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The Hydrolysis of Aqueous Hydroborate

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The kinetics of the hydrolysis of hydroborate has been studied over the pH range 3.8–14. The rate may be represented by the expression: $-d(BH_4^-)/dt = k_1(H^+)(BH_4^-) + k_2(BH_4^-)$, where $k_1 = 2.18 \times 10^{11}T$ (exp $- 4000/T$) M^{-1} min.$^{-1}$ and $k_2 = 1.72 \times 10^7 T$ (exp $- 10{,}380/T$) min.$^{-1}$. No evidence was found for stepwise hydrolysis of the hydroborate ion. The experimental data which have a bearing on the rate-determining step of the acid-catalyzed hydrolysis (k_1) are discussed. The data are consistent with a short-lived intermediate of composition BH_5 which decomposes to BH_3 and H_2.

Introduction

The hydrolysis of hydroborate

$$BH_4^- + H^+ + 3H_2O \longrightarrow 4H_2 + H_3BO_3 \qquad (1)$$

has been shown by Davis and Swain[2] to be an example of general acid catalysis. We have studied the kinetics of this reaction and have evaluated the heats and entropies of activation for the reaction paths in which hydroborate reacts with hydrogen ion and with water.

The rate constant reported by Kilpatrick and McKinney[3] for the reaction with hydrogen ion in solutions *ca.* 1 M in H^+ is lower by a factor of 10^6 than that reported by other investigators for solutions of pH > 7.5. We therefore extended our study of the reaction to as low a pH as conveniently possible (pH 3.8) to see if anything unusual occurs at lower pH values which might reconcile the data.

Because various workers[4] have reported that hydroborate hydrolyzes stepwise with formation of intermediates such as BH_3OH^-, we attempted to find supporting evidence for these claims.

The rate determining step of reaction of the hydrogen ion with the hydroborate ion is of considerable interest. Therefore we have examined and interpreted the available experimental data (including kinetic isotope studies which we report here) which have a bearing on this rate-determining step.

Experimental

Kinetics in Alkaline Solution.—The hydrolysis rate in alkaline solutions was measured by following the concentration of hydroborate in solutions of ionic strength 1.0 which either were buffered or contained a large excess of hydroxide. The hydroborate concentration was determined by analyzing aliquots by the iodate method.[5] All pH measurements were made with a Beckman pH meter, using a Type E glass electrode. A saturated calcium hydroxide solution was used as a pH standard.[6]

Metal Hydrides potassium hydroborate (>97%) was used without further purification. The buffered solutions were prepared using appropriate mixtures of K_2HPO_4 and K_3PO_4. The hydroxide solutions were prepared by dilution of a potassium hydroxide solution from which carbonate had been eliminated by addition of a slight excess of barium chloride. The ionic strength was adjusted to 1.0 with potassium chloride. Measurements were made at 10.5, 25.0, 37.9, and 49.7° using a thermostated bath which was regulated to ±0.1°.

The constants in the rate law

$$-\frac{d \ln (BH_4^-)}{dt} = k_1(H^+) + k_2 \qquad (2)$$

were evaluated by plotting $(H^+)/k'$ *vs.* $1/k'$, where $k' = -d \ln (BH_4^-)/dt$. The intercepts of the straight lines in such plots are equal to the reciprocals of k_1 and k_2. A plot of this type is given in Fig. 1, in which the hydrogen ion concentrations were obtained from the pH data. The antilogarithm of −pH was taken as the hydrogen ion concentration. Equation 2 may be rewritten

$$-\frac{d \ln (BH_4^-)}{dt} = \frac{k_a}{(OH^-)} + k_2 \qquad (3)$$

where k_a is equal to k_1 multiplied by the ion product for water. The constants k_a and k_2 were evaluated from a plot of $1/k'(OH^-)$ *vs.* $1/k^-$ (see Fig. 2).

Kinetics in Acid Solution.—The hydrolysis rate in acid solution was measured by determining the change in concentration of hydroborate when a hydroborate solution and

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[1] Taken from a thesis submitted by R. E. Mesmer in partial satisfaction of the requirements of the Ph.D. degree, 1962.

[2] R. E. Davis and C. G. Swain, *J. Am. Chem. Soc.*, **82**, 5949 (1960).

[3] M. Kilpatrick and C. E. McKinney, Jr., *ibid.*, **72**, 5474 (1950).

[4] J. Goubeau and H. Kallfass, *Z. anorg. allgem. Chem.*, **299**, 160 (1959); V. I. Mikheeva and W. Yu. Surs, *Dokl. Akad. Nauk SSSR*, **91**, 1133 (1953), *Chem. Abstr.*, **48**, 491 (1954); V. I. Mikheeva and V. Yu. Surs, *Dokl. Akad. Nauk SSSR*, **93**, 67 (1953), *Chem. Abstr.*, **48**, 7470 (1954); V. I. Mikheeva and E. M. Fedneva, *Dokl. Akad. Nauk SSSR*, **101**, 99 (1955), *Chem. Abstr.*, **49**, 10109 (1955).

[5] E. H. Jensen, "A Study of Sodium Borohydride with Special Reference to its Application in Organic Chemistry," Nyt Forsick Forlag, Arnold Bush, Copenhagen, 1954.

[6] R. G. Bates, V. E. Bower, and E. R. Smith, *J. Res. Natl. Bur. Std.*, **56**, 305 (1956).

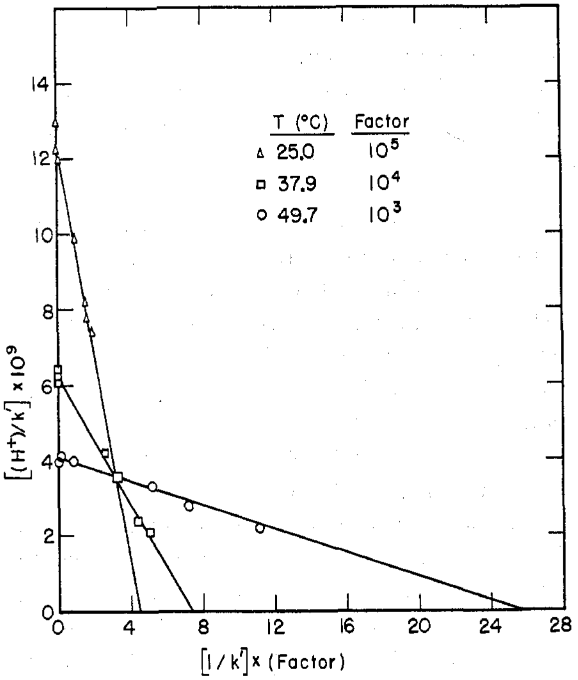

Fig. 1.—Plots for evaluation of rate constants k_1 and k_2, using pH data.

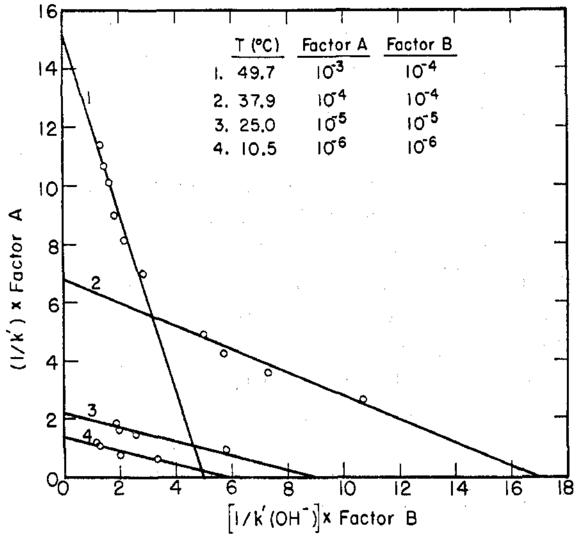

Fig. 2.—Plots for evaluation of rate constants k_a and k_2, using OH^- concentration data.

a buffer were mixed in a flow apparatus and the flowing mixture was passed into a reaction-quenching solution of sodium hydroxide. The flow apparatus was designed so that the hydroborate and buffer solutions were turbulently mixed at the top of a glass tube through which the reacting solution passed into a beaker of vigorously stirred sodium hydroxide solution. The reaction time was calculated from the flow rate and the volume of the reaction tube. The hydroborate was determined by the iodate method.

By assuming that the reaction rate could be expressed by eq. 2 (neglecting k_2), the rate constants tabulated in Table I were calculated.

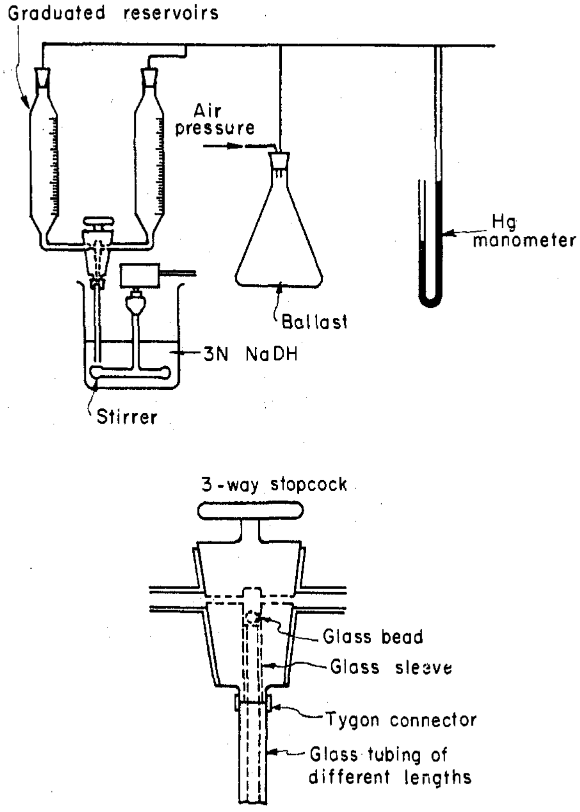

Figure 3.

TABLE I

RATE CONSTANTS MEASURED BY FLOW METHOD

pH	$k_1(M^{-1}\ \text{min.}^{-1} \times 10^7)$
6.88	4.2
6.53	4.4[a]
5.02	5.4[b]
3.83	>1.6[c]
0.0	$>10^{-3}$

[a] Average of five runs. [b] Average of three runs. [c] Average of two runs during which foaming occurred in the reaction zone.

Proton Magnetic Resonance.—A Varian V-4311 high resolution n.m.r. spectrometer (60 Mc.) was used in an attempt to find hydrogen-containing species other than BH_4^- and H_2O in partially decomposed hydroborate solutions. Solutions originally 1 M in hydroborate were allowed to hydrolyze until 55 and 30% of the reducing capacity remained. Neither solution gave a spectrum with any new features. It is estimated that a species such as $BH_2(OH)_2^-$ could have been detected at a concentration of 0.03 M.

Kinetic Isotope Effects.—The relative rates of hydrolysis of BH_4^- and BD_4^- were measured by both a competitive method and an absolute rate method. In the competitive method, an equimolar solution of KBH_4 and KBD_4[7] was allowed to hydrolyze for a certain time and then the evolved hydrogen and the remaining substrate were analyzed for deuterium. The data were treated by the method of

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(7) R. E. Mesmer and W. L. Jolly, *J. Am. Chem. Soc.*, in press.

(8) J. Bigeleisen and M. Wolfsberg, "Advances in Chemical Physics," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 15–76.

Bigeleisen and Wolfsberg.[8] The results are given in Table II. In the absolute rate method, separate solutions of KBH_4 and KBD_4, otherwise identical, were allowed to hydrolyze and the concentrations were followed as a function of time. The results are given in Table III.

TABLE II

KINETIC ISOTOPE EFFECTS OBTAINED BY "COMPETITIVE" METHOD

			$k_{BH_4^-}/k_{BD_4^-}$	
Solvent	t, °C.	pH or pD	From substrate analysis	From product analysis
H_2O	25	10.00	0.74	0.72
H_2O	50	9.80	.81	.81
D_2O	50	10.25	.74	.74

TABLE III

KINETIC ISOTOPE EFFECTS OBTAINED BY "ABSOLUTE RATE" METHOD

Solvent	t, °C.	pH or pD	Reducing agent	$k_{BH_4^-}/k_{BD_4^-}$
H_2O	50	9.80	BH_4^-	0.77
H_2O	50	9.80	BD_4^-	
D_2O	25	10.08	BH_4^-	.62
D_2O	25	10.08	BD_4^-	

It will be noted that essentially the same $k_{BH_4^-}/k_{BD_4^-}$ ratio for H_2O solutions at 50° was obtained by the two methods (0.81 and 0.77). The $k_{BH_4^-}/k_{BD_4^-}$ ratio for either solvent increased on going from 25 to 50°. The ratio was consistently higher in H_2O than in D_2O. In all cases, the ratio was appreciably less than 1.00, corresponding to an "inverse" isotope effect. Similar ratios, although not as a function of solvent and temperature, have been obtained and discussed by others.[9,10]

The rates of hydrolysis of KBH_4 in both H_2O and D_2O were measured in order to determine the solvent isotope effect. The runs were carried out simultaneously in buffered solutions at 25°. By assuming that the pH meter reading in the D_2O solution may be converted to pD by adding 0.4, we calculate 1.56 for the k_{H_2O}/k_{D_2O} ratio.[11] We cannot explain why our value differs markedly from those reported by Davis, *et al.*,[9] who reported ratios of 3.0 and 4.9. The reaction of hydroborate with ordinary phenol is four times faster than the reaction with phenol in which the active hydrogen has been replaced by deuterium.[10]

Results and Conclusions

Kinetic Studies.—From the plots shown in Fig. 1 (in which pH data were used), values for the rate constants k_1 and k_2 were obtained for the temperatures 25.0, 37.9, and 49.7°. From these data the following heats and entropies of activation were calculated: for k_1, $\Delta H_1{}^\ddagger = 7.9 \pm 1$ kcal./mole, $\Delta S_1{}^\ddagger = -4.0 \pm 3$ e.u.; for k_2, $\Delta H_2{}^\ddagger = 22.1 \pm 1$ kcal./mole, $\Delta S_2{}^\ddagger = -18.4 \pm 3$ e.u.

From the plots shown in Fig. 2 (in which OH^- concentration data were used), values for k_a and k_2 were obtained for the temperatures 10.5, 25.0, 37.9, and 49.7°. From these data the following heats and entropies of activation were calculated: for k_a, $\Delta H_a{}^\ddagger = 21.4 \pm 1$ kcal./mole, $\Delta S_a{}^\ddagger = -22.2 \pm 3$ e.u.; for k_2, $\Delta H_2{}^\ddagger = 20.6 \pm 1$ kcal./mole, $\Delta S_2{}^\ddagger = -22.3 \pm 3$ e.u. By subtracting the heat and entropy of ionization of water[12] from the corresponding activation parameters for k_a, we calculate[13] the following activation parameters for k_1: $\Delta H_1{}^\ddagger = 8.0 \pm 1$ kcal./mole, $\Delta S_1{}^\ddagger = -3.0 \pm 3$ e.u. These values are fortuitously close to the corresponding values obtained from pH data.

The average values of $\Delta H_1{}^\ddagger$ and $\Delta S_1{}^\ddagger$ (7.95 kcal./mole and −3.5 e.u., respectively) correspond to the analytical expression.

$$k_1 = 2.18 \times 10^{11} T(\exp - 4000/T) M^{-1}\ \text{min.}^{-1}$$

From this we calculate $k_1 = 9.7 \times 10^7\ M^{-1}$ min.$^{-1}$ at 25°. Our values for $\Delta H_1{}^\ddagger$ and $\Delta S_1{}^\ddagger$ are quite close to the corresponding quantities which may be calculated from the data of Pecsok,[14] *i.e.*, 9.0 kcal./mole and −4 e.u., respectively. We believe the values of $\Delta H_2{}^\ddagger$ and $\Delta S_2{}^\ddagger$ obtained from the OH^- concentration data are more reliable than, although in fair agreement with, the values obtained from the pH data. The former values correspond to the expression

$$k_2 = 1.72 \times 10^7 T(\exp - 10{,}380/T)\ \text{min.}^{-1}$$

From this we calculate $k_2 = 3.9 \times 10^{-6}$ min.$^{-1}$ at 25°.

According to the Brönsted catalysis law,[15] acid-catalyzed reactions that differ only in the reacting acids have free energies of activation that differ by the quantity $\alpha\Delta(\Delta F^0)$, where α is a constant characteristic of the type reaction and $\Delta\ (\Delta F^0)$ is the difference between the free energies of ionization of the acids. As a corollary of this

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[9] R. E. Davis and C. L. Kibby, *J. Am. Chem. Soc.*, **82**, 5950 (1960); R. E. Davis, E. Bromels, and C. L. Kibby, unpublished data.

[10] R. E. Dessy, E. Grannen, and Y. Okazumi, Paper 62 presented before the Division of Organic Chemistry at the 138th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1960 (p. 32-P, Abstracts of Papers). See *Chem. Eng. News*, **38**, 53 (Sept. 19, 1960); R. E. Dessy and E. Granner, Jr., *J. Am. Chem. Soc.*, **83**, 3953 (1961).

[11] P. K. Glasoe and F. A. Long, *ibid.*, **64**, 188 (1960).

[12] W. M. Latimer, "Oxidation Potentials," 2nd ed., Prentice-Hall, Englewood Cliffs, N. J., 1952.

[13] In so doing, we neglect the differences in the heat and entropy of ionization of water in our solutions of $\mu = 1.00$ and in a hypothetical 1 M solution with unit activities.

[14] R. L. Pecsok, *J. Am. Chem. Soc.*, **75**, 2862 (1953).

[15] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 218–231.

law, a similar relationship exists between the heats and entropies of activation and ionization. It will be noted that $\Delta H_2\ddagger - \Delta H_1\ddagger = 12.6$ kcal./mole, 94% of the heat of ionization of water (13.4 kcal./mole).[12] Similarly, $\Delta S_2\ddagger - \Delta S_1\ddagger = -18.8$ e.u., 98% of the entropy of ionization of water (−19.2 e.u.).[12] These results are in good agreement with the published rate constants for various acids,[2,16] which correspond to a value of 0.95 for α. Such a large value of α corresponds to an activated complex in which the reacting proton has almost completely broken its bond to the acid species. (In our studies, this corresponds to the breaking of an O–H bond.)

The good agreement of the rate constants measured by the flow method (Table I) with themselves and with the values of k_1 obtained for alkaline solutions is taken as evidence that the same rate law applies over the pH range 3.8 to 14. It seems certain, as Davis and Swain[17] have suggested, that Kilpatrick and McKinney[3] measured the rate of evolution of hydrogen from a supersaturated solution.

Goubeau and Kallfass and Mikheeva, *et al.*,[4] reported the formation of the species BH_3OH^-, $BH_2(OH)_2^-$, and $BH(OH)_3^-$ in hydroborate solutions undergoing hydrolysis. All our "first-order" plots (log (reducing power) *vs.* time), some of which were carried as far as 90% reaction, gave straight lines, with no suggestion of the formation of intermediates in amounts greater than 5% of the hydroborate initially present. Our proton magnetic resonance studies were also unsuccessful in detecting such intermediates.

The Rate-Determining Step of the Acid Hydrolysis.—When hydroborates react with acidic species in non-aqueous solvents, diborane generally forms in a molar amount equal to one-half the number of moles of hydroborate consumed. For example, consider the reaction of sodium hydroborate with concentrated sulfuric acid[18] and of lithium hydroborate with arsenic trichloride in ether.[19] It therefore is tempting to

$$NaBH_4 + H_2SO_4 \longrightarrow {}^1/_2B_2H_6 + H_2 + NaHSO_4 \qquad (4)$$

$$3LiBH_4 + AsCl_3 \longrightarrow {}^3/_2B_2H_6 + AsH_3 + 3LiCl \qquad (5)$$

postulate that borane (or its hydrate) and molecular hydrogen are the immediate products of the reaction of the hydroborate ion with the aqueous proton

$$BH_4^- + H^+ \xrightarrow{\text{slow}} BH_3 + H_2 \qquad (6)$$

However, a number of other rate-determining steps are conceivable (eq. 7–9) and we shall here discuss their compatibility with various experimental data.

$$BH_4^- + H^+ \rightleftharpoons BH_5 \xrightarrow{\text{slow}} BH_3 + H_2 \qquad (7)$$

$$H_3O^+ + BH_4^- \xrightarrow{\text{slow}} H_3OBH_3^+ + H^- \qquad (8)$$

$$BH_4^- + H^+ \xrightarrow{\text{slow}} BH_5 \rightarrow BH_3 + H_2 \qquad (9)$$

According to mechanism 7, the hydrolysis rate should be dependent only on the concentrations of hydroborate and hydrogen ions and independent of the concentrations of other acidic species such as bicarbonate, water, etc. Therefore the fact that the reaction is general-acid catalyzed rules out the possibility of mechanism 7. In addition, reactions of the type represented by mechanism 7 usually proceed faster in D_2O than in H_2O because of the weaker basicity of D_2O with respect to H_2O.[20] We found that the hydrolysis is faster in light water than in heavy water.

The facts that BD_4^- reacts faster than BH_4^- and that BH_4^- hydrolyzes faster in light water than in heavy water indicate that, in the formation of the activated complex, a B–H bond is "strengthened" and an O–H bond is "weakened." These results clearly are inconsistent with reaction 8, but they apparently are consistent with the other mechanisms.

When BH_4^- is hydrolyzed in D_2O, about 4% of the evolved hydrogen is H_2,[21] and when BD_4^- is hydrolyzed in H_2O about 1% of the hydrogen is D_2.[7] We believe that these results are more readily explained by mechanism 9 than by mechanism 6. It seems likely that, in a process such as mechanism 6, the reacting proton (which essentially plucks a hydride ion from the BH_4^- ion) always would end up in the molecular hydrogen.[22] However, the results quoted above are consistent

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[16] W. H. Stockmayer, R. R. Miller, and R. J. Zeto, *J. Phys. Chem.*, **65**, 1076 (1961).

[17] See footnote (5) in ref. 2.

[18] H. G. Weiss and I. Shapiro, *J. Am. Chem. Soc.*, **81**, 6167 (1959).

[19] E. Wiberg and K. Modritzer, *Z. Naturforsch.*, **12b**, 123 (1957).

[20] L. Melander, "Isotope Effects on Reaction Rates," Ronald Press Co., New York, N. Y., 1960.

[21] W. L. Jolly and R. E. Mesmer, *J. Am. Chem. Soc.*, **83**, 4470 (1961).

[22] Hydrogen is exchanged between the hydroborate ion and water,[21] but in order to account for the results described above using reaction 6 it would be necessary to assume that a disproportionate fraction of the exchanged hydrogen in the water reacts with hydroborate to form molecular hydrogen before being diluted by the solvent.

with intermediates of composition BH_4D or BD_4H, respectively, which mainly decompose to give HD and BH_3 or BD_3, but which decompose at a lower rate to H_2 and BH_2D or D_2 and BD_2H. Hence we believe that, of the two plausible mechanisms (6 and 9), the data favor mechanism 9.

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The Amine Complexes of Aluminum Hydride. IV. Bis-(dimethylamino borane)-bis-(dimethylamino) Alane

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A new compound, $HAl[N(CH_3)_2]_2 \cdot 2BH_2N(CH_3)_2$, has been prepared by the reaction of bis-(dimethylamino) alane with dimethylamino borane. The interaction of various other dimethylamino borane derivatives with dimethylamino derivatives of alane produced the same material. Its probable structure is discussed.

Only a few examples of complexes formed between boron and aluminum hydride derivatives have been reported. Perhaps the best known is aluminum borohydride. In this complex the boron and aluminum atoms are believed to be bonded together *via* hydrogen bridges.[1] Burg attempted to prepare amino derivatives of aluminum borohydride in which one of the hydride bridges was replaced by an amino group.[2] He observed that a complex reaction occurred between aluminum borohydride and dimethylamino borane. Although the products were not completely characterized, one fraction was tentatively identified as having the composition $BH_4Al[BH_3N(CH_3)_2]_2$. Based on the information reported, one cannot determine whether the dimethylamino group had been substituted for a terminal or a bridging hydride atom.

Preparation of Bis-(dimethylamino borane)-bis-(dimethylamino) Alane.—The possible existence of compounds containing a dimethylamino group bonded to both boron and aluminum prompted an investigation into the preparation of such materials. The interaction of dimethylamino borane and bis-(dimethylamino) alane[3] was found to produce a single product in excellent yield.

$$HAl[N(CH_3)_2]_2 + 2H_2BN(CH_3)_2 \longrightarrow HAl[N(CH_3)_2]_2 \cdot 2BH_2N(CH_3)_2 \quad (1)$$

Little or no side products were isolated nor did appreciable quantities of starting materials remain in the reaction mixture when the above stoichiometry was followed. The new compound was named bis-(dimethylamino borane)-bis-(dimethylamino) alane for reasons presented in the following section.

Bis-(dimethylamino borane)-bis-(dimethylamino) alane also could be prepared by the reaction of tris-(dimethylamino) alane with trimethylamine borane or by reaction of tris-(dimethylamino) borane with trimethylamine alane. Good yields of bis-(dimethylamino borane)-bis-(dimethylamino) alane were obtained in both reactions. Although the amount of trimethylamine liberated was in close agreement with the above stoichiometry, only fair yields of bis-(dimethylamino) alane were isolated, so that the presence of small amounts of other dimethylamino derivatives is not precluded.

$$2Al[N(CH_3)_2]_3 + 2BH_3 \cdot N(CH_3)_3 \longrightarrow HAl[N(CH_3)_2]_2 \cdot 2BH_2N(CH_3)_2 + HAl[N(CH_3)_2]_2 + 2N(CH_3)_3 \quad (2)$$

$$2B[N(CH_3)_2]_3 + 2AlH_3 \cdot N(CH_3)_3 \longrightarrow HAl[N(CH_3)_2]_2 \cdot 2BH_2N(CH_3)_2 + HAl[N(CH_3)_2]_2 + 2N(CH_3)_3 \quad (3)$$

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[1] W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1949).

[2] A. B. Burg and C. L. Randolph, *J. Am. Chem. Soc.*, **73**, 953 (1951).

[3] The nomenclature in this paper is an extension of that proposed in part I [*ibid.*, **82**, 2141 (1960)]. See *ibid.*, **83**, 1798 (1961) for Part III.