

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

**Ammonia-Triborane. The Heat Capacity, Heat of Transition and Thermodynamic Properties from 5 to 317°K.**

BY EDGAR F. WESTRUM, JR., AND NORMAN E. LEVITIN

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The heat capacity of pure ammonia-triborane has been measured over the range from 5 to 317°K. An apparently first-order transition involving an enthalpy of transformation of 1233 cal. mole<sup>-1</sup> and an entropy increment of 4.15 cal. mole<sup>-1</sup> deg.<sup>-1</sup> has been established at 297.10°K. A small anomaly in the heat capacity appears at a temperature of about 11°K. and involves a rather minor entropy increment of approximately 0.01 cal. mole<sup>-1</sup> deg.<sup>-1</sup>. Values of the thermodynamic functions derived from the heat capacity are given at rounded temperatures together with the smooth heat capacity data. The heat capacity at constant pressure, entropy, enthalpy increment and free energy function at 300°K. are: 38.22 cal. mole<sup>-1</sup> deg.<sup>-1</sup>, 39.90 cal. mole<sup>-1</sup> deg.<sup>-1</sup>, 6808 cal. mole<sup>-1</sup>, and -17.20 cal. mole<sup>-1</sup> deg.<sup>-1</sup>, respectively. The thermodynamic properties of the ideal gaseous ammonia-triborane are also given for 300°K.

The desirability of having data on the thermal and thermodynamic properties of a material with as many technological possibilities and fundamentally interesting physical properties as ammonia-triborane needs no argument. The preparation of this substance was reported by Kodama and Parry<sup>1</sup> in 1957. It is, unfortunately, rather difficult to prepare in high purity on the 20-g. scale at the present time and is sufficiently unstable as to require some care in its handling.

Very little information is presently available concerning the physical properties of this interesting compound. Nordman and Reimann<sup>2,3</sup> have made a single crystal X-ray diffraction study to elucidate its structural and crystallographic properties. They find that the NH<sub>3</sub>B<sub>3</sub>H<sub>7</sub> molecule contains a triangle of boron atoms with one side only slightly shorter than the other two. The NH<sub>3</sub> group is attached to the boron atom opposite the shortest boron-boron bond and is pointed at about a 65° angle out of the plane of the boron atoms. They also found evidence of a structural transformation taking place below room temperature but did not establish the temperature of the transition. In the present study the transition temperature was determined as 297.10°K.

**The Cryostat and Calorimeter.**—The cryostat and circuitry employed for the heat capacity measurements are very similar to those previously described by Westrum, Hatcher and Osborne.<sup>4</sup> The determinations of heat capacity were made by the adiabatic technique by measuring the temperature rise produced by a definite input of electrical energy. Current and potential measurements were made on the electrical heater during the energy input and on the capsule-type platinum resistance thermometer during drift periods. These measurements were made with an auto-calibrated White double potentiometer used in conjunction with a galvanometer having a rated sensitivity of 0.04 μv./mm. at 1 m. distance. The platinum resistance thermometer (laboratory designation A-3) was calibrated at the National Bureau of Standards by measuring its resistance at the boiling point of oxygen, the ice point, the steam point and the boiling point of sulfur. From these measurements made at fixed points on the International Temperature Scale the constants in the Callendar-Van Dusen equation were evaluated. Between 4 and 10°K. a provisional temperature scale<sup>5</sup> was established from the value of  $dR/dT$  at 10°K.,

the resistance of the thermometer at 10°K., and the resistance at the boiling point of helium, by evaluating the constants in the equation

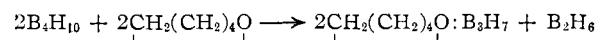
$$R = A + BT^2 + CT^6$$

It is believed that the temperature scale agrees with the thermodynamic scale within 0.1° from 4 to 14°K., within 0.02° from 14 to 90°K., and within 0.04° from 90 to 373°K.

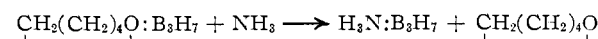
The calorimeter (laboratory designation W-17) has gold plating on the exterior and interior surfaces. It is similar in design to calorimeter W-6 previously described,<sup>6</sup> except that the inside is gold-plated to protect the calorimeter from possible corrosion by the sample and that the number of vertical conduction vanes is reduced from eight to two. Like W-6, this calorimeter also has a monel neck which permits the top to be soldered in place easily and without appreciably heating the calorimeter and contents. This avoids possible thermal decomposition of the sample (which takes place at temperatures above 320°K. at an appreciable rate). The calorimeter has an interior volume of about 60 ml. and weighs 33 g.

The calorimeter was loaded in the nitrogen atmosphere of the dry box, weighed and its top sealed in place with Cerro-seal-35 (indium-tin) solder. After evacuating the loaded calorimeter for an hour at room temperature through a small hole in the helium seal-off tube, 3.6 cm. pressure of pure helium gas was admitted through the hole which was then sealed with Cerro-seal solder with a small electric soldering iron fitted through the glass vacuum vessel. The amount of solder was adjusted carefully to that present during the determination of the heat capacity of the empty calorimeter and Apiezon-T stopcock grease weighed on to establish conductivity between the thermometer and the heater sleeve.

**Preparation and Purity of Ammonia-Triborane.**—The ammonia-triborane was prepared by a modification of the method described by Kodama and Parry.<sup>1</sup> Tetraborane and tetrahydropyran reacted at a temperature of about -120° (to moderate the reaction)



After excess tetrahydropyran was removed, the tetrahydropyran-triborane then was treated in ethyl ether with ammonia at -78°



The excess ammonia, ethyl ether and displaced tetrahydropyran were removed at room temperature. The product was dissolved in benzene and removed from the reactor. It was subsequently precipitated by addition of methylcyclohexane to the solution and was filtered under a nitrogen atmosphere. Further purification of the product was achieved by dissolving it in benzene, filtering the solution and precipitating the ammonia-triborane with a large excess of methylcyclohexane. The product then was dissolved in toluene and recrystallized at -95°. The product was filtered again in an anhydrous nitrogen atmosphere, and the adsorbed toluene was removed by evacuating for 2 hr. under high vacuum. The sample was stored under vacuum at

(1) G. Kodama and R. W. Parry, Transactions XVIIth Congress, Int. Union Pure and Applied Chemistry, Paris, July, 1957.

(2) C. E. Nordman, *Acta Cryst.*, **10**, 777 (1957).

(3) C. E. Nordman and C. Reimann, *THIS JOURNAL*, **81**, 3538 (1959).

(4) E. F. Westrum, Jr., J. B. Hatcher and D. W. Osborne, *J. Chem. Phys.*, **21**, 419 (1953).

(5) H. J. Hoge and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **22**, 351 (1939).

(6) G. Grenier and E. F. Westrum, Jr., *THIS JOURNAL*, **78**, 6226 (1956).

-196° until it was used. The yield of crude ammonia-triborane was between 70 and 80% of the theoretical, based on the tetraborane used; that of the finally purified product was approximately 50% of theoretical.

Chemical analyses for nitrogen, boron and active hydrogen were made with the following results: N<sub>2</sub>, 24.8% (theoretical, 24.9%); B, 57.4% (theoretical, 57.2%); and active H<sub>2</sub>, 12.47% (theoretical, 12.46%).<sup>7</sup> There is every indication then that the product was at least 99.8% pure. The absence of toluene (used as a recrystallizing solvent) was established by the absence of a hump in the heat capacity curve at or near the melting point of toluene. Further details of the 20-g. scale production of this compound are described elsewhere.<sup>7</sup>

**The Results of the Heat Capacity Measurements.**—The original values of the molal heat capacity of the sample of ammonia-triborane weighing 15.085 g. (*in vacuo*) are presented in chronological sequence, together with the mean temperature of the individual runs, in Table I and in Fig. 1. These data have been corrected to

TABLE I  
MOLAL HEAT CAPACITY OF AMMONIA-TRIBORANE  
(in cal./deg. mole)

T, °K.	C <sub>p</sub>	T, °K.	C <sub>p</sub>	T, °K.	C <sub>p</sub>
Series I					
	297.20 (2660)	6.72	0.021		
	298.87 (72)	7.52	.035		
147.26	18.81	302.36	37.81	8.40	.066
				9.25	.116
172.38	21.09	Series IV			
181.38	21.96	10.21	.195		
		11.72	.199		
		53.57	7.743	13.54	.306
174.40	21.27	56.07	8.185	15.20	.453
183.09	22.15	60.63	8.962	16.71	.609
192.18	23.03	66.06	9.831	18.16	.790
201.77	23.97	71.45	10.595	19.82	1.024
211.04	24.94	77.20	11.388	21.84	1.351
219.92	25.96	83.50	12.291	23.95	1.741
229.26	27.06	90.49	13.162	26.14	2.170
230.71	27.20	97.71	13.969	28.52	2.656
239.61	28.36	102.34	14.465	29.44	2.847
249.06	29.76	109.99	15.266	32.49	3.500
258.44	31.36	118.11	16.09	35.74	4.185
267.76	33.35	126.66	16.92	39.34	4.974
276.85	35.63	134.87	17.68	43.19	5.771
286.03	38.62	143.03	18.42	47.19	6.569
293.84	(84)	151.59	19.20	51.49	7.385
297.03	(2130)	160.51	20.01	56.09	8.180
		169.54	20.82	86.56	(12.29)
Series II					
	178.63	21.66	153.87	(19.31)	
	187.68	22.57	241.15	(29.36)	
282.75	37.70		297.31	(107)	
288.93	39.86	Series V			
294.46	(69)				
298.23	(400)	5.49	0.012	Series VI	
303.26	37.86	6.80	.026	250.73	30.02
308.78	38.54	7.35	.033	260.05	31.59
314.95	39.58	6.38	.018	269.49	33.59
		7.16	.028	278.69	35.98
Series III					
		8.03	.048	287.35	39.13
		8.76	.082	292.57	41.51
283.79	37.78	9.57	.140	298.74	(148)
288.27	39.62	6.13	.019	296.38	(213)
291.79	41.27	4.79	.008	297.09	(2270)
295.20	43.17	5.47	.011	297.20	(3150)
297.00	(2660)	6.06	.017		

(7) G. Kodama, R. W. Parry and J. C. Carter, *THIS JOURNAL*, **81**, 3534 (1959).

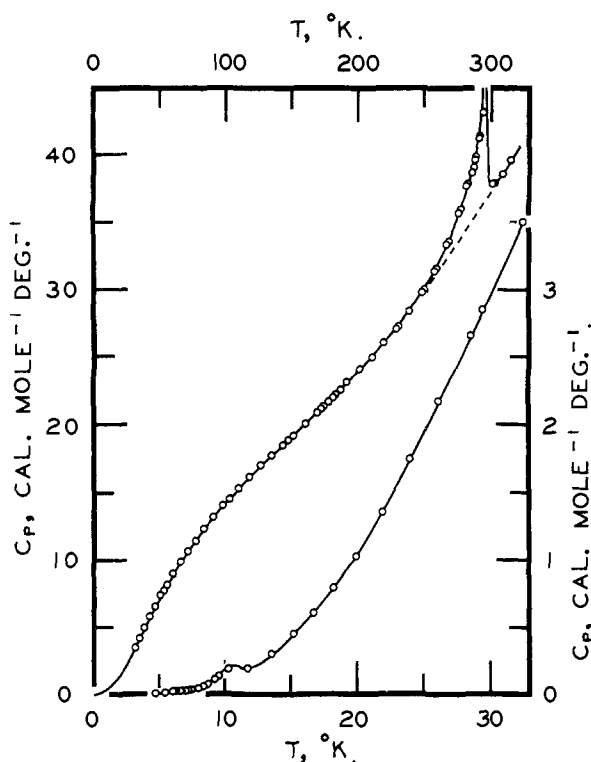


Fig. 1.—Low temperature heat capacity of ammonia-triborane as a function of temperature. The dashed line represents the assumed lattice contribution.

represent true heat capacities by applying a curvature correction for the finite temperature increments actually used in the measurements. The size of these temperature increments usually can be inferred from the mean temperature of the adjacent data points. The results are expressed in terms of a defined thermochemical calorie equal to 4.1840 absolute joules. The ice point was taken to be 273.15°K. and the gram formula weight of ammonia-triborane was taken to be 56.458 g.

The molal heat capacity and the thermodynamic functions derived from the heat capacity data are listed at rounded temperatures in Table II. These heat capacity values were read from a smooth curve through the experimental points, and they are estimated to have a probable error of approximately 0.1% above 25°, 1% at 14°K., increasing to about 5% at 5°K. The heat capacity was extrapolated below 5°K. using a Debye function. The effects of nuclear spin and of mixing of isotopes are not included in the entropy and free energy function. The estimated probable error in the entropy, heat content and free energy function is 0.1% above 100°K., but in order to make the table internally consistent and to permit accurate interpolation, some of the thermodynamic values are given to one more figure than is justified by the estimated probable error.

In addition to the numerical quadrature of points read from the smooth curve, the data of Table I were fed into a program on an IBM 650 calculator which independently evaluated the heat capacity at rounded temperatures and which performed the integration leading to the thermodynamic func-

TABLE II  
 MOLAL THERMODYNAMIC FUNCTIONS OF AMMONIA-TRIBORANE

$T, ^\circ\text{K.}$	$C_p$ cal./deg. mole	$S^\circ$ cal./deg. mole	$H^\circ - H_0^\circ$ cal./mole	$-(F^\circ - H_0^\circ)/T$ cal./deg. mole
5	(0.009)	(0.003)	(0.01)	(0.001)
10	.176	.036	0.29	.007
15	.435	.140	1.60	.033
20	1.052	.342	5.19	.082
25	1.946	.668	12.59	.164
30	2.967	1.112	24.83	.284
35	4.027	1.649	42.33	.439
40	5.109	2.258	65.18	.629
45	6.135	2.919	93.31	.845
50	7.102	3.616	126.43	1.087
60	8.857	5.070	206.41	1.630
70	10.412	6.551	302.9	2.224
80	11.820	8.035	414.2	2.858
90	13.080	9.502	538.8	3.516
100	14.215	10.940	675.3	4.187
110	15.27	12.344	822.8	4.864
120	16.27	13.716	980.5	5.545
130	17.23	15.056	1148.0	6.225
140	18.15	16.367	1324.9	6.903
150	19.06	17.650	1510.9	7.577
160	19.96	18.909	1706.0	8.247
170	20.86	20.146	1910.1	8.910
180	21.82	21.365	2123.4	9.568
190	22.82	22.571	2346.6	10.220
200	23.80	23.767	2579.7	10.869
210	24.83	24.953	2822.8	11.511
220	25.95	26.133	3076.7	12.148
230	27.12	27.313	3342.0	12.783
240	28.41	28.494	3619.6	13.412
250	29.90	29.683	3911.0	14.039
260	31.57	30.888	4218.3	14.664
270	33.76	32.120	4544.6	15.288
280	36.52	33.396	4895.5	15.912
290	40.24	34.740	5278.4	16.538
295	43.01	35.451	5486.6	16.853
300	38.22	39.895	6807.8	17.202
273.15	34.55	32.516	4652.2	15.484
298.15	(50)	(39.627)	(6727)	(17.065)

tions. In this manner a completely independent check has been obtained on the numerical values within the precision indices indicated in the above paragraph.

A third and final check on the measurements and the calculational technique is indicated in Table III. The enthalpy increments over relatively large increments of temperature were obtained in a series of runs made immediately subsequent to the Series V heat capacity determinations (*cf.* Table I) and compared with the integral over the corresponding ranges of temperature obtained by numerical quadrature of the smooth curve through the heat capacity data points. It will be noted that the agreement between the observed and the calculated values is excellent in all four instances.

**The Transition.**—Because of the slow rate of achievement of temperature equilibrium in the transition region, it was not possible to delineate heat capacity as a function of temperature with

 TABLE III  
 COMPARISON OF ENTHALPY INCREMENTS

Run	$T_{\text{final}}, ^\circ\text{K.}$	$T_{\text{initial}}, ^\circ\text{K.}$	$\overline{\Delta H}, \text{ cal. mole}^{-1}$ Obsd. <sup>a</sup>	Calcd. <sup>b</sup>
90	114.42	58.70	696.5	696.1
91	193.33	114.42	1531.8	1531.9
92	288.97	193.33	2814.6	2814.0
93	305.65	288.97	1785.8	1785.8
$\Sigma$	305.65	58.70	6828.7	6827.8

<sup>a</sup> From energy input of run indicated. <sup>b</sup> From numerical quadrature of smooth curve.

exactness. In order, therefore, to evaluate the thermodynamic functions more precisely, a number of energy inputs of varying magnitude were made in the transition region to obtain the enthalpy and entropy increments directly rather than the heat capacities. The findings from these runs are summarized in Table IV. The form of the material stable below the 297.10°K. transition temperature has been designated as the  $\alpha$ -form, and that stable above this temperature as the  $\beta$ -form. It will be noted that excellent agreement is characteristic of the entire set of transition runs.

 TABLE IV  
 ENTHALPY AND ENTROPY INCREMENTS AT THE  $\alpha$ - $\beta$  TRANSITION OVER THE RANGE 295–300°K.

Runs	$T_{\text{final}}, ^\circ\text{K.}$	$T_{\text{initial}}, ^\circ\text{K.}$	$\frac{H^\circ_{\beta 300} - H^\circ_{\alpha 295}}{\text{cal. mole}^{-1}}$	$\frac{S^\circ_{\beta 300} - S^\circ_{\alpha 295}}{\text{cal. mole}^{-1} \text{ deg.}^{-1}}$
22, 23	306.94	291.97	1321.8	4.443
30, 31,				
32, 33	300.49	293.52	1321.5	4.445
93	305.65	288.97	1320.6	4.442
100	303.88	293.59	1320.8	4.444
Av.			1321.2 $\pm$ 0.6	4.444 e.u.

It will be noted in Table I that the heat capacity near the transition temperature approximates  $3 \times 10^3$  cal. mole<sup>-1</sup> deg.<sup>-1</sup>, indicating that the transition is probably a first-order one or a very sharp lambda-type anomaly. However, there is a considerable pre-transitional rise in heat capacity. This fact renders rather difficult the evaluation of the entropy and enthalpy increments for the transition. To obtain these values, it is necessary to obtain a "normal" heat capacity curve for the substance in the absence of the aforesaid transition over a rather broad range. As a zeroth approximation to this "background" heat capacity, a smooth curve which is tangent to the observed heat capacities at 250°K. and again at 310°K. has been interpolated. The difference in the integral of the enthalpy along the observed curve minus that along the interpolated curve from 250 to 310°K. indicates an enthalpy increment of transition of 1233 cal. mole<sup>-1</sup>, and the corresponding transitional entropy increment is 4.15 cal. mole<sup>-1</sup> deg.<sup>-1</sup>. It is interesting to note that the transitional entropy increment approximates rather closely the value  $R \ln 8 = 4.13$  cal. mole<sup>-1</sup> deg.<sup>-1</sup>. This increment is consistent with the interpretation<sup>2,3</sup> of the possible configurations of the ammonia-triborane molecule in the  $\beta$ -form since the multiplicity of the general positions in the space group

14mm is eight, if the entropy increment associated with the 8% volume change is neglected.

The temperature of the  $\alpha$ - $\beta$  transformation was determined as  $297.10 \pm 0.04^\circ$  after a drift toward equilibrium of several hours duration in runs 31 and 32 (Table IV). Attempts to establish the transition temperature by cooling curves were unsuccessful in that the sample usually supercooled as much as  $5^\circ$  before undergoing the  $\beta \rightarrow \alpha$  transition and failed to reach the equilibrium temperature.

A thermal anomaly of unknown origin also was observed in the vicinity of  $11^\circ\text{K}$ . This appears to be a rather broad transformation with an entropy increment of about  $0.01 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ .

**Thermodynamic Properties of Gaseous Ammonia-Triborane.**—Measurements on the sublimation pressure of ammonia-triborane have been made<sup>8</sup> over the range  $304$  to  $327^\circ\text{K}$ . by an effusion technique. These data may be represented by the equation

$$\log P_{(\text{mm.})} = \frac{-3739}{T} + 9.200$$

This corresponds to a sublimation pressure of 5.46

(8) E. R. Alton, R. D. Brown, J. C. Carter and R. C. Taylor, *THIS JOURNAL*, **81**, 3550 (1959).

$\times 10^{-4} \text{ mm.}$  at  $300^\circ\text{K}$ . and a heat of sublimation of  $17.1 \pm 0.1 \text{ kcal. mole}^{-1}$ . Correction to the ideal gaseous state (at 1 atm. pressure) at  $300^\circ\text{K}$ . yields

$$\begin{aligned} (H^\circ - H_0^\circ)_{i.g.} &= 23.9 \pm 0.2 \text{ kcal. mole}^{-1} \\ S^\circ_{i.g.} &= 68.8 \text{ cal. mole}^{-1} \text{ deg.}^{-1} \\ - \left( \frac{F^\circ - H_0^\circ}{T} \right)_{i.g.} &= -10.9 \text{ cal. mole}^{-1} \text{ deg.}^{-1} \end{aligned}$$

The significance of these three values is subject, of course, to the usual uncertainties inherent in the interpretation of the effusion method of vapor pressure determination.

**Acknowledgments.**—The authors acknowledge their indebtedness to Professor R. W. Parry and Dr. G. Kodama for their interest and advice regarding the handling of the compound, to Mr. J. C. Carter for the preparation and the analysis of the sample and to Mr. H. G. Carlson and Miss Elfreda Chang for their assistance with the heat capacity determinations. This work was supported by Callery Chemical Company under a contract from the Bureau of Aeronautics, Department of the Navy.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

## Trimethylamine-Triborane. The Heat Capacity, Heat of Transition and Thermodynamic Properties from 5 to $350^\circ\text{K}$ .

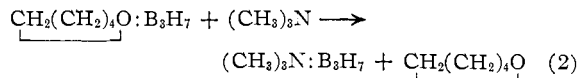
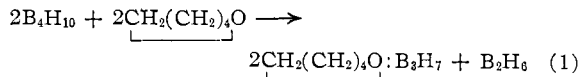
BY NORMAN E. LEVITIN, EDGAR F. WESTRUM, JR., AND JAMES C. CARTER

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The heat capacity of pure trimethylamine-triborane ( $(\text{CH}_3)_3\text{NB}_3\text{H}_7$ ) has been measured over the range from 5 to  $350^\circ\text{K}$ . with an adiabatic calorimeter. A sharp lambda-type transition was found at  $209.6^\circ\text{K}$ . It has a molal enthalpy of transformation of about  $843.4 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$  and an entropy increment of 4.0 e.u. Values of the thermodynamic functions derived from the heat capacity data are given at rounded temperatures together with the smooth heat capacity data. At  $298.15^\circ$ , the heat capacity at constant pressure, entropy, enthalpy increment and free-energy functions are:  $51.98 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ ,  $54.60 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ ,  $8732 \text{ cal. mole}^{-1}$  and  $-25.31 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ , respectively. The preparation of this compound on the 20-g. scale is described.

Ammonia-triborane ( $\text{NH}_3\text{B}_3\text{H}_7$ ) has been studied in this Laboratory by calorimetric<sup>1</sup> and X-ray diffraction techniques<sup>2</sup> and was found to undergo an interesting transition at  $297.10^\circ\text{K}$ . involving a disordering of the molecule in the crystalline lattice. The possible existence of a low temperature transformation in the trimethylamine-triborane ( $(\text{CH}_3)_3\text{NB}_3\text{H}_7$ ) provided an inducement for the investigation of its low temperature thermodynamic properties, despite some difficulty and hazard in its laboratory scale preparation. A transition of magnitude quite similar to that found in the ammonia triborane was found at  $209.6^\circ\text{K}$ .

**Preparation and Purity of Trimethylamine-Triborane.**—The trimethylamine-triborane was prepared by a suitable modification of the combined procedures of Edwards, Hough and Ford<sup>3</sup> and of Kodama.<sup>4</sup> The reactions are



The contents of a 500-ml. Pyrex reaction vessel were stirred by a magnetically-driven paddle and connected to a vacuum line and manometer through a  $195^\circ\text{K}$ . reflux condenser. Toluene (100 ml. of reagent dried over  $\text{CaH}_2$ ) as diluent and tetrahydropyran (100 ml., b.p.  $81$ – $82^\circ$ , refluxed over  $\text{CaH}_2$ ) were used in the reactor, and the system was cooled to  $77^\circ\text{K}$ . and evacuated. Tetraborane (50 ml. distilled *in vacuo* at  $188^\circ\text{K}$ ., and freed of diborane at  $147^\circ\text{K}$ .) was distilled into the reactor and the temperature slowly increased until evolution of diborane was noted, whereupon the reaction was quenched by immersion of the reactor in liquid nitrogen and upon gradual warming the diborane was distilled off and the reaction allowed to proceed more moderately. After most of the diborane was removed, the reactor was cooled to  $195^\circ\text{K}$ . and allowed to stand 10 hr. Then the remainder of the diborane, the excess tetrahydropyran and the toluene were distilled off. Ethyl ether (200

(1) E. F. Westrum, Jr., and N. E. Levitin, *THIS JOURNAL*, **81**, 3544 (1959).

(2) C. E. Nordman and C. R. Peters, Abstracts of Papers, 133rd Meeting of the American Chemical Society, San Francisco, Calif., 1958.

(3) L. J. Edwards, W. V. Hough and M. D. Ford, Transactions XVth Congress, Int. Union Pure and Applied Chemistry, p. 475, Paris, July, 1957.

(4) G. Kodama, Ph.D. Dissertation, University of Michigan, Ann Arbor, Mich., 1957.