Table V

Comparison of Bond Distances in $B_{10}H_{14}$, $B_{10}H_{13}(C_2H_5)$, and $B_{10}H_{13}I$

	Distance, A			
	$B_{10}H_{14}$[a]	$B_{10}H_{14}$[b]	$B_{10}H_{13}$-(C_2H_5)[c]	$B_{10}H_{13}I$
B_1–B_3	1.78	1.71	1.78	1.75
B_1–B_4 (B_1–B_2)	1.79	1.80	1.79	1.77
B_1–B_{10} (B_1–B_5)	1.74	1.78	1.77	1.77
B_3–B_4 (B_2–B_3)	1.81	1.78	1.78	1.77
B_3–B_8 (B_3–B_7)	1.74	1.77	1.745	1.74
B_4–B_8 (B_2–B_7)	1.74	1.80	1.79	1.80
B_4–B_9 (B_2–B_6)	1.73	1.72	1.71	1.73
B_4–B_{10} (B_2–B_5)	1.76	1.76	1.775	1.79
B_8–B_9 (B_6–B_7)	1.76	1.77	1.78	1.81
B_9–B_{10} (B_5–B_6)	1.78	1.77	1.78	1.78
B_5–B_{10}	2.01	2.01	1.96	2.01
B_7–B_8	2.01	2.01	1.98	1.93
Av esd	0.03	0.02	0.01	0.02

[a] J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Cryst.*, **3,** 436 (1950). [b] E. B. Moore, R. E. Dickerson, and W. N. Lipscomb, *J. Chem. Phys.*, **27,** 209 (1957). [c] A. Perloff, *Acta Cryst.*, **17,** 332 (1964).

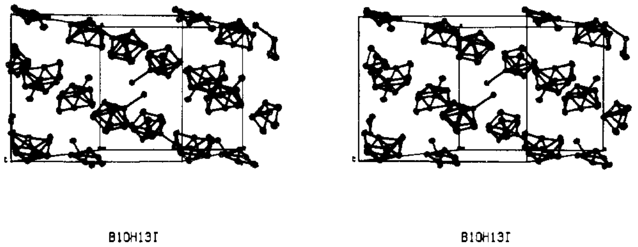

Figure 4.—Contents of one unit cell of $B_{10}H_{13}I$. The hydrogen atoms are not shown.

the B–B distances in $B_{10}H_{14}$,[13,15] $B_{10}H_{13}(C_2H_5)$,[16] and $B_{10}H_{13}I$. This comparison suggests that there are no important differences in B–B bond lengths among the three structures except possibly for the long B_5–B_{10} and B_7–B_8 bonds. The distances B_2–B_6 and B_4–B_9 appear consistently shorter in all three compounds. Interestingly, according to Lipscomb's three-center model of $B_{10}H_{14}$, this is the only two-center bond in the entire boron framework.

The average unbridged B–H distance is 1.20 (12) A as against that of 1.26 A in $B_{10}H_{14}$ and 1.11 A in $B_{10}H_{13}$-(C_2H_5). The average bridged B–H distance of 1.26 (13) A is closer to the value of 1.27 A observed in $B_{10}H_{13}$-(C_2H_5) than to that of 1.39 A in $B_{10}H_{14}$. The exact positions of the hydrogen atoms in this series of compounds must await a neutron diffraction investigation.

The crystal structure consists of the packing of discrete polyhedral cages of $B_{10}H_{13}I$ molecules which fall in sheets almost parallel to the (120) planes (see Figure 4). The iodine atoms protrude from the sheets, and pairs of iodines are in van der Waals contact at a distance of 4.3 A. The stacking of the sheets however is not entirely dependent on the I–I interactions, but on the I–H interactions as well. The cage opening in each molecule faces an iodine atom from a neighboring molecule, and the iodine seems to be in van der Waals contact with the bridge hydrogens of the former. The shortest I–H distances are ~3.4 A and are in good agreement with the sum of the van der Waals radii (3.35 A).

Acknowledgment.—We wish to thank Dr. M. Hillman of the Nuclear Engineering Department of Brookhaven National Laboratory for providing us with the crystals. We are also grateful to Mr. Sam J. La Placa for many useful suggestions. A. S. thanks the International Atomic Energy Agency for a Fellowship.

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[15] E. B. Moore, R. E. Dickerson, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 209 (1957).

[16] A. Perloff, *Acta Cryst.*, **17**, 332 (1964).

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Nuclear Magnetic Resonance Study of Aluminum Borohydride

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The nuclear magnetic resonance spectrum of aluminum borohydride has been studied at a temperature range −40 to 90°. A freshly distilled sample of $Al(BH_4)_3$ at room temperature has a single broad spectrum. Heating a sample in the liquid state leads to one of two changes in the nmr spectrum: (1) a reversible conversion from the broad spectrum to a quartet spectrum and (2) an irreversible conversion from a broad spectrum to a quartet spectrum. The experimental conditions contributing to these conversions are reported. A mechanism is proposed to account for the spectral observations and involves the formation of a new structure of $Al(BH_4)_3$.

Introduction

In exchange studies of aluminum borohydride with deuterium[2] and deuteriodiborane[3] results were obtained which might be explained on the basis of a structural change of the aluminum borohydride molecule when a sample is heated in the temperature range 50–80°. These results led us to examine critically the nuclear magnetic resonance spectrum of $Al(BH_4)_3$. Ogg and Ray[4] first reported the nmr spectrum of

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[1] Student participant sponsored by National Science Foundation Undergraduate Science Education Grant No. G-1210.

[2] P. C. Maybury and J. C. Larrabee, Abstracts of Papers, 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959, p 28M.

[3] P. C. Maybury and J. C. Larrabee, *Inorg. Chem.*, **2**, 885 (1963).

[4] R. A. Ogg and J. D. Ray, *Discussions Faraday Soc.*, **19**, 215 (1955).

aluminum borohydride, and found the spectrum to undergo a remarkable change when the substance was heated to moderate temperatures. Their results were interpreted in terms of the equilibrium

$$2Al(BH_4)_3 = Al_2B_4H_{18} + B_2H_6$$

It was stated that the "dimerized" form was observed to predominate at the higher temperatures which is evidenced by a sharp quartet spectrum, in contrast to the "normal" proton resonance spectrum of a single broad peak, with a width of half-maximum of about 300 cps, attributed to $Al(BH_4)_3$.

In view of these unusual and interesting spectral results, we have undertaken a further study of the aluminum borohydride magnetic resonance spectrum and associated temperature dependence as reported earlier. The results of our more detailed study have revealed certain differences from the earlier work and have permitted a more self-consistent interpretation of the phenomenon.

Experimental Section

Materials.—All samples of aluminum borohydride used in this study were obtained from a single source of the material, which was received from the National Aeronautics and Space Administration, Cleveland, Ohio. Purification of the hydride prior to reaction was accomplished by low-temperature fractionation of the compound to remove diborane and other impurities, followed by subsequent storage of the purified material at −80° until needed. In order to ensure that every sample of aluminum borohydride studied was in the "unmodified form" (which produces a broad nmr spectrum), all samples were expanded into the gas phase immediately prior to use. Benzene for use in studies to determine the concentration dependence of the spectral transformation was carefully distilled and was placed over sodium for storage.

Instrumentation and Procedures.—Early investigation was performed with the Varian DP-60 spectrometer at the University of Florida. Later work involved the use of our recently acquired Varian A-60 spectrometer which is equipped with the variable-temperature accessories. Most of the spectra were referenced externally to tetramethylsilane. Standard-wall, ground-glass sample tubes were utilized throughout and were modified for vacuum work and subsequent reuse *via* the addition of a 5-cm length of Pyrex tubing and standard taper. Great care was exercised to ensure uniformity and spinning symmetry of all tubes so constructed.

Pyrolysis Studies.—In order to evaluate more carefully the proposed equilibrium, a number of pyrolysis experiments were performed to obtain and quantify the decomposition products of aluminum borohydride. Samples of gaseous $Al(BH_4)_3$ were heated at 80° in 100-cc Pyrex bulbs for varying time intervals, after which the products were fractionated and their respective pressures were measured at ambient temperature in the constant volume of the system.

Temperature Dependence Studies.—The preliminary experiments of the temperature-induced transformation was performed with samples of $Al(BH_4)_3$ in the gaseous state. $Al(BH_4)_3$ at 20–30 cm pressure was condensed into 100-cc bulbs which had nmr side arms attached. After sealing the bulb from the vacuum system by torch, the sample was heated at 80° for 8–10 hr. Upon removal of the bulb from the bath, the nmr side arm was immersed in liquid N_2 to condense all bulb contents. The side arm was then warmed to −80° to allow any diborane present to volatilize and then the side arm was sealed off by torch for nmr analysis. It was subsequently discovered that this time-dependent conversion could be considerably increased in rate when the sample was heated at elevated temperatures in the liquid state. Accordingly, subsequent samples were prepared by simply filling an nmr sample tube from the purified hydride storage, after expansion into the gas phase, sealing the tube off from the vacuum system, and then heating the sample as before.

Previous reference[4] to a purely temperature-dependent modification of samples displaying the multiplet structure with decreasing temperature caused us to examine carefully proton spectra obtained for aluminum borohydride above and below ambient conditions with both "normal" and "modified" samples. Tubes were replaced with ethylene glycol for temperature and homogeneity adjustment at the elevated temperatures so as to limit the acceleration of the phenomenon by the simultaneous time-dependent process. Spectra were determined at each 10° interval from 30 to 90° for samples of "normal" hydride and to −40° for samples introduced in the quartet form. The samples studied at temperatures higher than 60° were filled with nitrogen at 30 cm pressure in order to retard boiling which interfered with the spectra. Methanol was used for low-temperature spectrometer adjustment. A 4-cps sweep rate provided the best compromise between resolution and exposure of the sample.

Gaseous-State Study.—The high-pressure sample, required to study the nmr spectrum in the vapor state, was prepared on the vacuum system by condensation of the required quantity of hydride into a sample tube followed by partial condensation of argon gas with liquid nitrogen. The tube was then sealed off from the system and slowly allowed to return to room temperature. The final pressure in the tube was estimated to be 5 atm.

Solvent Effect.—The hydride–benzene mixtures were prepared by pressure ratios of the benzene and hydride vapors in a known volume on the vacuum system, the resulting mixture being completely condensed into a sample tube and heated as previously outlined for pure samples. Several series of benzene–hydride mixtures were analyzed, holding either concentration or reaction time constant while observing the effect of varying the other.

Chemical Shift and Separation Studies.—Multiplet shift and separation with temperature were studied using benzene as an internal reference. A benzene–hydride sample was first analyzed at 25° to verify the characteristic broad continuum of normal $Al(BH_4)_3$. As expected, the benzene resonance remained a sharp singlet, indicating little or no sample–solvent interaction. The sample was then examined at 70° in conjunction with the variable-temperature apparatus and the spectrum recorded. The tube was then removed to a constant-temperature bath at 80° and the spectra at 25 and 70° were determined after a 30-min heating period. The sample was again immersed in the bath and heated an additional 60 min. Spectra were again determined at the indicated temperatures.

Infrared Studies.—A special Pyrex gas cell was constructed for the infrared investigations. The cell was equipped with a stopcock and standard taper for connection to the vacuum system and with a side arm of 10-cc volume separated from the cell body with another stopcock to serve as a reaction vessel. The cell was prepared with NaCl windows and had a path length of 5 cm. A small ~~oven~~ was constructed to warm the side arm for reaction. Hydride samples were condensed into the cell–side arm combination and the spectrum was recorded. The contents of the cell were then condensed into the side arm and heated for 8–10 hr. The intervening stopcock was then opened, and the spectrum was again recorded. All spectra were obtained with a Perkin-Elmer Model 337 spectrophotometer.

Results

Results of the decomposition experiments are shown in Table I.

It may be observed that only trace quantities of B_2H_6 were detected. Similar evidence was obtained from the infrared investigations, the spectrum in the 2.5–18.0-μ region remaining invariant to reactions attempted in the cell–side arm unit; only after prolonged periods of heating the hydride vapor could the characteristic

TABLE I

PYROLYSIS OF ALUMINUM BOROHYDRIDE AT 80°

Heating time, hr	Initial pressure (25°), cm $Al(BH_4)_3$	Final pressure (25°), cm $Al(BH_4)_3$	Final pressure (25°), cm B_2H_6
6	30.00	29.70	0.15
24	19.27	19.20	0.00
48	13.25	11.98	0.17

bands of diborane be distinguished. Several reactions were attempted using a heated cell as a reaction vessel but were unsuccessful as a result of increased window contamination by the hydride at elevated temperatures.

The proton resonance spectra obtained with samples of $Al(BH_4)_3$ heated in the gas phase were qualitatively identical with those of samples heated in the liquid phase. The transformations were followed only for the liquid phase because the rate of transformation was more conveniently studied and permitted a more meaningful comparison with the spectra obtained in benzene solution. Thus the results that are tabulated in this paper are based upon studies carried out in the liquid phase.

Proton resonance spectra obtained with the bath-reacted sample at 80° at various reaction times are given in Figure 1 (A–E). The broad singlet is shown in Figure 1A but begins to show definite structure after 25 min in the bath as seen in Figure 1B. Transformation continues with reaction time as evidenced in Figure 1C–E recorded at reaction times of 45, 70, and 110 min, respectively. Once modified, samples were observed to retain the quartet structure indefinitely when left in the sealed sample tubes. Under no circumstances could reversion to the broad continuum be accomplished. Prolonged treatment of several samples at cryogenic temperatures had no effect once the sample regained room temperature. The transformation appears to be extremely sensitive to experimental conditions. Cooling the tube too rapidly while attempting to quench the reaction had the effect of damping the multiplet; best results were obtained when the sample tube was removed from the bath and simply laid aside to cool for 2–3 min. The sample could then be wiped free of oil and analyzed without further mishap. Liquid samples, prepared from the purified source, were noted to transform at room temperature when left unattended over a period of 6–8 weeks to the multiplet structure.

A sample, known to give the sharp quartet structure, was broken in the vacuum system and its contents allowed to vaporize completely for 10–20 min. The material was then recondensed into a second sample tube, sealed off, and the spectrum redetermined. It was interesting to note that the spectrum obtained was the broad continuum.

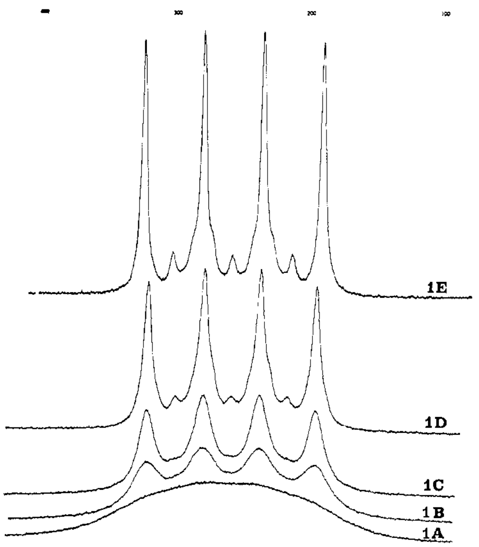


Figure 1.—Nuclear magnetic resonance spectra of $Al(BH_4)_3$ heated at 80° for: (A) 0 min (room-temperature spectrum), (B) 25 min, (C) 45 min, (D) 70 min, (E) 110 min.

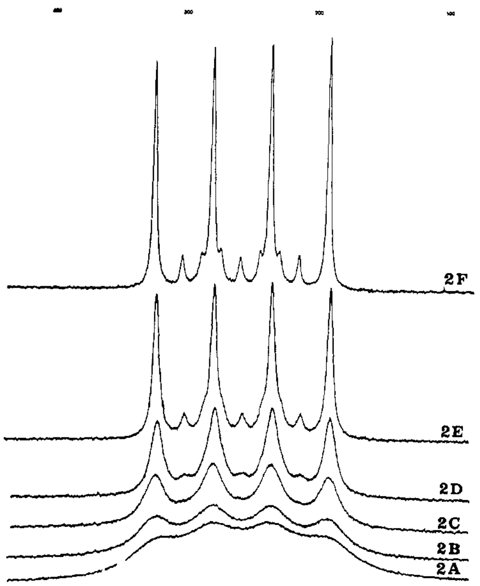


Figure 2.—Nuclear magnetic resonance spectra of $Al(BH_4)_3$ with temperature probe at: (A) 40°, (B) 50°, (C) 60°, (D) 70°, (E) 80°, (F) 90°.

Figure 2 illustrates the effect of increased probe temperature on a sample having a spectrum at 25° as in Figure 1A. Figure 2 (A–F) indicates that some instantaneous modification does occur and is readily apparent at a probe temperature of 40°. The temperature-dependent equilibrium increases in importance as the sample is heated through 50, 60, 70, 80, and 90° as seen in Figure 2B–F. At 90° the transformation is practically 100% achieved. Opposite but nearly parallel results were found for the modified sample exposed to decreasing probe temperatures as shown in Figure 3 (A–D). Figure 3A shows the sample at the normal operating temperature of 35°. At 0° the multiplet is visibly damped as seen in Figure 3B. Positive quenching is observed at −20° (Figure 3C), while at −40° the return to the broad singlet is complete as evidenced in Figure 3D.

Figure 4 is representative of samples prepared for coupling and shift measurements, the region scanned being offset so as to include the benzene resonance and several peaks of the quartet in a 500-c sweep width, rather than 1000 c as shown here. Duplicate spectra

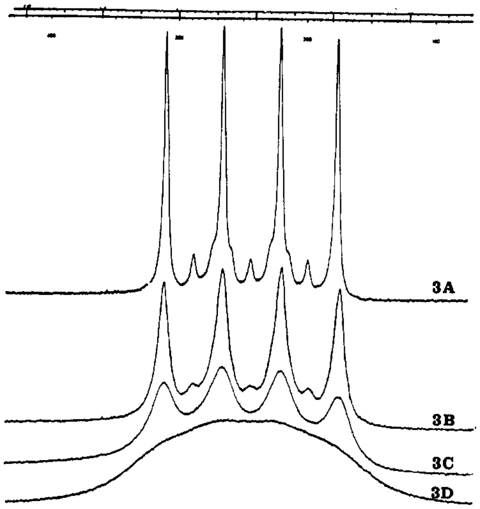


Figure 3.—Nuclear magnetic resonance spectra of modified $Al(BH_4)_3$ with temperature probe at: (A) 35°, (B) 0°, (C) −20°, (D) −40°.

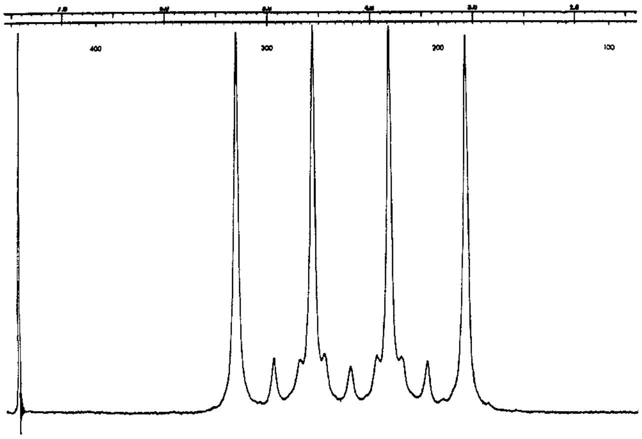


Figure 4.—Nuclear magnetic resonance spectrum of a solution of benzene and modified $Al(BH_4)_3$.

were swept at 1 cps following final adjustment of field homogeneity at the sample relative to the benzene singlet. Results of the measurements are given in Table II indexed to the center of the band.

TABLE II

Sample no.	Reaction time (80°), min	Probe temp, °C	Shift, cps	Multiplet sepn, cps
E-3	0	70	256.1	89.3
E-6	30	25	259.9	89.5
E-8	30	70	256.0	88.9
E-10	90	70	257.9	89.1
E-13, 14	90	25	259.3	89.3

The chemical shift of the strong quartet appears to be only slightly temperature dependent, exhibiting approximately 1.4-cps upfield shift with the 45° temperature change. Separation changes only *ca.* 0.2 cps within the same temperature interval. The shift difference between the probe-heated sample and the 90-min bath-heated (80°) sample is *ca.* 2 cps at 70°. Practically no difference in the values of the multiplet separation was noted. A comparison of the probe-heated sample to the sample heated for 30 min at 80° and recorded at a probe temperature of 70° gave no difference in chemical shift, although the separation dropped *ca.* 0.4 cps when the sample was run at the reduced temperature. The shift at 25° increased to 259.9 cps, or about 4 cps over the 70° recorded spectrum. Multiplet separation returned to *ca.* 89.3 cps when the sample was heated in the bath for the extra hour, perhaps indicating the sample heated at 80° for 30 min and recorded at 70° probe temperature to be nonrepresentative.

Several experiments were carried out with mixtures of aluminum borohydride and benzene. Mixtures containing 80, 60, and 20 mole % of $Al(BH_4)_3$ were heated for 1 hr at 80° in the liquid state and the nmr spectra were recorded. Each of the three samples was partially converted from the broad to the quartet form and the extent of conversion decreased from the 80% sample to the 20% sample. The 80% sample also evidenced less conversion than obtained by a pure sample of $Al(BH_4)_3$ under similar conditions.

Figure 5 is the vapor-phase proton spectrum of a sample that was heated at 80° for sufficient time so as to yield the quartet structure. Although the small number of protons results in a poor signal-to-noise ratio, the broad continuum is clearly in evidence.

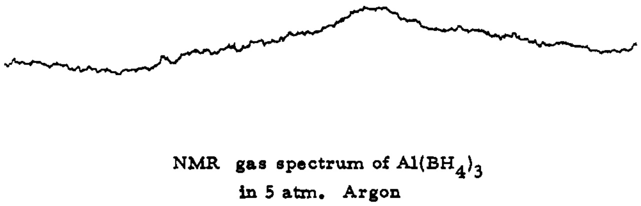


Figure 5.—Nuclear magnetic resonance gas-phase spectrum of $Al(BH_4)_3$ in 5 atm of argon.

Discussion

The nuclear magnetic resonance spectra of aluminum borohydride obtained in our laboratory at room temperature are essentially in agreement with the work of Ogg and Ray.[4] However, there are some differences noted in the higher temperature studies.

According to the earlier work,[4] liquid aluminum borohydride has a completely structureless proton resonance spectrum in the entire temperature range practically available (−64 to +44°). Our results show that the quartet structure begins to appear around +40° (Figure 2A) and increases in separation and height as the probe temperature is raised (Figure 2A–F). The fact that the "broad" form of aluminum borohydride is temperature dependent at higher temperatures would indicate that internal rotation of the borohydride groups might be possible. The continuous breaking and re-forming of the bridge bonds to aluminum which would occur during free rotation of the borohydride groups would result in spin–spin decoupling of the protons with the Al^{27} nucleus and the characteristic quartet of the borohydride group would appear. At temperatures lower than 40°, apparently the internal rotation of borohydride groups is markedly restricted and allows the borohydride groups to be spin–spin coupled to the central aluminum atom. The appearance of the broad continuum spectrum (Figure 1A) is thus a result of the spin–spin interaction of the borohydride groups and the Al^{27} nuclei with broadening due to the electric field gradient interactions with the large electric quadrupole moment of the Al^{27} nucleus. In order to account for the equivalency of both the terminal and bridge hydrogens, Ogg and Ray proposed a nonclassical penetration of the proton system through the hindering potential barriers, *i.e.*, the quantum mechanical "tunnel effect." At this point there is a definite need to maintain the tunnel exchange of protons as a suitable explanation of the equivalency of the protons in the molecule and at the same time account for the spin–spin interaction with the aluminum nucleus.

In the earlier work,[4] it was found that a quartet spectrum could be obtained when $Al(BH_4)_3$ was heated at 80° for 10 hr in the gaseous state and rapidly condensed with liquid N_2. When this sample was allowed to stand at room temperature for several days, they reported that the spectra would revert back to the broad continuum. However, when they condensed the sample with Dry Ice in the side-tip and then sealed it off, this reversion did not take place. Their explanation for these results was based upon the proposed equilibrium

$$2Al(BH_4)_3 = Al_2B_4H_{18} + B_2H_6$$

which being reversible would produce predominantly $Al(BH_4)_3$ at room temperature if the B_2H_6 were not removed. In our liquid-phase studies this equilibrium would not be important as the small gas volume available would prevent the formation of any significant quantity of diborane. The question as to whether aluminum borohydride yields B_2H_6 or H_2 upon heating might depend upon a specific catalyst in the system. However, we were unable to detect any appreciable amount of diborane formation either in the gas phase or the liquid phase. Further, it is apparent that reversion back to the broad form occurred only in those cases where $Al(BH_4)_3$ was allowed to remain in the gaseous state after heating. In our work, when aluminum borohydride was heated in the liquid state and then kept in a sealed sample tube in the liquid state, there was no reversion of the quartet spectrum to the broad continuum. This is consistent with the results of the sealed-off samples in the earlier work.[4]

It is interesting to note that samples of aluminum borohydride that were heated for several hours gave sharp quartet spectra that were identical with the spectra obtained when unmodified samples were heated by the temperature probe during the recording of their spectra. This latter transformation, from a broad continuum to a sharp quartet, was instantaneous; reversion to the broad form took place upon removal from the temperature probe, as evidenced by the fact that the broad form is obtained when the spectrum is reexamined (within 5 min) when the probe reaches room temperature.

Examination of the data in Table II clearly shows that the spectra obtained for aluminum borohydride with two different histories are practically identical in terms of chemical shift and coupling constants. This seems to indicate that both samples under the respective measurement conditions must have quite similar if not identical arrangements of hydrogen atoms surrounding each boron atom.

The results shown in Figure 3 are particularly interesting as they depict the effect of decreasing the temperature of samples which originally displayed the quartet structure. A progressive broadening to the single peak is seen to occur. This apparently corresponds to a decrease in the internal rotation of the borohydride ions and at the lowest temperature there exists spin–spin coupling with the Al^{27} nucleus. The temperature-induced conversion evidenced here is only temporary since the fourfold structure returns when the probe temperature rises to the normal operating temperature.

A similar conversion of the "quartet" form to the "broad" form is carried out by simply allowing the sample to expand into the gaseous state for 10 min or longer at room temperature. Conversion due to expansion is not characterized by a rapid return to the quartet structure but requires 6–8 weeks at 20° or 2 hr at 80° to form the quartet structure.

The broad single peak obtained in the high-pressure gas-phase study is consistent with the spectra obtained for samples previously expanded into the gas phase. It is for this reason that most investigators have reported the characteristic nmr spectrum of aluminum borohydride to be a single broad peak.

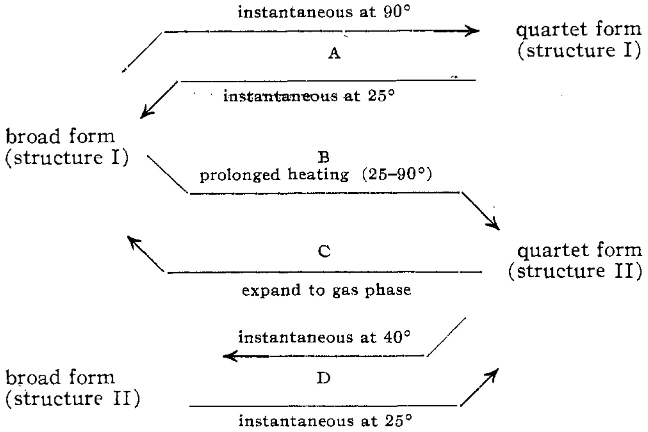
The several experiments carried out with benzene solution definitely have shown that the rate of conversion from the broad form to the quartet form is reduced when the concentration of $Al(BH_4)_3$ is lowered. The concentration effect is consistent with the longer times required for conversion when carried out in the gaseous state. Preliminary kinetic studies in our laboratories have confirmed the fact that the conversion is dependent upon concentration and temperature.

The spectrum in Figure 4 clearly shows the resolution of the splitting due to the naturally occurring B^{10} isotope which has a spin quantum number of 3 and yields the seven smaller peaks.

The experimental conditions responsible for the conversions between the broad form and the quartet forms are conveniently summarized in Scheme I.

Paths A and D are temperature-dependent reversible processes involving BH_4 rotation but not structural changes. Path B represents an irreversible process in pure liquid and in benzene solution, while C corresponds to the conversion of the quartet form to the broad form by expansion of the sample into the gas phase. Examination of the various conversion conditions shows that free rotation of the borohydride

SCHEME I



groups occurs at a lower temperature for structure II than for structure I. It is also observed that the instantaneously established conversion to a quartet form (path A) involves rotation at a rate much faster than the tunneling of the protons.

Two possible models have been proposed for the structure of aluminum borohydride, a prismatic structure and an octahedral structure, and they are shown in Figure 6. These models were first discussed by Longuet-Higgins.[5] Electron diffraction data obtained by Bauer[6] were shown to be more compatible with the prismatic model. Similar results favoring the prismatic model were obtained by infrared absorption studies carried out by Price.[7] According to Price it is difficult to reconcile the most plausible values for bond angles and distances with a regular octahedral model. The octahedral bond angles would have to be considerably distorted and this would require considerable energy.

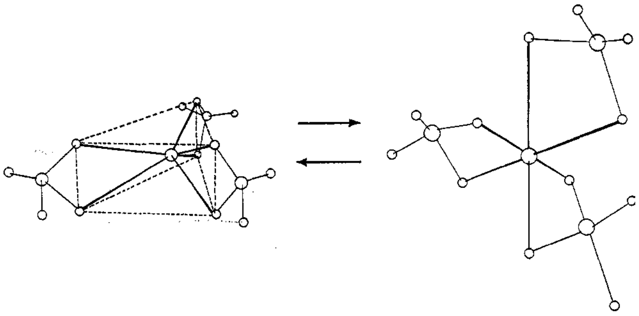


Figure 6.—Models for aluminum borohydride: left, prismatic; right, octahedral.

Although it is impossible for us to determine the correct structure for aluminum borohydride in our work, it is of interest to compare our results with the aforementioned models. Both the electron diffraction and the infrared studies were obtained on gas-phase samples of aluminum borohydride. According to our work aluminum borohydride exhibits the broad nmr spectrum in the gas phase and this would identify the broad form (structure I) with the prismatic model. None of these structural studies has been carried out on liquid samples of aluminum borohydride. Our experiments indicate that some modification of the aluminum borohydride structure occurs in the liquid state and this could represent a change from the prismatic structure to the octahedral structure; however, on the basis of our work we are unable to make a structural assignment of the modified form.

In order to obtain additional information concerning the structural change encountered in our nmr experiments, we are carrying out additional research including a kinetic study of the conversion from the broad form (structure II) and a study of the two structures by nmr in the solid state. It is hoped that these studies will help to elucidate the several structures of aluminum borohydride involved in this research.

Acknowledgments.—We wish to thank Professor Wallace Brey of the University of Florida for helpful advice and for carrying out some of the nmr spectra and Dr. James D. Ray for suggestions concerning the interpretation of our results.

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(5) H. C. Longuet-Higgins, *J. Chem. Soc.*, 14, 139 (1946).

(6) S. H. Bauer, *J. Am. Chem. Soc.*, **72**, 622 (1950).

(7) W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1949).