and 18-12-14 (Fig. 4 and 5) and 18-12-10 and 18-10-12 (Table II) were about equal with the transformations of state occurring at about the same temperature.

The solid condensed monolayers, which existed at 70 Å.^{2}, resemble in certain respects the mesomorphic monolayers of fatty acids and monoglycerides.[6,14] However, the monolayers are stable in this state only at 70 A.^{2} and within a narrow temperature range, which is just below the complete melting point.[6] At lower temperatures the monolayers are easily compressed, unstable, and exhibit hysteresis. Hysteresis indicates the presence of states or forms which are not in equilibrium. These properties and the uniformity of the area at 70 Å.^{2} are not commensurate with those of fatty acids and monoglycerides, which have an extremely high stability, a relatively low compressibility, low viscosity, and variable limiting areas.[9] It is interesting to note that the area of 70 Å.^{2} corresponds with the theoretical cross-sectional area of 69.9 Å.^{2} calculated for liquid crystals of tristearin in a β'-form. The absence of hydroxyl groups could account for the instability and rigidity of the films at this point.

Polymorphic transformation to higher melting forms did not occur in any of the monolayers, which remained fluid above the melting points and expanded to approximately 120 Å.^{2}. The excellent agreement between the melting points of the three-dimensional α-forms and the temperatures at which the condensed monolayers expanded to 120 Å.^{2} (Table III) is good evidence that the intermolecular forces in the condensed monolayer are similar to those in the α-form. If the temperature was not too far above the melting point, additional pressure condensed the expanded monolayers. An approximate calculation for dT/dP from the Clapeyron equation and an estimated heat of fusion shows that it should be possible to solidify the α-form of a triglyceride several degrees above its melting point (T_m) under a pressure of 20 dyne/cm. Although the curves do not represent a complete set of isothermals, several of them indicate that the temperature range from T_m to T_{cc} (temperature of critical crystallization) is approximately 5°. Above T_{cc} it was impossible to obtain a condensed monolayer and collapse resulted

in a constant pressure, the monolayer being fluid and in equilibrium with an oil lens. The absence of a stable β-form in the monolayers may be ascribed to the fact that this form requires a tuning-fork or chair arrangement of the chains with alternate molecular packing. Intra- and intermolecular packing of this nature would not be expected to occur in monolayers on water.

This investigation supports the generally accepted theory that the α-form is the only stable form in the condensed monolayers of triglycerides and confirms the presence of a second form, which is unstable under pressure and could be related to the β'-form.

The results also lead to the conclusion that the hydrocarbon chains of triglyceride molecules in the α-form are aligned in the same direction. The construction of a molecular model of a saturated triglyceride shows very little mechanical strain for such a structure. It is significant that the β- or β'-forms are always obtained by crystallization from a polar solvent in which the solute molecules have an unlimited degree of freedom with respect to each other. In the case of the pure compounds, rapid crystallization at low temperature of a completely liquid melt almost always produces the α- or β'-forms, whereas gradual cooling, which promotes a slow rate of crystal growth, usually yields the β-form. β-Forming compounds are very prone to supercooling and even though their crystal nuclei persist to some extent in a melt at temperatures slightly above the melting point, rapid cooling of such a melt usually results in a mixture of forms. When a large volume of liquefied tristearin is allowed to cool slowly to room temperature, there is considerable surface and internal eruption, which is visible evidence for inter- and intramolecular rearrangement during crystallization. This phenomenon is not observed in β' or α crystallizations, which as a rule occur with very little supercooling. Apparently the molecular structure of the liquid, α-, and β'-forms differs radically from that of the β-form. In view of these facts, X-ray data, and the results of this investigation it seems quite logical in theory to visualize a tuning-fork or chair structure for the β-form as opposed to coalignment of the chains in the α- and β'-forms.

The Unstable Species and the Isotope Effect in the Pyrolysis of Diborane in a Shock Tube[1]

By T. P. Fehlner and W. S. Koski

The pyrolysis of diborane has been examined using a chemical shock tube as a reactor. Additional evidence for the existence of hexaborane-12 and heptaborane-11 and -13 has been obtained. The presence of a large net normal isotope effect in the formation of tetraborane and hexaborane and a net inverse isotope effect in the formation of pentaborane-9 are observed. A mechanism, consisting of a series of competitive reactions and equilibria in which tetraborane is the precursor of pentaborane-11 and hexaborane but not of pentaborane-9, is shown to be compatible with the observed isotope effect. Data obtained by examining the pyrolysis of various mixtures of boron hydrides are also consistent with the mechanism.

Introduction

It has long been known that the boron hydrides are unstable with respect to heat[2] and their pyrolysis reactions have been the subject of considerable research in the past. The various studies have been summarized by Morey and Hill[3] and Lipscomb[4] and consequently will not be repeated in detail here. Briefly, however, kinetic studies[5] and work on the various isotopic exchange reactions[6] indicate that the initial two steps in the pyrolysis of diborane are the rapid borane equilibrium followed by a rate-determining at-

(1) This research was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Contract number AF 49(638)-481; and under the auspices of the United States Atomic Energy Commission.

(2) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(3) J. Morey and G. Hill, Tech. Report No. 1, Contract AF 49(638)-28, Fuel Technology Department, University of Utah, 1958.

(4) W. N. Lipscomb, Advan. Inorg. Chem. Radiochem., 1, 148 (1959).

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

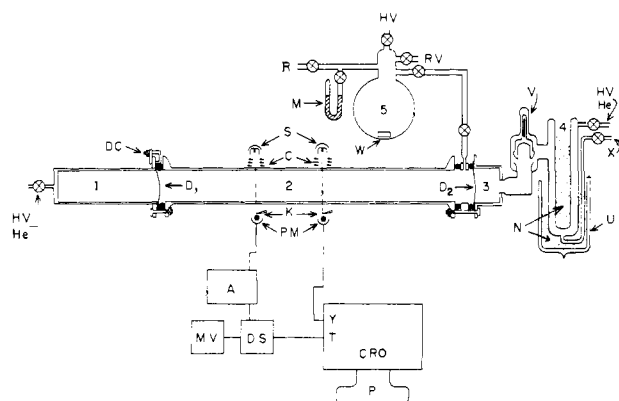(6) P. C. Maybury and W. S. Koski, J. Chem. Phys., 21, 742 (1953).

Fig. 1.—The shock tube and associated apparatus: 1, high pressure section; 2, reactant section; 3, dump section; 4, trap; 5, mix section; HV, high vacuum; RV, rough vacuum; He, helium inlet; X, to analysis; S, light sources; C, slit systems; PM, photomultipliers; K, knife edges; D_1, primary diaphragm; D_2, secondary diaphragm; DC, $^1/_3$ diaphragm clamp; M, manometer; RI, inlet for reactants; V, ball joint valve; W, Teflon-covered magnetic stirrer; A, amplifier; CRO, cathode-ray oscilloscope; P, Polaroid camera; T, trigger; Y, Y deflection plates; MV, multivibrator; DS, diode switch; N, liquid nitrogen; U, dewar; ⊗, stopcocks.

tack of BH_3 on diborane. However, the following steps whereby tetraborane, pentaborane-9 and -11, hexaborane, etc., are formed are in some doubt. For example, some authors[5,7] tend to write B_5H_{11} as being formed directly from diborane and an intermediate product, thought to be B_3H_7,[4] produced directly from diborane. However, it is Schaeffer's[8] view that the work of Klein, et al.,[9] on the decomposition of diborane in a hot–cold reactor tends to suggest that tetraborane is first formed from B_3H_7, subsequently being converted to B_5H_{11}. Kinetic studies on the conversion of tetraborane to pentaborane-11[10,11] indicate the possible existence of two intermediates, B_4H_8 and B_5H_7. Later work on the rate of formation of B_4H_8CO[12] tended to confirm the existence of the former. This species also seems a likely intermediate in the tetraborane–diborane exchange[13] and the pentaborane-11–diborane exchange.[14] In general, the existing evidence tends to favor a rather complex mechanism consisting of a series of competitive reactions and equilibria.

The present research was based on the idea that if the boron hydrides were subjected to a heat pulse of some type, one might expect to produce higher concentrations of intermediates for short periods of time. As a result of these higher concentrations and the short period of the temperature perturbation, new unstable boron hydrides could very well appear in the final products. In contrast, one would expect under the conditions at which the interconversion of the boron hydrides has been studied in the past (temperatures of the order of 100° and times measured in minutes) that unstable species would be destroyed nearly as fast as they are formed. Consequently, as the simple shock tube is a convenient means of producing heat pulses of varying strength in a mixture of gases, it was used in the work presented.

(7) K. Borer, A. B. Littlewood, and C. S. Phillips, J. Inorg. Nucl. Chem., 15, 316 (1960).

(8) R. Schaeffer, ibid., 15, 190 (1960).

(9) M. J. Klein, B. C. Harrison, and I. J. Solomon, J. Am. Chem. Soc., 80, 4149 (1958).

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

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

(12) F. L. Brennan and R. Schaeffer, ibid., 20, 205 (1961).

(13) J. E. Todd and W. S. Koski, J. Am. Chem. Soc., 81, 2319 (1959).

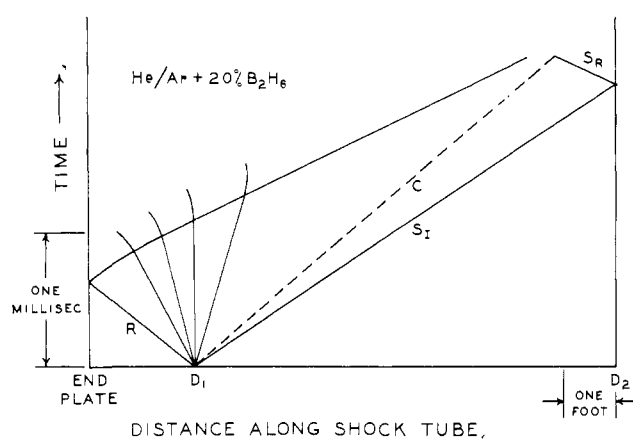(14) T. E. Larson, Thesis, The Johns Hopkins University, 1956.

DISTANCE ALONG SHOCK TUBE.

Fig. 2.—Distance vs. time for the principal waves in a typical 20% diborane in argon run; S_I, incident shock; S_R, reflected shock; C, contact surface; R, rarefaction; D, diaphragm.

Experimental[15]

The 2-in. i.d. shock tube used in this work and shown schematically in Fig. 1 consisted of a 2-ft. brass driver section separated from an 8-ft. Pyrex pipe reactant section by a 0.001 in. aluminum foil diaphragm. The end plate of the latter section was replaced by another 0.001-in. diaphragm which, when ruptured by the shock wave, allowed the products to enter a large evacuated trap at 77°K. This device allowed all the condensible products to be collected immediately after the shock perturbation had subsided. Provision was made for moving the products from this trap to the separation apparatus utilizing a stream of helium.

A driver pressure of about 1.5 atm. of helium or hydrogen initiated the shock wave by spontaneous diaphragm rupture in most cases. The reactant gas at a pressure of approximately 1 cm. generally consisted of a mixture of an inert gas and/or hydrogen with one or more of the volatile boron hydrides.

The velocity of the incident shock wave was measured utilizing a schlieren system. For He/Ar shock waves, the velocity compared favorably with that calculated from the diaphragm pressure ratio.[16] The measured velocity permitted the calculation of the temperature behind the incident wave using an average heat capacity, where available, for the boron hydride. Corrections were not made for the heats of reaction[17] as only an estimate of the shock strength was desired.

An indication of the conditions to which a typical sample is subjected is given by the wave diagram in Fig. 2, which was calculated for a typical run. It may be seen that the rarefaction wave overtakes the shock wave shortly after it reflects from the secondary diaphragm. It is probable that the diaphragm does not break immediately[18] and consequently the gas is subjected to the reflected wave which roughly doubles the temperature of the gas. If the diaphragm still has not broken, the interaction of the shock wave with the contact surface in this case would result in two shock waves moving in opposite directions. Further interactions become very complex, especially when the diaphragm ruptures allowing the gas to expand into the cold trap. For this reason it would not be very fruitful to try to trace the subsequent events. It suffices to say that it is doubtful that the cooling in the trap is efficient enough to prevent some reheating of the gas due to deacceleration at the trap walls. The rarefaction wave does aid in cooling the products, however. This was substantiated in the case of B_4H_{10} and H_2. With a H_2 driver, the wave diagram is about the same as that in Fig. 2 while with a He driver the rarefaction does not reach the secondary diaphragm until a relatively long time after the shock wave. Considerably more unstable products and less solid were formed in the former case than in the latter, other conditions being equal. Despite the vagueness of the actual history of the sample, it is subjected to a

(15) See J. N. Bradley, "Shock Waves in Chemistry and Physics," John Wiley Sons, Inc., New York, N. Y., 1962, and E. F. Greene and J. P. Toennies, "Chemische Reactionen in Stosswellen," D. Steinkopff, Darnstadt, 1959, for a complete description of the principles and operation of shock tubes.

(16) E. L. Resler, S. C. Lin, and A. Kantrowitz, J. Appl. Phys., 23, 1390 (1952).

(17) S. R. Gunn and L. G. Green, J. Phys. Chem., 65, 2173 (1961).

(18) For equivalent initial conditions, substitution of this diaphragm for the normal end plate did not change the gross product distribution appreciably, indicating a bursting time of sufficient duration for the reflected wave to process the gas.
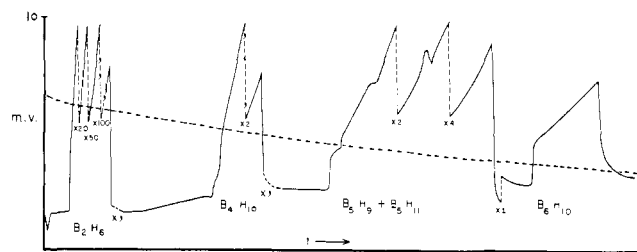
Fig. 3.—A typical distillation record.

temperature perturbation of short duration which, as this study was initiated along preparative lines, was the desired result.[19]

The separation of the products was accomplished using a "codistillation fractionation apparatus" constructed essentially as described by Cady and Seigwarth.[20] The general operation of this apparatus is as follows. The products are carried by a stream of helium gas from the shock tube trap to a copper U-tube packed with magnesium metal filings to which a temperature gradient between 77 and 300°K. has been applied. The vertical position in the tube where the various substances condense depends on the boiling points of the substances. The temperature gradient is gradually raised allowing the rings to move toward the bottom of the U-tube. Upon reaching this point they distil off and are carried away by the helium stream. As the compound leaves the column it is detected by a thermal conductivity cell that forms one arm of a bridge circuit. The unbalance of the bridge is monitored with a recorder giving a visual record of the distillation. A typical record is shown in Fig. 3. The vertical dotted lines refer to the scale changes shown, while the decaying curve is the output of a copper–constantan thermocouple attached to the base of the column.

A schematic diagram of the actual apparatus constructed for this research is shown in Fig. 4 and the parts used are given in the legend. Selected products could be efficiently trapped in the detachable spiral glass traps and carried to the mass spectrometer for identification.

This method of separation is very suitable for separating unstable volatile compounds such as the boron hydrides for two reasons. First, the column contains no absorbing substances that may hold water and it may be baked out under vacuum. Secondly, the entire distillation is finished before the column reaches 0°, eliminating the problem of decompostion.[21] It was particularly applicable to this work as about 5×10^{-7} mole of a stable product could be trapped and identified on the mass spectrometer. The mass spectrometer showed that compounds purified in the apparatus had total impurities of less than 0.2%.

As the area under each curve on the distillation record (Fig. 3) is proportional to the amount of material present, the composition of the mixture of volatile products could be determined with suitable calibration. The area of each peak was taken to be the height times the width at half-height. Peaks were trapped and the area per unit pressure determined. As a check on the procedure, the composition of a run was determined by area and also by trapping. The total amount of material was equal within 1%; however, the pentaboranes were over 3% off, which is not surprising as one peak falls practically on the other.

The amount of solid produced in a given run was taken as the total amount of volatile material collected in a blank run minus the amount collected in a normal run. The blank run and the normal run were corrected for any differences in starting pressures and the calculations were done in terms of moles of boron. The absolute accuracy of this method of composition determination is probably not better than 10% of the composition values and is particularly bad for small peaks in that it tends to give too small percentages. However, all that was desired was a relatively easy way to compare various runs and for this purpose the accuracy is quite sufficient.

The diborane of normal isotopic content used in the pyrolysis experiments was purchased from the Callery Chemical Co., Callery, Penna. It was purified by trap-to-trap distillation before use. The tetraborane was obtained from the same company. It was found to contain small amounts of hydrocarbon and alkyl substituted diboranes; consequently, it had to be purified on the distillation apparatus described above. The pentaborane-9 used was some that had been previously prepared in the laboratory.[22] The pentaborane-11 was prepared as adequately described by

(19) Many of these difficulties could be eliminated by the use of a *single-pulse* shock tube (H. S. Glick, J. J. Klein, and W. Squire, *J. Chem. Phys.*, **27**, 850 (1957); A. Lifshitz, S. H. Bauer, and E. L. Resler, *ibid.*, **38**, 2056 (1963).

(20) G. H. Cady and D. P. Seigwarth, *Anal. Chem.*, **31**, 618 (1959).

(21) J. J. Kaufman and W. S. Koski, *ibid.*, **29**, 1032 (1957).

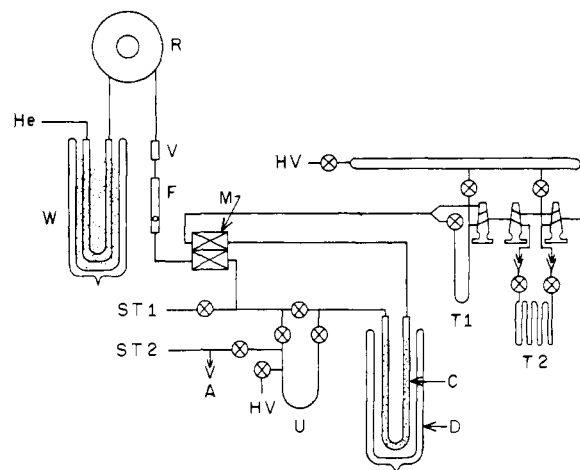(22) W. S. Koski, P. C. Maybury, and J. J. Kaufman, *ibid.*, **26**, 1992 (1954).

Fig. 4.—Fractionation codistillation apparatus: HV, high vacuum; R, pressure regulator; T_1, Pyrex trap (for large amounts of stable product); T_2, Pyrex spiral trap (for small amounts stable and unstable products); M, Gomac microcell (Model JDC-307-thermistor); ST_1, to shock tube trap; ST_2, from shock tube trap; U, sample freeze-out for auxiliary samples; A, standard taper for auxiliary samples; F, flowmeter (predictability: 0–40 ml./min.); V, check valve; He, from helium tank; W, water trap (0.5 in. × 2 ft. copper tubing packed 70–80 mesh Mg filings); C, column ($^3/_{16}$ in. x 3 ft. copper tubing packed 70–80 mesh Mg filings); D, dewar (1 pt.); ⊗, stopcocks (high vacuum).

Burg and Stone.[23] The hexaborane used was prepared in the shock tube and purified on the distillation apparatus. The deuterated B^{11} diborane was some that was previously prepared in this laboratory.[24]

For the driver gas, helium obtained from Air Reduction Corp. was used. Helium from the same source was used with the fractionation apparatus except it was run through a drying tube and large packed copper column at 77°K. before entering the flow system. These precautions were taken in the latter case as much larger amounts of helium were involved.

The argon used was Matheson reagent grade which was certified 99.99% pure argon. Electrolytic hydrogen was also obtained from Matheson while the deuterium was obtained from the Stuart Oxygen Co.

Results and Discussion

The volatile products B_2H_6, B_4H_{10}, B_5H_9, and B_5H_{11} were all separated and identified as described above. Considerable amounts of solid were produced in these runs and samples were analyzed on, the mass spectrometer. $B_{10}H_{14}$ was present along with possible traces of $B_{20}H_{26}$.[25,26] Most of this solid material was nonvolatile, however.

Detection of Unstable Products.—Besides these "normal products," unstable products were formed and their identity was determined as follows. In certain runs (low shock strength, excess hydrogen) the distillation record had several peaks that were not due to known hydrides. As the magnitude of the difference in thermal conductivity between the reference and sample cells of the detector is directly proportional to the vapor pressure of the substance distilling at a certain column temperature, an unknown vapor pressure can be determined with suitable calibration. It was found that the temperature at which the vapor pressure of a compound was 0.1 mm. corresponded to the temperature at which the compound first appeared on the distillation record. This is shown in Table I for a few selected runs. Vapor pressures for the boron hydrides are given in ref. 27 and 28. As can be seen, the

(23) A. B. Burg and F. G. A. Stone, *J. Am. Chem. Soc.*, **75**, 228 (1953).

(24) J. J. Kaufman and W. S. Koski, *J. Chem. Phys.*, **24**, 403 (1956).

(25) A. Quayle, *J. Appl. Chem.*, **9**, 395 (1959).

(26) L. H. Hall and W. S. Koski, *J. Am. Chem. Soc.*, **84**, 4205 (1962).

(27) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

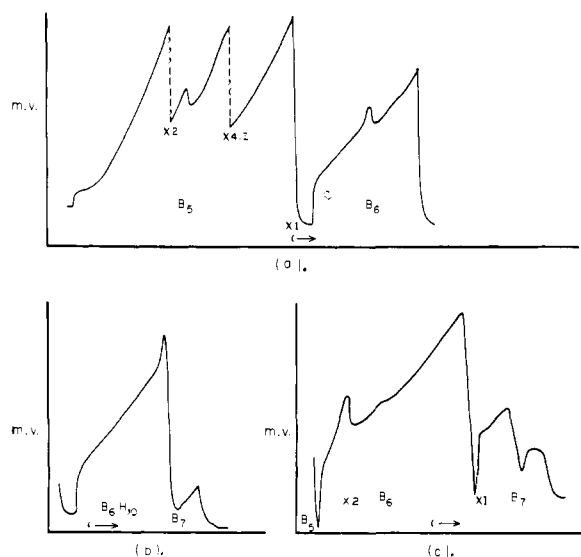(28) S. G. Gibbins and I. Shapiro, *J. Chem. Phys.*, **30**, 1483 (1959).

Fig. 5.—Partial distillation curves showing unstable products.

Fig. 6.—Partial fragmentation patterns of two heptaboranes.

correspondence is very good and is quite reproducible. It is felt that the values determined for the unstable products are as good.

The most abundant intermediate found was B_6H_{12}. This molecule was first suggested by Stock,[2] and later some mass spectral evidence for its existence was offered by Gibbins, et al.[29] The latter consisted of ion peaks at m/e 77 and 78 in the spectrum of freshly prepared hexaborane.

In Fig. 5a, a reproduction of the distillation curves of the pentaboranes and hexaboranes from a 16% B_2H_6, 57% H_2, 27% Ar run is shown. Using selective trapping and mass spectral analysis of the cuts, the first portion (before the first maximum) of the pentaborane curve was shown to consist of a mixture of B_5H_9 and B_5H_{11}, while the second portion was B_5H_9 alone. The second part of the hexaborane curve was shown to be B_6H_{10}. The first part of the hexaborane peak has a mass spectrum containing ion peaks at m/e 77 and 78 not unlike the ion peaks at m/e 65 and 66 in the mass spectrum of B_5H_{11}.[30] These peaks were not caused by instrumental peculiarity as both fractions were run in succession. One sample had m/e 77 and 78, and one did not. The sample size admitted to the mass spectrometer had no effect on the existence of these peaks either. By comparison with the case of the pentaboranes, it is evident that the first part of the hexaborane distillation curve consists of a mixture of B_6H_{10} and B_6H_{12}. It is obvious that in order to obtain a pure sample of B_6H_{12} by this method of separation it would be necessary to prepare it in greater amounts than B_6H_{10}. Unfortunately, no conditions in these experiments led to the formation of B_6H_{12} in excess.

In Table I, it can be seen that the vapor pressure of B_6H_{12} seems to be slightly larger than that of B_6H_{10} for a given temperature although this is not obvious from the distillation curve shown in Fig. 5a.[31]

Besides B_6H_{12}, one or more heptaboranes were formed in shock waves through B_4H_{10} and H_2. A partial mass spectrum of a heptaborane believed to be B_7H_{12} has been published.[32] Similar evidence for other heptaboranes has also been put forward.[25,29,33] The evi-

(29) S. G. Gibbins and I. Shapiro, J. Am. Chem. Soc., 82, 2968 (1960).

(30) T. P. Fehlner and W. S. Koski, ibid., 86, 581 (1964).

(31) R. Schaeffer (145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963) also finds this to be the case.

(32) R. W. Schaefer, K. H. Ludlum, and S. E. Wiberley, J. Am. Chem. Soc., 81, 3157 (1959).

(33) M. Hillman, D. J. Mangold, and J. H. Norman, Advances in Chemistry, No. 32, American Chemical Society, Washington, D. C., 1961, p. 151.
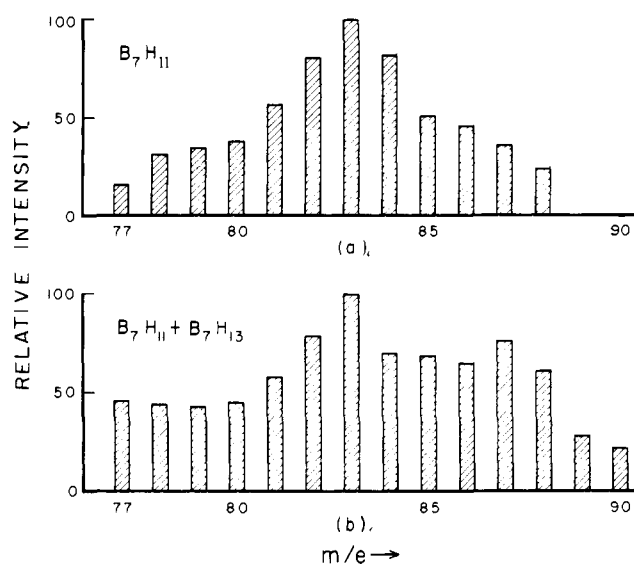
dence for B_7H_{12} consists of ion peaks at mass numbers 77–89 with the principal peak at m/e 83 in a mass spectrum of a mixture of B_4H_{10}, B_5H_9, B_5H_{11}, and B_6H_{10}.

TABLE I

TEMPERATURES AT WHICH THE VAPOR PRESSURES OF THE BORON HYDRIDES EQUAL 0.1 MM.

Substance	Temp., °C., at which vapor pressure equals 0.1 mm.	Temp., °C., at which substance first appears during distillation			
		A	B	C	D
B_4H_{10}	−110	−113	−114	−118	−118
B_5H_9	−88	−89	−91	−87	−87
B_5H_{11}	−80	−80		−82	−79
B_6H_{12}				−59	
B_6H_{10}	−57	−58	−61	−57	−56
B_7H_{11}				−44	−41
B_7H_{13}					−36

In Fig. 5b and c are reproductions of the B_6H_{10} distillation curves including peaks attributed to heptaboranes. Attempts were made to trap these peaks singly; however, none was successful. The resulting mass spectra consisted of mixtures of small amounts of B_2H_6, B_4H_{10}, and B_5H_9, indicating decomposition had occurred. This is not too surprising as the total area of the peak trapped represented about 5×10^{-7} mole of material. This amount of B_6H_{10} could be trapped and identified; however, a sample of B_5H_{11} of similar size suffered considerable decomposition.

To identify these peaks, the hexaborane and heptaborane were trapped together. In this way, it was hoped that the B_6H_{10} would both "carry" the heptaborane into the inlet of the mass spectrometer and also "protect" it from decomposition, especially on the metal walls of the expansion chamber. This turned out to be the case and the partial spectrum of B_7H_{11} is shown in Fig. 6a while that of a mixture of B_7H_{11} and B_7H_{13} is shown in Fig. 6b. It is to be noted that the envelope of the fragment ion distribution of B_7H_{11} is similar in shape to that of B_6H_{10}. This may indicate that B_7H_{11} has a structure similar to B_6H_{10} except with seven borons in the basal ring. The spectrum in Fig. 6b is very similar to the one previously published for B_7H_{12}.[32]

The temperatures at which the heptaboranes have vapor pressures of 0.1 mm. are given in Table I and as the difference between the values given is small they probably differ by two hydrogens. Therefore it is
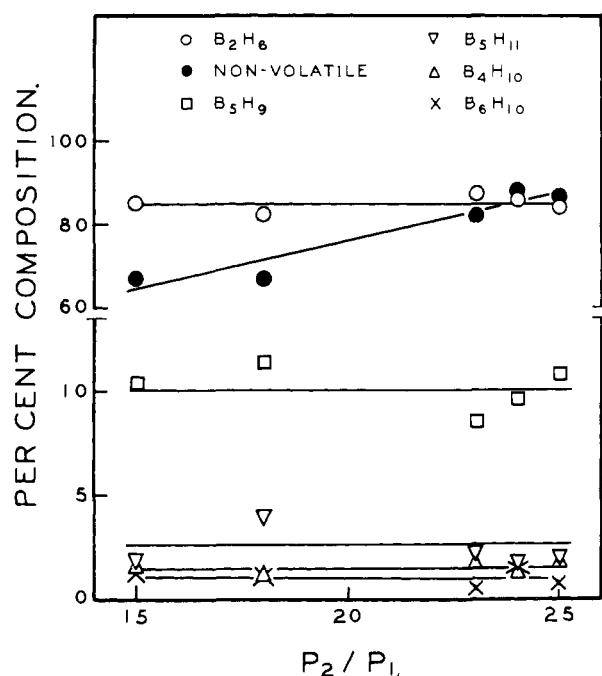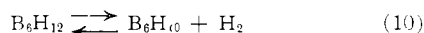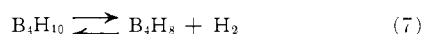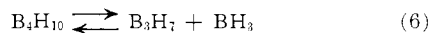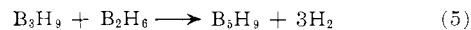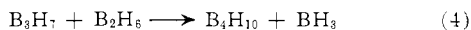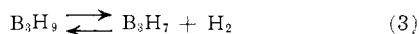
Fig. 7.—Product distribution *vs.* incident shock strength for 20% diborane in argon runs. The main volatile products are shown as percentages of the total amount of volatile material recovered. The nonvolatile material is shown as the percentage of the starting boron hydride that did not appear as volatile products. P_2/P_1 refers to the pressure ratio across the incident shock and corresponds to a temperature range of 800–1200°K.
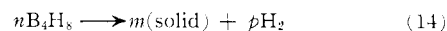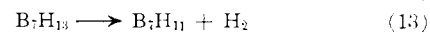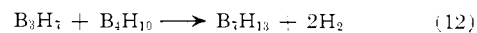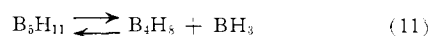
thought that these compounds are B_7H_{11} and B_7H_{13}, although the pair B_7H_{13}, B_7H_{15} is also possible.

The Mechanism and Isotope Effect.—The effect of shock strength on the product distribution was examined initially. Figure 7 shows that there is no real change in the volatile product distribution with increasing shock strength.[34] However, the amount of solid material produced increased. The invariance of the volatile product distribution suggests that the distribution may be thought of as a "steady state" distribution in the production of solid. This is interesting in that it suggests that the solid is not produced directly from diborane but it is the end product of several steps. It also implies that molecules once formed can easily decompose and re-enter the decomposition scheme.

To provide a basis for the discussion of the results, a proposed mechanism for the pyrolysis of diborane is given below. It is composed partly of steps previously set forth by workers in this field and partly of the authors' proposals.

$$B_2H_6 \rightleftarrows 2BH_3 \qquad (1)$$

$$BH_3 + B_2H_6 \longrightarrow B_3H_9 \qquad (2)$$

$$B_3H_9 \rightleftarrows B_3H_7 + H_2 \qquad (3)$$

$$B_3H_7 + B_2H_6 \longrightarrow B_4H_{10} + BH_3 \qquad (4)$$

$$B_3H_9 + B_2H_6 \longrightarrow B_5H_9 + 3H_2 \qquad (5)$$

$$B_4H_{10} \rightleftarrows B_3H_7 + BH_3 \qquad (6)$$

$$B_4H_{10} \rightleftarrows B_4H_8 + H_2 \qquad (7)$$

$$B_4H_8 + B_2H_6 \longrightarrow B_5H_{11} + BH_3 \qquad (8)$$

$$B_4H_8 + B_2H_6 \longrightarrow B_6H_{12} + H_2 \qquad (9)$$

$$B_6H_{12} \rightleftarrows B_6H_{10} + H_2 \qquad (10)$$

(34) It should be noted that because of a certain amount of mixing occurring at the contact surface, some of the reactant will not be heated at all. Consequently the values for starting material recovered will be somewhat high.

$$B_5H_{11} \rightleftarrows B_4H_8 + BH_3 \qquad (11)$$

$$B_3H_7 + B_4H_{10} \longrightarrow B_7H_{13} + 2H_2 \qquad (12)$$

$$B_7H_{13} \longrightarrow B_7H_{11} + H_2 \qquad (13)$$

$$nB_4H_8 \longrightarrow m(\text{solid}) + pH_2 \qquad (14)$$

The short reaction times available in this study require that the initial and propagating steps in the reaction mechanism be very fast. It is possible then that under "normal" pyrolysis conditions other slower reaction steps could contribute to the formation of products. However, it is reasonable to expect that in the latter case the fast reactions would also dominate.

Evidence to support this mechanism is found from the examination of the isotope effect occurring during pyrolysis. This was done in the following manner. Shock waves were run through mixtures of $B^{11}_2X_6$, X_2, and Ar at about the same shock strength $(X = H,D)$. These compounds contained various amounts of the isotope H. The products were trapped as before and the % H determined from their mass spectra. Unfortunately, the B_5X_{11} was present in amounts too small to be separated completely from B_5X_9. However, an upper limit for the % H in B_5X_{11} could be determined. To obtain the % H, the spectrum was run about 1 v. above the appearance potential of the parent peak. This automatically gave the distribution of ions containing all D, all D except 1 H, etc. In the cases where the parent peak was too weak for this procedure, corrections had to be applied for the various contributions to a peak. Because of the somewhat arbitrary nature of this correction, the resulting values are not as good as those of the first method in an absolute sense. However, they are as good for comparative purposes.
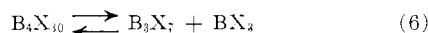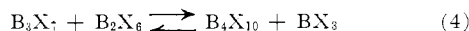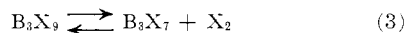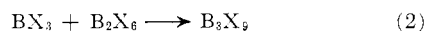
Two different isotopic contents were used in the runs made. The first, type I, employed mixtures of 10–20% deuterated diborane containing 1.6% H, 60–70% deuterium gas containing 1.01% H, and 10–20% argon. The average protium contents of the products of three runs under nearly the same conditions are: diborane, 1.4% H; tetraborane, 11% H; pentaborane-9, 1.0% H; pentaborane-11, <3% H; and hexaborane-10, 25% H. It is fairly evident that the protium which appears in the tetraborane and hexaborane is part of the protium lost by diborane. As the latter compound is in considerable excess, the total amount of protium lost is more than sufficient to account for that found.

The type II run was made in a mixture of 16% deuterated diborane containing 20% H, 60% deuterium gas containing 30.8% H, and 24% argon. The results were: residual diborane, 26% H; tetraborane, 30% H; pentaborane-9, 28% H; and hexaborane-10, 48% H. In this case complications arise as the diborane may gain protium by exchange with the hydrogen gas and this seems to have occurred.

The explanation of this striking example of the isotope effect is intimately connected with the mechanism of the reaction. Unfortunately, the unavailability of reaction times and the molecular parameters of some of the species involved render any rigorous theoretical consideration of this effect on the basis of the proposed mechanism virtually impossible. It may be observed, however, that the end result of the entire reaction is analogous to a process of isotopic enrichment. As the proposed mechanism consists of a series of steps, each of which may exhibit the normal or inverse isotope effect, the following considerations are enlightening.

Consider the hypothetical system in which only the reactions leading to the formation of tetraborane are allowed to occur. These are essentially 1, 2, 3, 4,

and 6, which may be written

$$B_2X_6 \xrightleftharpoons{} 2BX_3 \tag{1}$$

$$BX_3 + B_2X_6 \longrightarrow B_3X_9 \tag{2}$$

$$B_3X_9 \xrightleftharpoons{} B_3X_7 + X_2 \tag{3}$$

$$B_3X_7 + B_2X_6 \xrightleftharpoons{} B_4X_{10} + BX_3 \tag{4}$$

$$B_4X_{10} \xrightleftharpoons{} B_3X_7 + BX_3 \tag{6}$$

Initially let the system contain n moles of B_2H_6, n' moles of B_2D_6, m moles of H_2, and m' moles of D_2. Reaction is then allowed to occur at a certain temperature with no mixing of isotopic species until a steady state is reached. Provided 2, which is generally accepted as the rate-determining step in diborane pyrolysis, is a slow step with respect to the other reactions and diborane and hydrogen are in large excess, one can write the following equation for the protium content of tetraborane.

$$\frac{N}{1 - N} = \frac{k_2 K_3 K_4 m'}{k_2' K_3' K_4' m} \left[\frac{N_0}{1 - N_0}\right]^2$$

Here N is the mole fraction of H in the product, N_0 is the mole fraction of H in the diborane before reaction, K_i is the equilibrium constant for reaction i, where $i = 1, 3,$ and 4, k_2 is the rate constant for reaction 2, and the primes refer to parameters of the deuterated compounds. In general, the protium content of the product will not equal that of the reactants.

In an enrichment process, the final enrichment may be written in terms of an enrichment factor, R, defined by Evans[35] as

$$R = \frac{N/(1 - N)}{N_0/(1 - N_0)}$$

N and N_0 will have the same significance as above if the reactant diborane is considered as the original mixture and the products as the enriched or impoverished fractions. If there is more than one step in the process, R is the product of the enrichment factors for the individual steps. As the equation above for the protium content of tetraborane may be rearranged in a form equivalent to the equation for a process of enrichment (or impoverishment) with an enrichment factor

$$R = \frac{k_2 K_3 K_4 m'}{k_2' K_3' K_4' m} \left(\frac{N_0}{1 - N_0}\right)$$

the analogy of this system to a process of isotopic enrichment becomes evident.

An estimate of the expected enrichment on the basis of this model could be made if the k's and K's were known. As k_2/k_2' for D and T has been estimated as 1.6, 1.7 would be an acceptable value for H and D.[36] If K_1/K_1' is calculated from the vibrational frequencies contained in ref. 3 and 37, a value of 1.7 is obtained at 298°K., decreasing with higher temperatures. It is not unreasonable that K_3/K_3' and K_4/K_4' would have approximately the same value. If, in fact, one uses $k_2/k_2' = 1.7$ and $K_i/K_i' = 1.6$ and substitutes in the expression above values for N_0 and m'/m corresponding to the reactant mixtures used, a protium content of 10% is found for type I runs and 37% for type II as compared to observed values of 11 and 30%, respectively. Models similar to the proposed mechanism may also be set up for pentaborane-9 and -11 and hexaborane. Agreement here for both types of runs is as reasonable as with tetraborane. In the non-equilibrium system, products once formed can decompose and re-enter the reaction scheme. Therefore,

(35) R. D. Evans, "The Atomic Nucleus," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 269.

(36) J. S. Rigden and W. S. Koski, J. Am. Chem. Soc., **83**, 3037 (1961).

(37) R. C. Lord and E. Nielsen, J. Chem. Phys., **19**, 1 (1951).
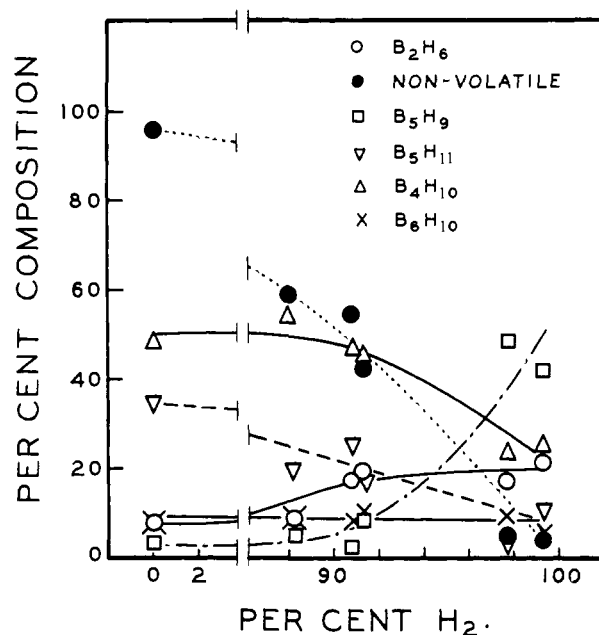

Fig. 8.—Product distribution vs. percentage hydrogen in reactant mixture for tetraborane runs. The product distributions are plotted as in Fig. 7. The incident shock temperature is about 400°K.

the possibility exists that a greater effective number of steps than those shown could be involved in the formation of a final product. In this case, even a small difference in the rate constants for the two isotopes would yield a measurable effect.

If nothing else, the agreement of the model with two different sets of data shows that this large, apparently abnormal, isotope effect is not at all unreasonable for this type of mechanism. In spite of the additional complexity, both in the mechanism and the reacting system, it is evident that the mechanism presented could very well yield the enrichments found.

Evidence that products once formed can undergo additional decomposition and reaction is obtained when the various possible products are themselves subjected to the conditions behind the shock wave. In contrast to the invariance of the product distribution with change in shock strength, a large effect in the distribution was observed on changing the concentration of initial reactants. The results are quite interesting when interpreted in light of the above mechanism.

Tetraborane was the compound examined most thoroughly as it was found that this compound produced larger amounts of the unstable species described above than did diborane. Figure 8 shows the product distributions as a function of the percentage H_2 in the initial mixture. The run with 0% H_2 contained 91% He to retain approximately the same conditions. The basic trends on H_2 addition can be explained as follows. Reaction 7 is probably faster than 6 in the absence of hydrogen.[12,13] Most likely a large excess of hydrogen would considerably slow the production of B_4H_8 which in turn would lower the production of solid. This corresponds to the observations. The reduction in the rate of 7 would allow 6 to contribute effectively to the decomposition at large H_2 concentrations. The presence of the hydrogen, however, would remove the B_3H_7 in reaction 3. The B_3H_9 thus formed accounts for the increase in B_5H_9 observed. The increasing contribution of 6 should also increase (B_2H_6)[38] due to

(38) For brevity in the discussion the symbol (X) will be used to denote the concentration of X in per cent of the total amount of volatile material recovered.
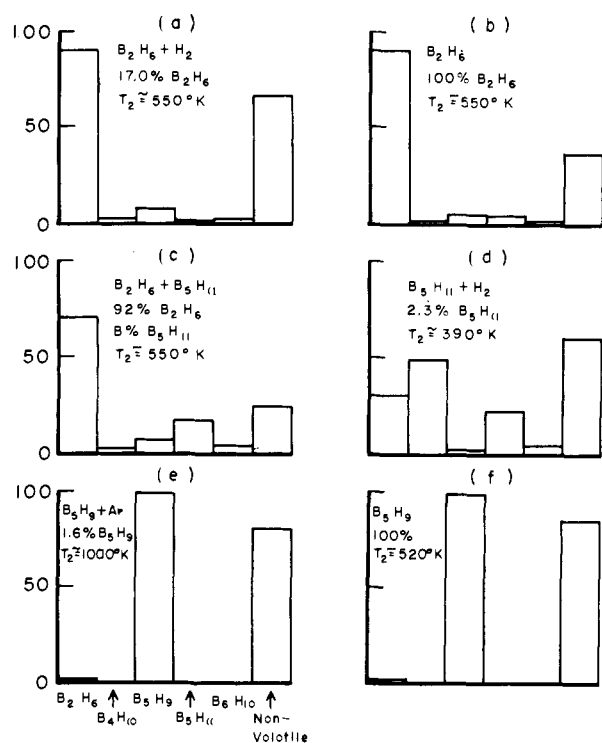
Fig. 9.—Composition profiles for selected runs. The product distributions are plotted as in Fig. 7 and the temperatures listed are for the gas behind the incident shock.

BH_3 recombination with increasing (H_2), and this too appears to be the case. Finally, (B_5H_{11}) decreases at high (H_2) in agreement with 8 while (B_6H_{10}) also seems to decrease slightly as indicated by 9 and 10.

As tetraborane systems produced by far the most unstable products, it is thought that tetraborane or an intermediate derived directly from it is involved in their formation. (B_6H_{12}) decreases with increasing (H_2) suggesting reaction 9 for its formation. The low concentrations of the heptaboranes were independent of (H_2) indicating their production by reactions 12 and 13.

In the search for new products, there was occasion to study briefly several other systems. Results of selected runs are shown in the composition profiles in Fig. 9. Shock waves in B_2H_6–H_2 mixtures show little change from B_2H_6–Ar mixtures (Fig. 9a) although hexaborane-12 and traces of heptaborane, which were never obtained using inert gas alone, were observed. Pure diborane (Fig. 9b) is also nearly the same except that considerably more B_5H_{11} and less solid is formed. This could be the result of changed reaction conditions but it is believed to result from the excess B_2H_6 eliminating some of the B_4H_8 via 8 and 9 thereby increasing (B_5H_{11})

and decreasing the solid. The fact that (B_6H_{10}) remains about the same implies that 8 is faster than 9. This may account for the fact the B_6H_{10} has not been prepared by pyrolysis without the formation of large amounts of B_5H_{11} in spite of the apparent stability of hexaborane when pure.

Figure 9d is the profile of a B_5H_{11}–H_2 run. In spite of the large concentration of H_2, 60% of the initial B_5H_{11} went to solid. This confirms that B_5H_{11} decomposes via 11 with the production of B_4H_8 and is thus unaffected by hydrogen concentration.

Figure 9c shows the results of a run with B_2H_6 and B_5H_{11}. The only marked change between this and pure B_2H_6 is an increase in (B_6H_{10}). B_5H_{11} decomposing via 11 yields higher B_4H_8 concentrations producing more B_6H_{10} and of course B_5H_{11}. It is interesting to note that in this case considerable B_6H_{12} was produced along with some heptaborane while with B_5H_{11}–H_2 none was produced.

It was found that the addition of a small amount of B_6H_{10} to a B_4H_{10} and H_2 run tripled the amount of B_6H_{12} produced. This suggests that 10 is reversible and much of the added B_6H_{10} was converted to B_6H_{12}.

The results of shocking B_5H_9 and Ar and pure B_5H_9 are shown in profiles 9e and f. For all practical purposes no volatile products are produced, although considerable amounts of solid are. As postulated in the mechanism, this strongly suggests that 5 is not reversible because, if it were, other products should be observed. A white-blue flash was observed with strong shocks in B_5H_9 which may indicate the presence of excited BH.[39] It is quite possible that the following reaction takes place.

$$B_5H_9 \longrightarrow BH^* + B_4H_8 \quad \text{solid}$$
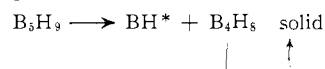
Although several specific steps in the proposed mechanism are still open to debate, it has been shown that the pyrolysis of diborane may be described as a series of competitive reactions and equilibria in which pentaborane-9 is formed by a different route from that of tetraborane and hexaborane and in which tetraborane is a precursor of hexaborane. The actual steps are consistent with the product distributions obtained by pyrolyzing various mixtures of the boron hydrides. Also hexaborane-12 and two heptaboranes were identified and it appears that hexaborane-12 is intermediate in the formation of hexaborane-10.

(39) G. Herzberg, "Molecular Spectra and Molecular Structure," Prentice–Hall, Inc., New York, N. Y., 1939.