Discussion

Preparative Methods.—In a new modification, gradual addition of AgNCO or AgNCS to excess cyclo-$C_6H_{11}SiH_3$ furnishes cyclo-$C_6H_{11}SiH_2NCO$ and some cyclo-$C_6H_{11}Si(NCO)_3$, or cyclo-$C_6H_{11}SiH_2NCS$ and some cyclo-$C_6H_{11}Si(NCS)_3$, respectively. This partial reaction corresponds to the partial reaction with $HgCl_2$ or AgCl to obtain cyclo-$C_6H_{11}SiH_2Cl$. In these halogenoids of silicon there is evidence for an isothiocyanate structure[8] but the oxygen analog could be either an isocyanate or a cyanate.

Both cyclohexylfluorosilanes hydrolyze very slowly in pure water at 20°, while the other halides hydrolyze readily. Thus shaking of warm, concentrated HF with cyclo-$C_6H_{11}SiCl_3$ gives cyclo-$C_6H_{11}SiF_3$ easily in one step. A two-step method is more typical of earlier syntheses[9] $R_2SiCl_2 + 2R'OH = R_2Si(OR')_2 + 2HCl$ and then $R_2Si(OR')_2 +$

(8) H. H. Anderson, THIS JOURNAL, **69**, 3049 (1947).

(9) N. S. Marans and others, *ibid.*, **73**, 5127 (1951).

$2HF = R_2SiF_2 + 2R'OH$, although they also list $R_3SiCl + HF = R_3SiF + HCl$.

Preparation of cyclohexylsilane from cyclo-$C_6H_{11}SiCl_3$ and $LiAlH_4$ in ether appears more convenient than the successive preparations of SiH_4, then of SiH_3Br and finally of cyclo-$C_6H_{11}SiH_3$.[6]

Molar Refractions and Bond Refractions.—Excluding the value for less-pure cyclo-$C_6H_{11}SiH_2F$, Table I lists calculated molar refractions with an average error of 0.48%. These calculations include Vogel's values for C–H, C–C, Si–C, Si–Cl, Si–Br, Si–O and Si–H and for[10] Si–N, C=N and C=O. They include 1.95 for the Si–F bond refraction[4] and 17.53 for Si–NCS.[3]

Acknowledgment.—Messrs. John E. Zlupko and Bernard Zuckerman kindly assisted in some preparations of cyclohexylsilane.

(10) A. I. Vogel and others, *J. Phys. Chem.*, **58**, 174 (1954); *J. Chem. Soc.*, 531 (1952).

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The Nature of Boron Hydride Solids[1]

BY I. SHAPIRO[2] AND ROBERT E. WILLIAMS

The reaction of diborane and decaborane in the liquid phase results in the formation of non-volatile yellow solids; no intermediate boron hydride compounds could be detected by mass spectrometry. The ratio of hydrogen evolved to diborane consumed is four. By application of the isotopic boron technique the molar ratio of reactants has been found to be unity. Infrared analysis indicates loss of bridge hydrogens; diborane is pictured as completing the icosahedron structure of decaborane followed by polymerization and rearrangement. The solid loses about one-half of its hydrogen as a function of temperature up to 180–200°; much higher temperatures are required to remove the remainder of the hydrogen. Hydrolysis of the solid yields trace amounts of tetraborane and hexaborane.

From the classical works of Alfred Stock and his collaborators to present-day studies, the literature on boron hydrides is sprinkled with remarks about the formation of "yellow solids," but apparently no concerted effort to study these solids has been reported. One reason, of course, is the difficulty of obtaining a truly reproducible sample. The pyrolysis of diborane produces a number of volatile boron hydride products in addition to yellow solids.[3,4] Yellow solids also are formed from the decomposition of the unstable higher boron hydrides. The color of such solids has been ascribed as "light yellow," "dark yellow," "light brown," "dark brown" or even "black," depending upon the previous history of the solids. Stock[3] has reported that the average ratio of boron to hydrogen in the (unheated) yellow solids is approximately unity, and the formula $(BH)_x$ is commonly used.

From the structure of the various boron hydrides it was conceivable that the diborane molecule might complete the icosahedron structure of the decaborane molecule. Decaborane heated alone

(1) Presented at the 132nd Meeting of the American Chemical Society, New York, September, 1957.

(2) Hughes Tool Company, Aircraft Division, Culver City, California.

(3) A. Stock and W. Mathing, *Ber.*, **69**, 1469 (1936).

(4) A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **55**, 4009 (1933).

to 100°, *i.e.*, just above its melting point, is stable, and the rate of disappearance of diborane (alone) at this temperature is comparatively slow. However, when diborane is heated in the presence of liquid decaborane, the rate of disappearance of diborane is greatly accelerated; a liquid phase reaction takes place. A solid product, soluble in decaborane, remains after the decaborane is sublimed from the reactor. That the product is not formed by pyrolysis of the diborane alone is shown by the fact that no intermediate boron hydride products are detected in the mass spectrum; hydrogen is the only gaseous product. Although the non-volatile solid is colored yellow when prepared under normal conditions, the color approaches white under mild thermal conditions, *i.e.*, short reaction time at 100°.

Since this method for forming the yellow solid appeared to be reproducible, a detailed study was undertaken in order to gain an insight of the nature of the solid.

Experimental

Materials: Diborane.—Isotopically labeled diboranes were prepared in the conventional manner[5] and stored in the vapor phase at room temperature. The diborane was frac-

(5) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, *ibid.*, **74**, 901 (1952).

tionated immediately prior to use, and its purity checked mass spectroscopically.

Decaborane.—This material was obtained as a product from the pyrolysis of diborane and purified by sublimation. Purity was checked mass spectroscopically.

Apparatus.—Standard high-vacuum equipment and techniques were used for the preparation and reaction of the boron hydrides. Description of a special glass reactor is given under Procedure. Mass spectral recordings were taken with a Consolidated Model 21-103 mass spectrometer operating at 70 volts. Infrared recordings were taken with a Perkin–Elmer Model 21 Infrared Spectrophotometer equipped with NaCl optics.

Procedure: Formation of Boron Hydride Solids.—The apparatus consisted of a small glass reaction tube connected by a capillary section to one leg (upper) of a Y-tube. The other upper leg was connected to the high vacuum system, and the lower leg of the Y was connected through a needle valve to a mercury reservoir. After evacuation of the system, decaborane was introduced into the reaction tube by sublimation from a sidearm which then was sealed off from the reactor. Next a measured amount of diborane was introduced into the reactor (liquid nitrogen trap), and then the reactor was isolated from the rest of the system by mercury whose level was brought above the fork in the Y. The reactor was surrounded by a constant temperature oil-bath and mercury was fed continuously from the reservoir into the Y in order to maintain a constant volume in the reactor. Thus the Y served as a manometer whose pressure was read as a function of time. After completion of the reaction, all volatile materials were removed and measured. The reaction vessel was replaced between experiments except when it was desired to learn the effect of solids-coating on the reactor walls.

Thermal Aging.—A weighed amount[6] of yellow solid was heated at predetermined temperatures for definite periods of time in a quartz tube which was connected to the vacuum system. Since hydrogen is evolved upon heating, a quartz wool plug was used to keep the solid within the heating zone. The temperature of the furnace was electronically controlled, and the temperature of the quartz tube was recorded on a strip chart. The hydrogen evolved was removed continuously by a Toepler pump and measured in a gas buret. After heating to 350° in the furnace, the quartz tube was heated with a torch in order to remove the remaining hydrogen from the solid.

Isotopic Analysis.—The molar ratio of reactants was determined by the isotopic boron technique, i.e., interaction of boron hydrides of different isotopic boron content and then determination of the resultant isotopic boron content of the product. The advantage of such a technique is that one need not measure quantitatively the amount of reactants used or products formed but measure only the relative ratio of the boron isotopes in the product. The application of this technique, of course, depends upon the absence of boron exchange between reactants.

After diborane and decaborane of different isotopic boron content were heated, the excess decaborane was removed by sublimation, and the yellow solids hydrolyzed and ignited to boric oxide. The B^{10} content of the oxide was determined by conversion of the oxide either to boron trifluoride or to diborane and then examination of their mass spectra. Boron trifluoride was generated from boric oxide by heating the latter with calcium fluoride in a stainless steel tube (prepared from a large syringe needle) contained in a (evacuated) quartz tube. Temperatures up to the softening point of quartz have been found necessary before a substantial amount of boron trifluoride is generated. A more satisfactory method of analysis is the conversion of the oxide to diborane.

Infrared Spectrum.—The KBr pellet technique for obtaining the infrared spectrum of the yellow solids was unsatisfactory because of the high reactivity of the solids to moisture. In a number of attempts the infrared spectra were found to contain appreciable amounts of boric acid. However, an acceptable infrared spectrum of the solids was obtained by a new technique carried out entirely under high-vacuum conditions. The yellow solids were prepared by the reaction of diborane and decaborane in a side arm of an IR gas cell. After removal of all volatile material from the

solids, pentaborane was condensed onto the solids; upon warming, the pentaborane dissolved the yellow solids. Next the entire gas cell was maneuvered in such a manner that the pentaborane solution was poured into a recess cut into the inner surface of a NaCl window. Thus the pentaborane did not come in contact with the glyptal window sealant. Finally, the pentaborane was pumped from the cell so that the solids formed a fine deposit over the window.

Results

Hydrogen–deuterium exchange in addition to reaction was found when deuteriodiborane and decaborane were heated together for 30 minutes at 100° or for 10 seconds at 200°. Large amounts of D_2, HD and H_2 were formed but no trace of any intermediate boron hydride could be detected mass spectroscopically. B^{10}-enriched diborane was substituted for deuteriodiborane and, although a large amount of diborane disappeared during the reaction, no exchange of boron between the recovered diborane and decaborane could be detected. In contrast, boron exchange has been observed when diborane is heated with either tetraborane or pentaborane.

The reaction of diborane and decaborane was followed gasometrically with the results given by Fig. 1. In a typical experiment a measured amount of diborane and an excess of decaborane were heated to 100° in a reaction vessel; the rate of pressure increase of the system initially was rapid but decreased with time although never actually reaching zero. After 160 hours the evolution of hydrogen still could be detected. The curves for three typical experiments give a measure of the reproducibility of these experiments. A solids-coating on the reactor had no influence on the shape of the curves. At the first increase in pressure the colorless liquid decaborane became tinged yellow, and after the removal of the unused decaborane a yellow non-volatile solid remained. The slow increase in pressure of the system with time is attributed to the thermal decomposition of the yellow solid to give hydrogen. By extrapolation of the curves in Fig. 1 to zero time in order to correct for the hydrogen due to decomposition of the solids, one finds a final reaction pressure which is approximately four times the initial diborane pressure. The cross-hatched zone gives a measure of the uncertainty in this extrapolation. Although there is this degree of uncertainty, the value of 4 for the ratio of hydrogen evolved to diborane consumed is regarded as significant, especially in view of other related data.

A sample of B^{10}-enriched diborane (96% B^{10}, 4% B^{11}) was heated with an excess of isotopically normal decaborane (20% B^{10}, 80% B^{11}),[7] and the B^{10} content of the product was determined. Several analyses by both the boron trifluoride and diborane methods resulted in values of 32–33% for the B^{10} content.

The infrared spectrum of the yellow solids obtained by the "vacuum" technique exhibited a

(6) The solids are highly reactive to air or water; all material transfers and weighings were carried out in an inert atmosphere.

(7) Recent studies[3] on the natural isotopic abundance ratio of boron indicates that the B^{10} content is closer to 20% than to the previously accepted value of 18.82%; however, for the analyses reported here the slight difference in value does not affect the final results.

(8) W. Lehmann and I. Shapiro, to be published; also see ref. 10 of I. Shapiro and J. F. Ditter, J. Chem. Phys., **26**, 798 (1957).
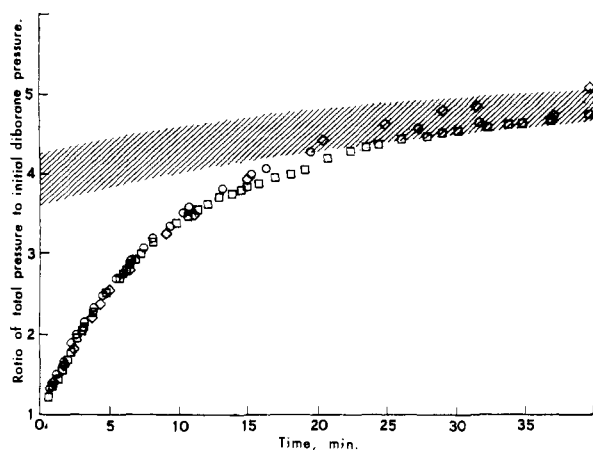
Fig. 1.—Change in pressure of system containing diborane and decaborane at 100° as function of time. Initial diborane pressure (100°) is 70 mm.: □, ○, ◇ represent three separate experiments.

Fig. 2.—Change in composition of boron hydride solids as a function of temperature.

sharp intense peak at 2560 cm.$^{-1}$, with no bands suspected of being due to crystal formation. The spectrum also contained several low intensity absorptions which are assigned to decaborane. There were no absorption bands which could be attributed to bridge hydrogens in the yellow solids.

When the yellow solid is exposed to moisture, the characteristic boron hydride odor is detected. Addition of trace amounts of water to yellow solids in the high vacuum system results in the formation of tetraborane and lesser amounts of hexaborane in addition to hydrogen.

Thermal Aging of Solids.—When a sample of the solids was heated in a closed (evacuated) container at a constant temperature, for example 150°, the pressure increased rapidly at first, but then tended to level off with time. When the hydrogen was pumped out of the container and the solids reheated at the same temperature, again the pressure increased rapidly with the rate of pressure increase tapering off with time. This cycle was repeated a number of times. This influence of hydrogen on slowing the rate of decomposition of the solids has also been noted at several different (low) temperatures. If, at any pressure, the hydrogen is removed and replaced by an equal pressure of nitrogen, the solid behaves as though no gas were present, i.e., there still is an initial pressure increase. In order to study the uncomplicated rate of hydrogen evolution, effect of hydrogen back-pressure was substantially eliminated by modifying the apparatus so that the evolved hydrogen could be removed continuously from the system with an automatic Toepler pump. The hydrogen evolved at any given time was measured in a gas buret.

When the solid is subjected to continuous pumping at a constant temperature, the solid loses a definite amount of hydrogen over a prolonged period of time. The bulk of the hydrogen that does come off at any one temperature does so over a period of several hours. Consequently for this study, the practice of heating the solids at each temperature level was set at four hours for one series and seven hours for another series. The
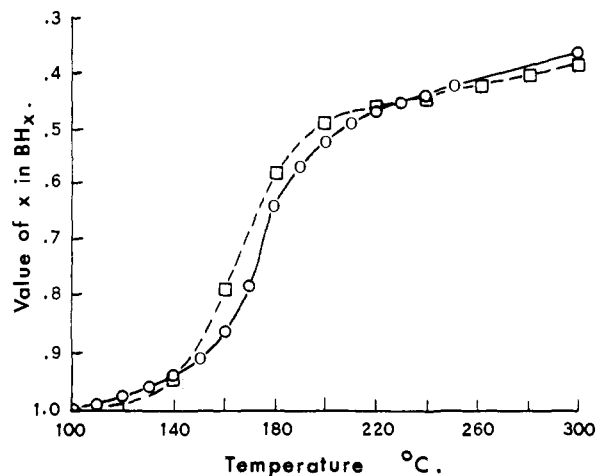
results are shown in Fig. 2 where the amount of hydrogen lost is plotted in terms of the empirical formula BH_x. The shape of the two curves is similar. The amount of hydrogen evolved increases with the temperature to about the region of 200°. From 200 to 310° there is a flattening off portion, and above 310° hydrogen again commences to evolve in an appreciable quantity.

Discussion

The pronounced increase in rate of disappearance of diborane in the presence of liquid decaborane without any other volatile boron hydride being detected is attributed to an interaction of the two boron hydrides rather than a decomposition of either one. From the isotopic boron technique the observed B^{10} content (32–33%) of the solids agrees very well with the value expected for an equimolar ratio of reactants (Table I). Such a ratio

TABLE I

CALCULATED ISOTOPIC COMPOSITION OF SOLID AS FUNCTION OF MOLAR RATIO OF REACTANTS

Moles $B_2{}^{10}H_6$	Moles $B_{10}{}^nH_{14}$	% B^{10} in solids
2	1	41.7
1	1	32.7
1	2	26.9

of reactants also would yield four moles of hydrogen per mole of diborane in agreement with the data in Fig. 1. The reaction can now be written

$$B_2H_6 + B_{10}H_{14} \longrightarrow 4H_2 + (BH)_{12}$$
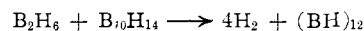
The $(BH)_{12}$ simultaneously and continuously loses additional hydrogen to become a more hydrogen deficient polymer.

The diborane molecule can attach itself to the decaborane molecule either by completing the icosahedron with loss of the bridge hydrogen atoms of the decaborane molecule, or by attaching itself to the outside of the decaborane basket. In this latter case all of the boron or hydrogen atoms would

not be equivalent; one would not expect to get four moles of hydrogen per mole diborane consumed. The infrared spectrum of the solid shows a predominant peak at 2560 cm.$^{-1}$ which corresponds to the B-H$_{terminal}$ frequency. The absence of any absorption attributable to a B–H$_{bridge}$ frequency favors the structure of the completed icosahedron.

Although theoretical considerations[9] based on the electronic structure of a regular icosahedron of boron atoms leads to the conclusion that a discrete molecule of B$_{12}$H$_{12}$ is fundamentally unstable, the existence of such a molecule should not be ruled out since the same theory predicts instability for the remarkably persistent framework structures of tetragonal boron and boron-enriched boron carbide.[10] Obviously, the yellow solid is not stable at elevated temperatures employed in this study; however, it appears reasonable to retain the concept of a B$_{12}$ building block such as found in elementary boron[10] and boron carbide.[11] Thus, upon heating, the "building blocks" lose hydrogen between adjacent units and/or undergo rearrangements resulting in a polymer. The lattice structure of the solid is such that about one-half of the hy-

drogens can be lost easily upon heating to temperatures of 180–200°. Past this point some of the hydrogens are no longer accessible. Thus much higher temperatures become necessary to effect structural rearrangement so that the remainder of the hydrogen atoms can be released. The actual role of hydrogen in affecting the rate of hydrogen evolution from the solid is still not understood since the loss is apparently non-reversible.

The solubility of yellow solid in pentaborane (indicating limited polymerization) suggests that further studies at lower temperatures might yield B$_{12}$H$_{12}$ as an identifiable molecular species. At any rate such studies should yield a product deserving of structural investigation by X-ray methods.

The formation of tetraborane or hexaborane from the hydrolysis of yellow solids is not surprising since it has been observed that hydrides can be formed from protons upon breaking of boron–boron bonds,[12] and in this case the yellow solid has retained the basic boron hydride structure.

(9) H. C. Longuet-Higgins and M. de V. Roberts, *Proc. Roy. Soc. (London).* **A230.** 110 (1955).

(10) J. L. Hoard, R. E. Hughes and D. E. Sands. This Journal. **80,** 4507 (1958).

(11) H. K. Clark and J. L. Hoard, *ibid.,* **65,** 2115 (1943).

(12) I. Shapiro and H. G. Weiss, *J. Phys. Chem.,* **63,** 1319 (1959).