triplets by some process that did not produce *trans*-stilbene triplets would proportionally inhibit both reactions causing no net color change under these conditions. The observed bleaching must therefore be due to selective sensitization of reaction II → III by *trans*-stilbene triplets. However, *trans*-stilbene triplets must be much less efficient in sensitizing this bleaching process than sensitizer triplets, for otherwise *trans*-stilbene inhibition of sensitized bleaching would not occur with the lower energy sensitizers. This low sensitization efficiency strongly suggests that *trans*-stilbene triplets have a substantially shorter lifetime than sensitizer triplets. Since quenching of sensitizer triplets by dissolved atmospheric oxygen ($[O_2] = 4 \times 10^{-4} M$) is close to diffusionally controlled ($k \sim 3 \times 10^9$ 1. mole^{-1} sec.$^{-1}$),[7] the sensitizer triplet lifetimes must be about 8×10^{-7} sec. ($1/k[O_2]$) and the *trans*-stilbene triplet lifetime must be even shorter.[8]

The method thus appears to be a simple sensitive test for compounds having exceptionally short-lived triplet states. Its use in the demonstration of exceptionally short lifetimes for, *inter alia*, the tetraphenylallene, diphenylacetylene, stilbene, and tetraphenylethylene triplets will be discussed in a future publication.

(7) (a) R. Livingston and D. W. Tanner, *Trans. Faraday Soc.*, **54**, 765 (1958); (b) G. Porter and M. W. Windsor, *Proc. Roy. Soc.* (London), **A245**, 238 (1958).

(8) This is in accord with the maximum *trans*-stilbene triplet lifetime of 7.7×10^{-7} sec. estimated by G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

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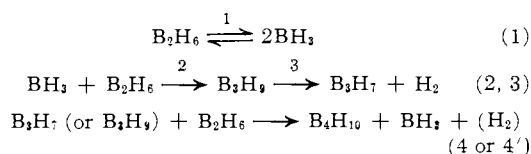CENTRAL RESEARCH DIVISION
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Mass Spectrometric Investigation of the Pyrolysis of Diborane. Triborane and Tetraborane Intermediates[1]

Sir:

The results of many investigations on the pyrolysis mechanism of diborane have been published since the pioneering work of Stock.[2a] The present state of affairs has been adequately summarized by Lipscomb.[2b] The initial stages of the polymerization are believed to proceed by the following mechanism.

$$B_2H_6 \underset{1}{\rightleftharpoons} 2BH_3 \qquad (1)$$

$$BH_3 + B_2H_6 \xrightarrow{2} B_3H_9 \xrightarrow{3} B_3H_7 + H_2 \qquad (2, 3)$$

$$B_3H_7 \text{ (or } B_3H_9) + B_2H_6 \longrightarrow B_4H_{10} + BH_3 + (H_2)$$
$$(4 \text{ or } 4')$$

The postulation of reactions 1 and 2 as the most probable initial steps is based on kinetic evidence. Thus, the initial stages of the B_2H_6 pyrolysis reaction[3-5] and the B_2H_6–B_2D_6[6] and B_2H_6–$^{10}B_2H_6$[7] exchange reactions

(1) Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1, 1964.

(2) (a) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933; (b) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

(3) J. K. Bragg, L. V. McCarty, and F. J. Norton, *J. Am. Chem. Soc.*, **73**, 2134 (1951).

(4) R. P. Clarke and R. N. Pease, *ibid.*, **73**, 2132 (1951).

(5) S. H. Bauer, *ibid.*, **78**, 5775 (1956).

(6) P. C. Maybury and W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1953).

(7) I. Shapiro and B. Keilin, *J. Am. Chem. Soc.*, **77**, 2663 (1955).

are all observed to be kinetically of three-halves order with respect to the diborane concentration. This agrees with eq. 1 and 2 if one assumes that a steady-state concentration of BH_3 is obtained. The recently reported detection of both BH_3 and BH_2[8] is not necessarily in contradiction to this mechanism. This aspect, however, has to be discussed further elsewhere.

Although a triborane species, B_3H_9 or B_3H_7, is the most readily imagined product formed in the propagation step, direct observation of either has so far not been accomplished.

Another important question in the B_2H_6 pyrolysis reaction is the "first stable intermediate" problem discussed by Schaeffer[9] and by Enrione and Schaeffer.[10] These authors conclude that reaction 3 is rate determining and that the very reactive triborane-7 reacts with B_2H_6 to give the "first stable intermediate," B_4H_{10}, plus BH_3. Under conventional experimental conditions, this B_4H_{10} is too reactive to be isolated prior to decomposition to a postulated B_4H_8, which in turn reacts with B_2H_6 to produce the observed[3] B_5H_{11}.

Using a mass spectrometric technique, we have investigated the B_2H_6 pyrolysis reaction in an endeavor to observe directly any mono-, tri-, or tetraborane species.

An Inghram-type mass spectrometer[11-13] was used. Diborane was introduced into a baffled[14] $^3/_4$ in. i.d. stainless steel crucible. Contact time for diborane was 0.04 sec. and did not necessarily correspond to attainment of equilibrium at the higher pressures. A movable beam defining slit ("shutter")[11] provided unambiguous identification of species emerging directly from the crucible orifice. This arrangement is a general method for investigation of gas-phase reaction intermediates over wide temperature and pressure ranges. The mass analyzer could detect 10^{-9} atm. of diborane in the crucible. Furthermore, it could resolve boranes from background; e.g., the triplet at mass peak 36 ($H^{35}Cl$, $^{12}C_3$, and $^{10}B_3H_6$) was resolved to the base line. This is most important, since, even with a base pressure of 3×10^{-8} torr, large "background" peaks, not readily eliminated by reducing the ionizing electron voltage, are always present between mass peaks 28 and 45.

Differential pumping was provided between the furnace (500 1./sec *in* the compartment), ion-source (20 1./sec), and analyzer (20 1./sec) chambers. Pressure drops of $5000:1:^1/_{20}$ were maintained between the furnace, furnace chamber, and ion source. Temperature was measured with three thermocouples spotwelded to the furnace.

Only species whose ions and neutral progenitors were identified by mass spectrum, mass *defect*, dependence on inlet valve setting, temperature dependence, and "shutter" profile[11] are considered. In all experiments, all peaks up to at least mass 130 were scrutinized.

(8) (a) T. P. Fehlner and W. S. Koski, *ibid.*, **86**, 2733 (1964); (b) G. Herzberg and J. W. C. Johns (National Research Council, Ottawa, private communication) report a rotational analysis of the BH_2 spectrum; (c) R. W. Diesen (private communication) reports a mass spectrometric identification of BH_3 in a shocktube (cf. R. W. Diesen, *J. Chem. Phys.*, **39**, 2115, 2121 (1964)).

(9) R. Schaeffer, *J. Inorg. Nucl. Chem.*, **15**, 190 (1960).

(10) R. E. Enrione and R. Schaeffer, *ibid.*, **18**, 10377 (1961).

(11) M. G. Inghram and J. Drowart, in "High Temperature Technology," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

(12) W. A. Chupka and M. G. Ingraham, *J. Phys. Chem.*, **59**, 100 (1955).

(13) Nuclide Analysis Associates, State College, Pa., Model-12-60 H. T.

(14) J. Berkowitz, *J. Chem. Phys.*, **36**, 2533 (1962).

The pyrolysis mechanism was studied by following the reaction parameters (loss of B_2H_6, formation of new species) as a function of temperature at successively increasing pressures of diborane in the furnace.

With a pressure of diborane of 5×10^{-8} to 2×10^{-7} atm. in the furnace, the B_2H_6 was 50% decomposed at 750°K. and the presence of a new monoborane species was detected.[15] No hydrides heavier than B_2H_6 were present. Increasing the B_2H_6 pressure to 5×10^{-6} atm. caused 50% B_2H_6 decomposition at only 525°K.; ions containing three, but not four, five, or more boron atoms were detectable.

At $\approx 10^{-4.5}$ atm. B_2H_6 pressure and 425°K. triborane ion peaks were clearly observed at masses 34 through 39. Simultaneously, the presence of "shutterable" peak intensities between masses 46 and 52 (in the ratios $0.5:1.0:1.0:0.5:0.2:(<0.07):(<0.03)$, respectively) and the absence of peaks corresponding to ions with five or more borons showed that a tetraborane was present, but B_5 and higher hydrides were not. In contrast with the known mass spectrum of tetraborane-10,[3,16] the peaks at masses 36–38 were 50% larger than any tetraborane peak between masses 46 and 50.

With the same pressure, an increase in temperature was accompanied by a slight decrease in the B_3 intensities, an increase in the B_4, and a very rapid increase in the B_5 intensities.

Interpretation of the mass spectra and temperature dependence of the B_3-B_4-, and B_5-boron containing ions indicate the presence of triborane and a new tetraborane. First, the mass spectrum at peaks 46–52 given above is different from the well-characterized B_4H_{10} spectrum,[3,16] where the ratios of peak intensities are $0.6:0.9:1.0:1.0:1.0:0.2:0.1$, respectively. Since this mass spectrometer has systematically reproduced the mass spectra of other known compounds, this is good evidence for a new tetraborane with fewer hydrogens than B_4H_{10}.

This offers the possibility that the B_3H_x ions are produced by fragmentation of this new tetraborane species, which is possibly B_4H_8. However, on electron impact, all the known boron hydrides produce ions of greatest intensity which contain the same number of boron atoms as the parent molecule. Since at times the B_3-containing ions were at least 50% larger than any B_4-containing ion, and the B_3, B_4, and B_5 ions had different temperature dependence, the conclusion that a neutral triborane species is formed is reasonably justified. The formation of a tetraborane prior to pentaborane is in accord with the arguments of Schaeffer,[9] Lipscomb,[17] and others,[18] as well as the tentative observation in ref. 3, footnote 7. However, we are at present unable to prove conclusively whether the observed tetraborane is B_4H_8 or a mixture of $B_4H_8 + B_4H_{10}$, and whether it is produced via reaction 4 or 4'.

Although to date no other direct observation of B_4H_8 has been made, evidence exists that it may play an important role in the formation of B_5H_{11}. Independent kinetic studies[19,20] of the $B_4H_{10} + B_2H_6$ reaction indi-

cate that B_4H_8 is almost certainly the first reaction product of B_4H_{10} prior to its conversion to B_5H_{11}. More recently, Brennan and Schaeffer[21] observed the thermal decomposition of B_4H_{10} in the presence of carbon monoxide. They isolated B_4H_8CO as the major reaction product. The close agreement between the kinetics of the B_4H_{10}–CO and B_4H_{10}–B_2H_6 reactions also indicates that the same intermediate, B_4H_8, is common to both systems.

(20) R. K. Pearson and L. J. Edwards, Abstracts, 132nd National Meeting of the American Chemical Society, New York, N. Y., 1957, p. 15N.

(21) G. L. Brennan and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **20**, 205 (1961).

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The Chemistry of Alane. IV.[1]
Dimethylaminodialane, $(CH_3)_2NAl_2H_5$[2]

Sir:

We wish to report the synthesis of the first known derivative of dialane, Al_2H_6, the aluminum analog of diborane, by the reaction of sodium aluminum hydride with dimethylaminochloroalane[3] in tetrahydrofuran (THF) according to eq. 1. The precipitation of so-

$$NaAlH_4 + (CH_3)_2NAlH(Cl) \xrightarrow{\text{THF}}$$
$$NaCl\downarrow + (CH_3)_2NAl_2H_5 \quad (1)$$
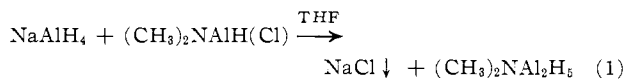
dium chloride was quantitative and evaporation of the solvent yielded a white, chloride-free solid corresponding to $(CH_3)_2NAl_2H_5 \cdot THF$. *Anal.* Calcd.: Al, 30.80; active H, 2.88; H/Al, 2.50. Found: Al, 31.00; active H, 2.88; H/Al, 2.49. Almost all of the associated THF could be removed by precipitating the product from its THF solution with pentane. Dimethylamino-dialane was a white solid which decomposed without melting at 130°. Its molecular weight, determined cryoscopically in benzene, was found to be 100 as compared to the calculated value of 103 for the monomer.

The direct reaction of alane and dimethylamino-alane in diethyl ether was found to be a second method for the preparation of dimethylaminodialane. It is well-known that ether solutions of alane are unstable and precipitate polymerized diethyl ether· alane.[4,5] When an equimolar solution of dimethylaminoalane was added to freshly prepared diethyl ether alane in ether, no precipitation occurred during 1 week of stand-

(1) Paper III: R. Ehrlich, A. R. Young, II, and D. D. Perry, to be published.

(2) This research was supported by the Advanced Research Projects Agency under ARPA Order No. 24-60 and by the Air Force Flight Test Center, Air Force Systems Command, Edwards Air Force Base, Calif., under Contract AF33(616)-5935 (1960).

(3) The dimethylaminochloroalane was prepared from dimethylamino-alane and mercuric chloride by the method of J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 1798 (1961), and its composition was confirmed by quantitative hydrolysis of its THF solution.

(4) *Cf.* A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

(5) R. Ehrlich, A. R. Young, II, B. M. Lichstein, and D. D. Perry, *Inorg. Chem.*, **2**, 650 (1963).

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

(16) I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehmann, Advances in Chemistry Series No. 32, American Chemical Society, Washington, D. C., 1961, p. 127.

(17) W. N. Lipscomb, *Advan. Inorg. Radiochem.*, **1**, 149 (1959).

(18) R. P. Clarke and R. N. Pease, *J. Am. Chem. Soc.*, **73**, 2132 (1951).

(19) J. A. Dupont and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **15**, 310 (1960).