The comparison cannot be made at lower pD because of the unidentified X bands at pD 7.9 and 8.4 (Figures 1E and 1F). However, it seems relevant to this point that the resonance frequencies of both bands I and II move upfield ~0.5 ppm in going from the pD 9.9 ^{31}P spectrum to the pD 9.4 spectrum, but they remain constant from pD 9.4 to 8.4. This sudden change between pD 9.9 and 9.4 could be due to an increased ligand exchange rate between non-ST and ST complexes, *if* the non-ST band is slightly upfield of, and hidden by, the normal band II of structure **3**. Unfortunately, we cannot verify this conjecture, for as noted above, we cannot identify a ^{31}P non-ST band alone. However, consistent with this view are the sudden very large intensity changes of bands I (55% → 19%) and II (18% → 51%) between 9.9 and 9.4 (Table I), while III increases only 3%. Thus, it seems that the major reaction which occurs when the pD is made less than ~9.9 is

$$\mathbf{2} \xrightarrow[\text{pD} <9.9]{} \text{non-ST complex(es)}$$

To reconcile the constancy of the ^{31}P data (*i.e.*, chemical shifts and relative areas) between pD 8.4 and 9.4 (r = 3.8–4.2) with the definite changes in the pmr spectra in this region we would first note that this region is the first half of the third, relatively steep buffer region in the titration (Figure 3). This is also the region in which the pmr spectra contain the unidentified X bands. We suggest, purely as speculation, that as the pD is decreased below 9.9 several reactions occur. First, protonation of one of the ribose hydroxyl-oxygen atoms (probably 2′) occurs, weakening the ST-type of chelation and causing the formation of non-ST complex(es) according to the previous equation. As the non-ST complex concentration increases mixed complexes form. For instance, a 2:2 dimer may form in which one uranium atom is attached bidentately to the phosphate of one AMP molecule and also (bidentately) to the 3′ oxygen and one phosphate oxygen of a second AMP, while this latter phosphate group is also bidentate to a second uranium as in **3**. Such a dimer should give both the II band of **3** and the non-ST band, which, we suggested earlier, may be near the location of II. Thus, as the reaction, **3** → mixed dimer, proceeds with decreasing pD, the change in the ^{31}P spectrum may be only slight. On the other hand, the pmr spectrum should change because of the breaking of the $U{-}O_{2'}$ bond. The X bands may be mixed complex bands.

Our interpretation of the nmr spectra may be coupled with the earlier titration results[3] to give the following summarizing series of reversible reactions (several of which may overlap) as a description of the equimolar U–AMP system from pH 2 to 11.5. (Equations are not balanced.)

$$H_2A + UO_2{}^{2+} \xrightarrow[\text{pH} <4.5]{2OH^-} A{\equiv}UO_2(\text{ppt}^3) \xrightarrow[\text{pH} \sim 6]{\sim 0.4OH^-} \text{olated gel} \xrightarrow[\text{pH} \sim 7.5]{\sim 0.6OH^-}$$

$$\text{non-ST complex (soluble)} \xrightarrow[\text{pH } 7\text{–}9.5]{OH^-}$$

$$\text{mixed complex} \xrightarrow[\text{pH} \sim 10]{\sim 0.5OH^-} (\mathbf{2} + \mathbf{3}) + A^{2-} \xrightarrow[\text{pH} \sim 11]{\sim 0.5OH^-} \mathbf{1}$$

Hydrolysis of a Borane Cation Derived from Ethyl N,N-Dimethylglycinate[1]

N. E. Miller

Contribution from the Department of Chemistry, University of South Dakota, Vermillion, South Dakota 57069. *Received February 7, 1970*

Abstract: The rate of hydrolysis of $(CH_3)_3NBH_2N(CH_3)_2CH_2CO_2C_2H_5{}^+$ was determined by monitoring hydrogen evolution in an apparatus which requires only micro quantities of substrate. After an induction period, the hydrogen evolution was fit by first-order decay of substrate, with $k = 6.5 \times 10^{-4}$ sec^{-1} at 29.8°. Temperature dependence and kinetic isotope effects were explored, and syntheses of several possible intermediates were attempted. A mechanism consistent with all the experimental data invokes saponification of the ester function to produce a polar intermediate, $(CH_3)_3NBH_2N(CH_3)_2CH_2CO_2$, as a first step. Slow intramolecular loss of trimethylamine governed by k gives a cyclic intermediate, $(CH_3)_2\overline{NCH_2CO_2B}H_2$, which then undergoes a second-order step and subsequent fast hydrogen-producing steps. The cyclic intermediate was isolated from a hydrolysate in dilute base and was characterized.

The class of borane cations, $H_2B(NR_3)_2{}^+$, derived from tertiary amine bases has been shown to be exceptionally inert to hydrolysis, even under forcing conditions.[2] It has now been found that a cation derived from an amino acid ester is hydrolyzed in base, and this observation opens interesting questions about

---

[1] Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 13–18, 1969.

[2] N. E. Miller and E. L. Muetterties, *J. Amer. Chem. Soc.*, **86**, 1033 (1964).

structure and reactivity in the cations of tertiary amines. A salt of this cation, trimethylamine–dimethyl(carbethoxymethyl)aminedihydroboron(1+) hexafluorophosphate, I, evolves hydrogen in strong base after a short induction period at a rate conveniently followed by volumetric techniques. This is a well-characterized

$$(CH_3)_3NBH_2N(CH_3)_2CH_2CO_2C_2H_5{}^+PF_6{}^+$$

I

salt[3] which is readily prepared, so a detailed investigation was begun to develop insight into the reactivity of borane cations of tertiary amine bases.

Experimental Section

Infrared spectra were recorded with a Perkin-Elmer 237B grating spectrophotometer, nmr spectra with a Varian A60-A. Microanalyses were obtained from Peninsular ChemResearch, Gainesville, Fla.

Hydrolyses were conducted in an apparatus (see Figure 1) nominally similar to the classic Warburg apparatus. The essential novelty is a large diameter manometer that is completely immersed in a temperature bath. The vessel has a volume of nearly 15 ml and is connected by a thick-wall capillary to a 5-mm i.d. precision bore manometer–buret having a measuring range of nearly 2 ml of gas. A larger diameter (*ca.* 10 mm) glass tubing forms the open leg of the manometer.

To keep the ionic effects sensibly constant, a background ionic strength of 0.90 was maintained with potassium chloride. A standard stock solution, 1.000 *M* potassium chloride, was prepared from a weighed amount of dry, reagent-grade salt and deionized distilled water. The sodium hydroxide used was a carbonate-free, commercial analytical solution diluted to 1.000 *M* with deionized distilled water. The hydroxide stock solution was stored in polyethylene bottles contained in a larger sealed can containing an open bottle of 0.5 *M* sodium hydroxide to remove carbon dioxide traces and to prevent concentration of the stock solution by evaporation.

Several modes of bringing the substrate and reaction media together were tried. It was most convenient generally to add hydroxide to a solution of I in the requisite amount of potassium chloride solution pipetted into a 10.0-ml volumetric flask at bath temperature. The hydroxide solution was added by pipet, and the solution was made to volume with deionized water. Time zero was marked with a Precision Scientific interval counter at the vigorous shaking of the volumetric flask to mix the contents. The reaction mixture was then quickly transferred to the reaction vessel through a small funnel. The flask contained a small Teflon-coated magnetic stirring bar and a portion of powdered glass. After assembling the flask to the manometer, the apparatus was positioned in the temperature bath with the stopcock open. The stopcock was closed after a few minutes of thermal equilibration and volume readings were begun. Times for the first volume readings were 100–200 sec.

Temperature control to better than 0.1° was provided by a water bath equipped with a Haake Model ED Unitherm circulator–regulator. Temperatures were read to 0.1° with a mercury-in-glass thermometer which was compared with calibrated thermometers.

Buret readings were made through a telescope from a distance of several feet to minimize parallax. The manometric fluid was 0.9 *M* potassium chloride solution rather than water in order to minimize systematic error arising through water transport from manometer to reaction solution. A scale divided in $^1/_{50}$th-in. ruling was attached to one apparatus, and a nonrational milk glass scale from a thermometer was attached to another apparatus. The first scale is especially facile, as its divisions correspond to 0.01 ml to 5 parts per 1000 accuracy with the 5.0-mm i.d. buret. The second scale had 100 divisions marked for an 0.895-ml volume.

As gas is evolved, the total pressure increases as a result of an increasing water head in the manometer. It is not necessary to correct observed volumes to the initial pressure condition if the volume data are to be fitted to first-order plots. The correction for the evolved gas volumes is well represented as proportional to the evolved volume, ΔV. These corrections only shift the straight-line intercepts with no effect on slope. Representing the correction as $\Delta = \alpha\Delta V$, the corrected evolved volume is $(1 + \alpha)\Delta V$. Thus, the slopes of plots of corrected volumes are identical with those using uncorrected volumes, $(\log (1 + \alpha)\Delta V_1/(1 + \alpha)\Delta V_2)/\Delta t = (\log \Delta V_1/\Delta V_2)/\Delta t$.[4]

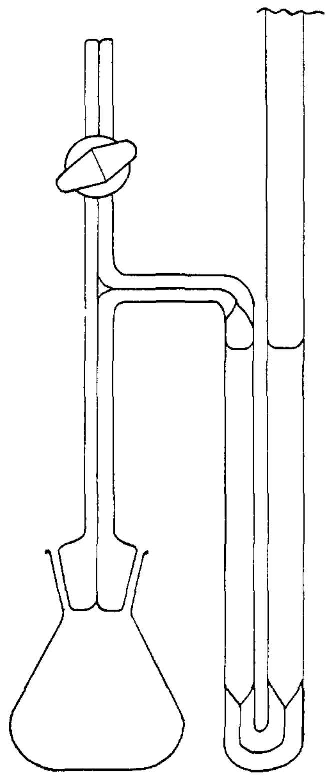


Figure 1. Hydrolysis apparatus.

$(CH_3)_3NBH_2N(CH_3)_2CH_2CO_2C_2H_5{}^+PF_6{}^-$ was prepared by addition of ethyl N,N-dimethylglycinate to a chloroform solution of trimethylamine–iodoborane followed by the usual work-up and conversion to the hexafluorophosphate salt.[3] The $>BD_2$ analog was similarly prepared from $(CH_3)_3NBD_2I$ obtained by reaction of iodine on $(CH_3)_3NBD_3$. Deuteriodiborane, liberated from $LiBD_4$ in tetraglyme, bis[2-(2′-methoxyethoxy)ethyl] ether, by addition of 0.5 mol equiv of iodine, was used to prepare $(CH_3)_3NBD_3$. Portions of the intermediate $(CH_3)_3NBD_2I$ were purified by sublimation for use in hydrolysis studies.

The infrared spectra of the deuterated compounds were free of B–H absorption and had strong B–D absorption near 1800 cm^{-1}. Important bands (cm^{-1}) are listed for mineral oil mulls (abbreviations: s = strong, m = moderately strong, w = weak, vw = very weak).

$(CH_3)_3NBD_2N(CH_3)_2CH_2CO_2C_2H_5PF_6$. 1870 (w), 1785 (vw), 1735 (s), 1200 (m), 1170 (vw), 1120 (vw), 1035 (m), 1005 (vw), 985 (vw), 970 (w), 960 (w), 930 (m), 850 (s).

$(CH_3)_3NBD_2I$. 2480 (vw), 1920 (w), 1890 (m), 1850 (vw), 1820 (w), 1805 (m), 1755 (w), 1735 (m), 1405 (m), 1255 (w), 1240 (w), 1120 (m, multiplet), 1070 (w), 1005 (m), 980 (s), 895 (m), 880 (m), 855 (m), 810 (s).

Rate constants were determined graphically from log plots of $V_\infty - V_t$ against time. The data were linear to 90% completion.

---

[3] N. E. Miller, D. L. Reznicek, R. J. Rowatt, and K. R. Lundberg, *Inorg. Chem.*, 8, 862 (1969).

[4] The correction, $\Delta = \alpha\Delta V$, does vary somewhat with ΔV, depending on the size of the dead gas volume between the hydrolysate surface and the manometer surface. In our apparatus the dead volume was between 5 and 10 ml and α changed about 10% as ΔV varied from 0 to 1.0 ml. Since α was about 0.048 in our apparatus, the true ratio of evolved volumes, $(1 + \alpha_2)\Delta V_2/(1 + \alpha_1)\Delta V_1$, is within 4 parts per 1000 of the uncorrected volume ratio, $\Delta V_2/\Delta V_1$, or within the reading error of the buret.

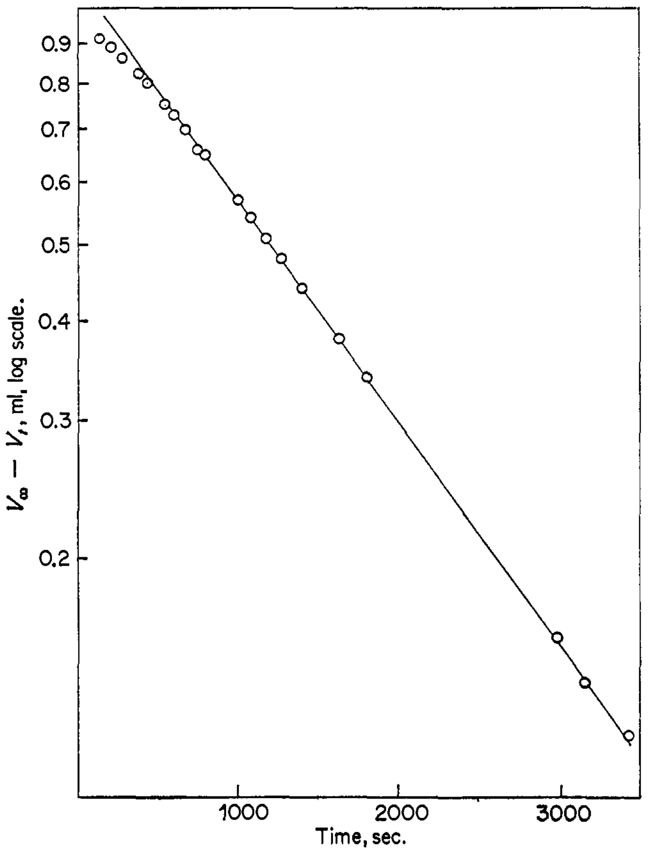
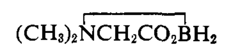


Figure 2. Log plot; hydrolysis of I in 0.3 M OH^-, ionic strength 0.9, T = 29.8°.

Because of the inherent inaccuracy of evolved volumes ($V_\infty - V_t$) below 0.10 ml, the best lines were drawn through volume data equal to or greater than 0.10 ml. The data spanned three half-lives. Activation energy was obtained from the Ahrennius plot using primarily the rate constants at 38.1, 29.8, and 25.4°.

The completeness of hydrolysis was examined with several runs with no supporting electrolyte. After more than ten half-lives had elapsed, the solutions were acidified with dilute nitric acid and treated with silver nitrate solution. An immediate darkening evidenced the presence of B–H groups. These observations agreed with the calculations that only 85–95% of the hydridic hydrogen had been released. Apparently some boron hydride species were present which were decomposing only very slowly.

Isolation of $(CH_3)_2NCH_2CO_2BH_2$ (II). A solution of 0.5 g of I in 500 ml of water was prepared. Half was made to 0.01 M in OH^- by addition of 2.5 ± 0.1 ml of standard 1.0 M sodium hydroxide with vigorous stirring. The mixture was stoppered and allowed to stand at 25° for 700–1000 sec before neutralizing to pH 7.0. Water was removed at 27° using a film evaporator over a 3-hr period, the last traces under high vacuum. The wet solid that remained was extracted with small quantities of methylene chloride, and the extract evaporated to give 50 mg of a slush-like residue. Sublimation at 80–100° under high vacuum gave 41 mg of white $(CH_3)_2NCH_2CO_2BH_2$ (II), mp 118–120°. The sublimed material was soluble in benzene, insoluble in hexane.


$(CH_3)_2NCH_2CO_2BH_2$

II

Anal. Calcd for $(CH_3)_2NCH_2CO_2BH_2$ (II): C, 41.8; H, 8.8; N, 12.2. Found: C, 41.6; H, 8.5; N, 11.9.

^1H nmr resonances at 2.76 and 3.45 ppm downfield from $(CH_3)_4Si$ in methylene chloride solution are assigned to N–CH_3 and N–CH_2–CO_2 protons, respectively. The observed intensity ratio of 3:1 supports the assignment. Infrared absorptions of a mineral oil mull were (exclusive of those masked by mineral oil): 2450 (m), 2350 (m), 2220 (w), 1790 (w), 1730 (s), 1330 (m), 1300 (m br), 1270 (m), 1220–1200 (m, doublet), 1150 (m), 1110 (m), 1030 (w), 1020 (w), 975 (w), 920 (w), 880 (m), 840 (m), 730 (m).

The mass spectrum (run by Morgan-Schaffer Corp., Montreal) displayed highest major peaks at *m/e* 114 and 113 in abundance ratio near that expected for ^{11}B and ^{10}B. Absence of a significant parent at 115 indicates facile loss of H^+. The rest of he fragmentation pattern above 40 is given in as *m/e* (intensity): 115 (3), 114 (50), 113 (13), 72 (1), 71 (4), 70 (4), 69 (1), 59 (5), 58 (100), 57 (5), 56 (15), 55 (5), 54 (6), 45 (3), 44 (7), 43 (3), 42 (24), 41 (5), 40 (5).

The other half of the substrate solution was treated with 148 mg of sodium chloride, neutralized, and evaporated in an identical manner as the first half. A precipitate appeared before the water had all been removed. It was separated by filtration and identified as I by its infrared spectrum. The yield was 216 mg.

Reaction of $(CH_3)_4N^+(CH_3)_2NCH_2CO_2^-$ with $(CH_3)_3NBH_2I$. A solution of $(CH_3)_4N^+OH^-$ was prepared from 1.1837 g (7.69 mmol) of $(CH_3)_4N^+Br^-$ using a strong base anion exchange column in OH^- form. This solution tested Br^--free using acidified silver nitrate. To this solution was added 1.0130 g (7.22 mmol) of ethyl N,N-dimethylglycinate, and the mixture was allowed to stand 3 days before evaporation. The nonvolatile solid residue was taken up twice in about 20 ml of dry chloroform, evaporated to dryness to remove traces of water, and gave a white residue weighing 1.3 g. Its proton nmr showed three resonances, 3.48, 2.92, and 2.30 ppm downfield from internal $(CH_3)_4Si$ in chloroform, assigned to $(CH_3)_4N^+$, CH_2, and $(CH_3)_2N$ protons, respectively. The intensity ratio of the signals was the expected 6:1:3 ratio.

A solution of the $(CH_3)_4N^+(CH_3)_2NCH_2CO_2^-$ in about 10 ml of chloroform was mixed with a chloroform solution of 1.4 g of $(CH_3)_3NBH_2I$, whereupon a solid immediately precipitated. The mixture was stirred for several hours and filtered, giving 1.9 g of insoluble $(CH_3)_4N^+I^-$ (theory, 1.6 g) and a clear solution. Evaporation of the filtrate produced a clear oil mixture denoted M-1. The ^1H nmr spectrum had two significant signals at 2.97 and 2.67 ppm downfield from $(CH_3)_4Si$ (~1:3 ratio) in addition to $(CH_3)_2NBH_2CO_2BH_2$ (II) peaks at 3.47 and 2.78 ppm. Judging from the peak areas M-1 is about 70% $(CH_3)_2NCH_2CO_2BH_2$ (II).

Reaction of N,N-Dimethylglycine with $(CH_3)_3NBH_2I$. Dimethylglycine was prepared by hydrolysis of 1 ml of $(CH_3)_2NCH_2CO_2C_2H_5$ in water at 80° for 8 hr. Evaporation produced a white solid that was then mixed with 3 ml of ether and 2 ml of $(CH_3)_3SiCl$ for 2 hr to remove traces of water. Evaporation followed by sublimation gave 368 mg (3.56 mmol) of dimethylglycine. It was insoluble in aprotic solvents. It was mixed with 693 mg (3.48 mmol) of freshly sublimed $(CH_3)_3NBH_2I$ and dry chloroform, *ca.* 10 ml, was added. The mixture was stirred for 8 hr; during the first hour the insoluble portion changed to a more dense solid that settled readily. Filtration yielded 444 mg of insoluble solid identified as $(CH_3)_3NH^+I^-$ from its infrared spectrum. The filtrate, upon evaporation, left a very viscous clear melt designated M-2. This dissolved readily in water with gas evolution. The ^1H nmr spectrum of a chloroform solution of M-2 showed multiplet and broad peaks near 2.7 ppm downfield from $(CH_3)_4Si$, and a singlet at 3.50 ppm. A small amount of $(CH_3)_2NCH_2CO_2BH_2$ (II) was sublimed out by heating to 130° for 2 hr under high vacuum.

Results and Discussion

The rate of hydrogen evolution upon hydrolysis of I in strong base showed a first-order relationship. Plots of log $V_\infty - V_t$ against t were linear within experimental error for the most part to three half-lives, after an induction time that varied from 400 to 1000 sec. The fit of the first-order kinetic law is displayed in Figure 2 and Table I for a run with 0.3 M hydroxide.

It was not possible to analyze directly for substrate, so the increase of the product hydrogen was followed and related to substrate decay by the volume function $V_\infty - V_t$. The first-order decay of the function observed, however, may be that of some intermediate rather than I. An explanation of the induction period, in fact, almost necessitates such an intermediate.

Table I. Hydrolysis Data of $(CH_3)_3NBH_2N(CH_3)_2CH_2CO_2C_2H_5{}^+$-$PF_6{}^-$, Fit to Two Consecutive Rates[a]

Time, sec	Obsd 100 × $(V_\infty - V_t)$, ml	Calcd[b] $V(k)$	Calcd[b] $V(k_i)$	$V(k) - V(k_i)$	|Deviation|[c]
152	90	97.1	7.3	89.8	0.2
248	87	91.4	4.4	87.0	0
344	83	85.9	2.7	83.2	0.2
401	81	82.9	2.0	80.9	0.1
540	75	75.9	1.0	74.9	0.1
589[d]	73	73.6	0.8	72.8	0.2
660	70	70.3	0.5	69.8	0.2
775	65	65.3	0.4	65.0	0
955	58	58.2	0.3	58.1	0.1
1024	56	55.7	0.1	55.7	0.3
1075	54	53.9	0.09	53.9	0.1
1164	51	51.0	0.05	51.0	0
1254	48	48.1		48.1	0.1
1392	44	44.1		44.1	0.1
1561	39	39.6		39.6	0.6
1799	34	34.0		34.0	0
2992	16	15.9		15.9	0.1
3160	14	14.3		14.3	0.3
3715	1.5	10.0		10.0	0.5
4010	8.0	8.3		8.3	0.3
4676	6.0	5.4		5.4	0.6
5330	3.0	3.6		3.6	0.6

[a] Temperature 29.8°, $I = 0.9$, $[OH^-] = 0.3$ M. [b] Volumes calculated from graphically derived equations: $\log V(k) = -2.7676 \times 10^{-4}t + 2.0294$, $k = 6.4 \times 10^{-4}$ sec^{-1}; $\log V(k_i) = -2.23 \times 10^{-3}t + 1.201$, $k_i = 1.7 \times 10^{-2}$ l. mol^{-1} sec^{-1}. [c] Absolute deviation between $V(k) - V(k_i)$ and $100(V_\infty - V_t)$. Standard deviation is 0.27 for the 22 times listed. [d] End of induction period observed in graphic analysis.

The data of the induction period can be resolved into sums of two exponentials, as required by consecutive reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Exact, integrated rate laws for this mechanism are known.[5] The expression for the instantaneous concentration of C can be rearranged to simulate (A).

$$(A_0 - C) = A_0\left[\frac{k_1}{k_1 - k_2}e^{-k_2t} - \frac{k_2}{k_1 - k_2}e^{-k_1t}\right] \quad (1)$$

If k_1 and k_2 are sufficiently different, the function $(A_0 - C)$, which corresponds to $(V_\infty - V_t)$ in these hydrolyses, can be resolved graphically as a difference between two exponentials. Since this expression is invariant to subscript change, one is not able to order the two rate constants in the mechanism by rate data where product is monitored. Let us designate $k_2 > k_1$, so at large values of t, eq 1 reduces to $(A_0 - C) = A_0'e^{-k_1t}$.[6] Calculated values of $(A_0 - C)$ can now be obtained for small values of t in the induction period. If observed values of $(A_0 - C)$ are subtracted from the calculated values, the differences, Δ, should fit the expression $\Delta = \Delta_0e^{-k_2t}$. Thus, k_1 can be obtained from simple log plots of Δ *vs.* t.

The data for runs at several hydroxide concentrations were resolved as described and fit graphically to two rate constants. It was found that the large rate, k_i, is second order, first order in hydroxide, and the smaller constant, k, is first order. The best values at 29.8° are $k_i = 1.7 \pm 0.5 \times 10^{-2}$ l. mol^{-1} sec^{-1}, and $k = 6.5 \pm 0.2 \times 10^{-4}$ sec^{-1}. A summary of the experiments is presented in Table II. It was not possible to resolve data by this method for runs with $[OH^-]$ much less than 0.1 M, where the data form well-curved log plots. Runs with 0.1 and 0.056 M base were fit by a varying parameter method to the consecutive reaction rate law, with a standard deviation of 0.004 ml, about twice the minimal reading error. In the 0.056 M run, a function

Table II. Rate Constants for Hydrolysis of I at 29.8°; Ionic Strength, 0.9

$10^3[I]$, M	$[OH^-]$, M	10^2k_i, l. mol^{-1} sec^{-1}	10^4k, sec^{-1}
1.6	0.1	1.4	6.3
1.7	0.2	2.7	6.6
1.8	0.2		6.2
1.8	0.3	1.7	6.4
1.8	0.4		6.6
4.6	0.4	1.6	6.7
		Av 1.7 ± 0.5	6.5 ± 0.2

$$f = \frac{k_2}{k_2 - k_1}e^{-k_1t} - \frac{k_1}{k_2 - k_1}e^{-k_2t}$$

was calculated for $k_1 = 6.5 \times 10^{-4}$ sec^{-1}, with k_2 taking on values from 7×10^{-4} to 10^{-3} sec^{-1} in 3×10^{-4} increments, for selected values of t from 200 to 3500 sec. Plots of $\log f$ *vs.* time were made, and the curve best representing the experimental data (by superimposition) had $k_2 = 10^{-3}$. Other sets of f were evaluated, this time varying k_1 from 5.8×10^{-4} to 7.0×10^{-4} in increments of 0.2×10^{-4}, and varying k_2 from 9.1×10^{-4} to 10.9×10^{-4} in increments of 0.3×10^{-4}. In all, 49 sets of f were obtained, each evaluated for 27 recorded experimental times. By superimposition of f on the experimental graph, the best visual fit was made and the value of A_0 obtained. With this, theoretical values of $V_\infty - V_t$ were evaluated as A_0f. A minimum in the standard deviation between A_0f and $(V_\infty - V_t)$ observed was then sought, beginning at $k_1 = 6.6 \times 10^{-4}$ and $k_2 = 10^{-3}$. In this way values for $k_1 = 6.6 \times 10^{-4}$ and $k_2 = 9.4 \times 10^{-4}$ were determined. See Table III for final tabulated data. Identifying k_1 with k and k_2 with $k_i[OH^-]$ leads to $k = 6.6 \times 10^{-4}$ sec^{-1} and $k_i = 1.7 \times 10^{-3}$ l. mol^{-1} sec^{-1}, in excellent agreement with previous values obtained at higher base concentration.

---

(5) See discussion by A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1953, p 153 ff.

(6) For a k_2/k_1 ratio of 5, t must be greater than seven times the short half-life related to k_2 if the Δ terms are to be less than 0.2% A_0.

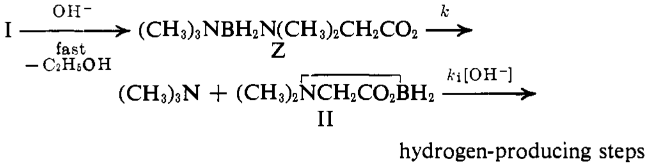
The problems of ordering the rate constants k and k_i and developing a plausible mechanism require more experimental data. Ancillary evidence bearing on the problems was amassed from studies of isotope effects and from isolation and synthesis of intermediates.

The possibility that the induction step is the saponification of the ester moiety can almost be eliminated out of hand in that the rates observed are less than one-tenth that for the saponification of ethyl acetate.[7] A saponification rate larger than that for ethyl acetate and more like those of quaternary ammonium esters would be expected. Rates of quaternary ammonium esters are known to be 200 or more times that of ethyl acetate. Ethoxycarbonylmethyltriethylammonium ion, for example, has a 25° rate of 31 l. mol^{-1} sec^{-1}, or about $2000k_i$.[8] This quaternary ammonium ion is structurally related to I, having the $(CH_3)_3NBH_2$ group replaced by ethyl. It is not likely that the decrease in $+I$ inductive effect caused by the replacement would account for the factor of 2000 decrease in rate.

Experimental evidence confirms that k_i is not for saponification. A solution of I was treated with 0.01 *M* OH$^-$ for *ca.* 800 sec, and then neutralized precisely and evaporated to dryness, but no starting salt was recovered. Instead, a new cyclic borane, $(CH_3)_2NCH_2CO_2BH_2$ (II), was isolated, and its characterization and importance are discussed later. A control solution of I, containing the equivalent amount of NaCl that would have been produced in the neutralization of the 0.01 *M* OH$^-$ run, was taken to pH 7 and evaporated in an identical manner. This time 86% of I was recovered. It can therefore be concluded that the 0.01 *M* OH$^-$ treatment destroyed I. If k_i were saponification, the most that should have been saponified under the conditions would be about 15%. A saponification rate in excess of 0.2 l. mol^{-1} sec^{-1} is therefore inferred, and clearly k_i is too small for saponification.

The d_2 isomer of I was synthesized and its hydrolysis studied, see Table IV. Within experimental error there was no isotope effect with k; the inductive rate k_i is too imprecise to ascertain any effect. The species that is decaying by rate constant k does not, therefore, primarily involve B–H bonds in the transition state.

A mechanism can be described that is supported by all the ezperimental data. Key evidence for this mechanism is the controlled-hydrolysis experiment with 0.01 *M* OH$^-$, in which a 50% yield of cycle compound II, 3,3-dimethyl-2-boryla-3-azoniatetrahydrofuranone-5, was isolated. It is a sublimable, crystalline solid which is stable in air and neutral or acidic solution. In the vapor state it appears to be monomeric as judged by a large P − 1 mass spectrum peak at m/e 114, but in benzene some association occurs. Hydrolysis of II is second order, first order in hydroxide, with $k = 1.8 \pm 0.2 \times 10^{-2}$ l. mol^{-1} sec^{-1}, identical with k_i within experimental error.



$$\mathrm{I} \xrightarrow[\substack{\text{fast}\\ -C_2H_5OH}]{OH^-} \underset{\mathrm{Z}}{(CH_3)_3NBH_2N(CH_3)_2CH_2CO_2} \xrightarrow{k}$$

$$(CH_3)_3N + \underset{\mathrm{II}}{(CH_3)_2NCH_2CO_2BH_2} \xrightarrow{k_i[OH^-]}$$

hydrogen-producing steps

Table III. Hydrolysis of I at 29.8° in D_2O[a]

Time, sec	Obsd $100(V_\infty - V_t)$, ml	Calcd[b] A_0f	Deviation $\lvert 100(V_\infty - V_t) - A_0f \rvert$
218	64	65.0	1.0
332	62	63.9	1.9
535	60	61.4	1.4
626[c]	59	60.0	1.0
770	57	57.8	0.8
897	55	55.5	0.5
1019	53	53.3	0.3
1141	51	51.0	0
1194	50	50.0	0
1253	49	48.9	0.1
1304	48	48.0	0
1363	47	46.8	0.2
1477	45	44.7	0.3
1530	44	43.7	0.3
1741	40	39.9	0.1
1917	37	36.8	0.2
2032	35	34.9	0.1
2208	32	32.0	0
2340	30	30.0	0
2412	29	28.9	0.1
2740	24	24.4	0.4
3044	20	20.8	0.8
3235	18	18.7	0.7
4366	9.8	9.8	0
4545	8.0	9.0	1

[a] Ionic strength, 0.95; [OD$^-$], 0.056 *M*. [b] Calculated from $A_0f = 65.9[(9.4/2.8)\exp(-6.6 \times 10^{-4t}) - (6.6/2.8)\exp(-9.4 \times -10^{-4t})]$. [c] Standard deviation was calculated only for times greater than 626 sec because the first volumes seem to be systematically high—possibly from lag in temperature equilibration. Standard deviation of the last 21 points is 0.4. Standard deviation for the entire set of 25 points is 0.7.

Table IV. Hydrolysis of d_2-I, $(CH_3)_3NBD_2N(CH_3)_2CO_2C_2H_5{}^+PF_6{}^-$, at 29.8°; Ionic Strength, 0.9

[OH$^-$], *M*	10^2k_i, l. mol^{-1} sec^{-1}	10^4k, sec^{-1}
0.2	2.0	6.7
0.2	1.6	6.9
0.4	1.8	6.4

In most of the kinetic runs where [OH$^-$] ⩾ 0.2 *M*, the concentration of II would be quite small, since k_i [OH] > k, but in the controlled experiment at 0.01 *M* OH$^-$ appreciable concentrations could be expected. The first saponification step probably proceeds with a second-order rate constant near 1 sec^{-1} M^{-1} and would be expected to be essentially complete in 700–1000 sec. Less than 50% of the Z formed will decompose to II, and of this, less than 2% will be hydrolyzed. During the long evaporation (several hours) in neutral solution, the cyclization, k step, will go to completion with no loss by the k_i step.

---

(7) The second-order rate constant in 1 *M* KCl is 0.113 l./mol^{-1} sec^{-1} at 25°: "International Critical Tables," Vol. VII, McGraw-Hill, New York, N. Y., 1963, pp 129–130.

(8) (a) R. P. Bell and F. J. Lindars, *J. Chem. Soc.*, 4601 (1954), studied saponification of $(C_2H_5)_3NCH_2CO_2C_2H_5{}^+Cl^-$; (b) G. Aksnes and J. E. Prue, *ibid.*, 103 (1959), studied hydrolyses of four esters with quaternary nitrogen in acid and base.

The intermediate zwitterion Z should be present in significant concentrations relative to the amount of I taken. Two attempts to extract this intermediate from hydrolyzing solutions were unsuccessful. This intermediate should be polar and very soluble in water; attempts, therefore, to solvent extract it from aqueous solution would be hindered by low distribution coefficients between organic and aqueous phases. The synthesis of Z was therefore attempted by combining $(CH_3)_3NBH_2I$ and $(CH_3)_4N^+(CH_3)_2NCH_2CO_2^-$. The calculated amount of $(CH_3)_4N^+I^-$ was found, but the chloroform-soluble material was a mixture designated M-1 containing II and probably Z, as judged from its ^1H nmr spectrum. The mixture dissolves readily in water with slow hydrogen evolution. Basic hydrolysis of M-1 (Table V) could be analyzed as two simultaneous reactions, one first order and the other first order in substrate and hydroxide. The slower rate is essentially identical with k for I, but the faster rate is 40% greater than k_i. Possibly some impurity species which is very base sensitive to hydrolysis is also present. A slow hydrogen release observed for the mixture in neutral solution would suggest the presence of an impurity since II does not hydrolyze in neutral solution, and it is unlikely that Z does either, being structurally so similar to the inert bistertiary amine–borane cations.

Table V. Hydrolysis of Reaction Mixture M-1 at 29.8°; Ionic Strength, 0.9

$[OH^-]$, M	10^2k_a, l. mol^{-1} sec^{-1} [a]	10^4k_b, sec^{-1} [b]
0.2	2.3	5.8
0.4	2.33	6.3
0.5	2.5	6.9
	2.4 ± 0.2	6.3 ± 0.5

[a] k_a = pseudo-first-order constant/$[OH^-]$. [b] First-order constant for parallel reaction.

Another possible intermediate, $(CH_3)NBH_2OCOCH_2N(CH_3)_2H^+$, was sought by reaction of dimethylglycine, $(CH_3)_2N^+HCH_2CO_2^-$, with $(CH_3)_3NBH_2I$. Unexpectedly, a significant yield (67%) of chloroform-insoluble trimethylammonium iodide was isolated, along with a transparent, water-soluble oil, denoted M-2. This oil had complicated ^1H nmr and ir spectra.

The hydrolysis of M-2 in basic solution was studied (see Table VI). Very rapid (less than 60 sec) release of about 40% of hydrolytic hydrogen occurs in neutral solution. Addition of base leads to the release of the remaining hydrogen in a second-order process, first order in hydroxide, with a rate constant of $1.7 \pm 0.4 \times 10^{-2}$ l. mol^{-1} sec^{-1}.

A small amount of II was isolated from M-2, and its presence can be accounted for in a simple way.

$$(CH_3)_3NBH_2OCOCH_2N(CH_3)_2H^+ \longrightarrow II + (CH_3)_3NH^+$$

Other species besides the desired $(CH_3)_3NBH_2OCOCH_2N(CH_3)_2H^+$ are probably present.

Table VI. Hydrolysis of Reaction Mixture M-2 at 29.8°; Ionic Strength, 0.9

Sample size, mg	$[OH^-]$, M	10^2k_c, l. mol^{-1} sec^{-1} [a]
6.9	0.3	1.9
6.7		1.5
13.2	0.6	2.6[b]
3.1		1.8
		1.7 ± 0.4

[a] k_c = pseudo-first-order constant/$[OH^-]$. [b] The large sample size is believed responsible for the high value.

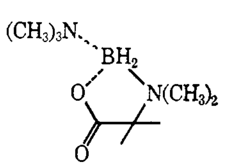
Temperature dependence and salt effects of the hydrolysis of I were also investigated. The activation parameters appear in Table VII; they are consistent with an activation process for the k step envisioned as a concerted cyclization and amine elimination.

Table VII. Temperature Dependence in Hydrolysis of I[a]

Temp, °C	10^4k, sec^{-1}	10^3k_i, l. mol^{-1} sec^{-1}
13.1[b]	0.6	
25.4	3.71	
	3.78	
29.8	6.5	1.7
38.1	16.1	38
	15.9	40 ± 10

Activation Parameters[c]
E_a = 20.3 ± 0.5 kcal/mol
$\Delta H^{\ddagger}$ = 19.8 ± 0.5 kcal/mol
$\Delta S^{\ddagger}$ = −8.1 eu

[a] Ionic strength, 0.9; $[OH^-]$, 0.2 M. [b] Only one run made at this temperature. Since V_∞ had to be calculated, the rate constant is very suspect and was not used to determine activation parameters. [c] Calculated and obtained graphically: $E_a = -4.567 \times$ slope, plot of log k *vs.* $1/T$; $\Delta H^{\ddagger} = -4.576 \times$ slope, plot of log k/T *vs.* $1/T$; $\Delta S^{\ddagger} = 4.576(\log k - 10.75 - \log T + 20.3 \times 10^3/4.576T)$, $k = 3.75 \times 10^{-4}$ sec^{-1} interpolated for T = 298.2°K.



A simple dissociative loss of trimethylamine is less likely, in that the very reactive trigonal boron site produced would be expected to react with the media very rapidly.[9]

There is little evidence that the dissociation is reversible. Results of an nmr search for an equilibrium of II with trimethylamine were negative. Proton nmr of II in water or methylene chloride shows no additional resonances on treatment with trimethylamine up to 2.5 M concentration (in 0.6 M II). Neither was there

---

[9] K. C. Nainan and G. E. Ryschkewitsch, *J. Amer. Chem. Soc.*, **91**, 330 (1969).

any kinetic evidence for reversibility. Addition of trimethylamine (up to 0.3 *M*) into hydrolyzing solutions of I did not appreciably change the slope. Much longer induction times were encountered, however, but it is apparent that this is a property of the k_i step rather than the k step. Hydrolyses of II in either trimethylamine or $(CH_3)_2NCH_2CO_2^-$ up to 0.3 *M* show enhanced induction periods (about 200 sec as opposed to about 60 sec without amine added).

A small normal salt effect is evident at 29.8° (Table VIII). No attempt was made to relate the effect to activities because of the lack of precision, and because the ionic strengths are too large, well out of range of usual treatments. There is little specific salt effect as shown by small change in k when CsCl rather than KCl is used as the supporting electrolyte. Only a small general salt effect is expected, however, for the proposed mechanism.

Table VIII. Effect of Ionic Strength on Hydrolysis of I[a]

Ionic strength	10^4k	10^3k_i
	29.8°	
0.2	7.3	1.8
	6.7	
0.4	7.1 ± 0.2	2.8
	6.85	2.0
0.9	6.5	1.7
0.9 (0.5 *M* CsCl, 0.4 *M* OH^-)	6.9	
	38.1°	
0.2	16.0	35
0.9	16.0	39

[a] $[OH^-] = 0.2$ *M*.

The only mechanistic information for the k_i step that can be deduced from the kinetic data for I is that it is approximately first order in substrate and hydroxide. Preliminary kinetic data on isolated II (see Table IX) show an induction step and some evidence for equilibria. Log $V_\infty - V_t$ plots are not linear for time greater than three half-lives. A detailed study of the chemical properties of this compound and a study of the hydrolysis kinetics are the objects of continuing investigation.

The possibility that $(CH_3)_3NBH_2OH$ is formed in the hydrolysis of I by loss of glycinate base was explored. While $(CH_3)_3NBH_2OH$ is not an isolable compound, it might be presumed to result from displacement of iodide by hydroxide in the hydrolysis of $(CH_3)_3NBH_2I$ in base. The hydrolysis of trimethylamine–iodoborane was therefore investigated and found to proceed with first-order kinetics with small isotope effect, $k_H/k_D = 1.2$ (see Table X). The rate constant at 29.8° is $4.5 \pm 0.3 \times 10^{-3}$ sec^{-1}. The poor precision attained in the hydrolysis was attributed to solubility problems. It was difficult to know if all the material had dissolved before data were collected. Small traces of solid floating on the top or caught on the vessel side walls could have been slowly dissolving during the first part of the run. Nearly complete hydrolysis occurred, as contrasted to only 85–95% hydrolysis of I.

The present data, while insufficient to distinguish between $(CH_3)_3NBH_2OH$ or $(CH_3)_3NBH_2I$ as the species involved in the rate step for $(CH_3)_3NBH_2I$ hydrolysis, do exclude $(CH_3)_3NBH_2OH$ as an early intermediate in the hydrolysis of I. Even if $(CH_3)_3NBH_2I$ did undergo a dissociative rate step, $(CH_3)_3NBH_2OH$ must then be formed by solvation and proton abstraction and produce hydrogen by much faster steps. The hydrolysis rate constant of $(CH_3)_3NBH_2OH$, whether the observed 4.6×10^{-3} sec^{-1} or much faster, is larger than k; consequently $(CH_3)_3NBH_2OH$ could only be present in minute amounts from a competitive reaction.

Table IX. Hydrolysis of $(CH_3)_2\overline{NCH_2CO_2B}H_2$ at 29.8°; Ionic Strength, 0.9

10^2[substrate], *M*	$[OH^-]$, *M*	Pseudo-first-order constant, sec^{-1}	10^2k_i, l. mol^{-1} sec^{-1} [a]
1.8	0.2	3.46×10^{-3}	1.73
1.8	0.4	6.50×10^{-3}	1.62
2.4[b]	0.2	3.48×10^{-3}	1.72
2.2[c]	0.2	3.92×10^{-3}	1.97
2.6	0.2	3.76×10^{-3}	1.86
2.3	0.3	5.90×10^{-3}	1.94
2.2[d]	0.3	4.90×10^{-3}	1.63
2.6[d]	0.3	5.10×10^{-3}	1.70
2.4	0.3	5.35×10^{-3}	1.78

[a] Pseudo-first-order constant/$[OH^-]$. [b] Solution 0.13 *M* in added trimethylamine. [c] Solution 0.25 *M* in added trimethylamine. [d] Solution 0.06 *M* in added $(CH_3)_2NCH_2CO_2^-$.

Table X. Hydrolysis of $(CH_3)_3NBH_2I$ and $(CH_3)_3NBD_2I$ at 29.8°; Ionic Strength, 0.9

Compound	$[OH^-]$, *M*	$10^3k'$, sec^{-1}
$(CH_3)_3NBH_2I$	0.0	4.2
	0.2	4.6
	0.3	4.8
	0.4	5.3
	0.7	4.3
		Av 4.6 ± 0.3
$(CH_3)_3NBD_2I$	0.3	3.78
	0.6	4.0
		3.78
		3.28
		Av 3.71 ± 0.3

The hydrolysis of I appears distinctly different in character than the hydrolyses of primary and secondary amine–borane cations. Shchegoleva and coworkers,[10] for example, find that the latter cation types are stable in acid but evolve hydrogen slowly in neutral solution and rapidly in base. From rate studies of solvolyses in alcohol and water, they conclude that solvent dis-

---

(10) T. A. Shchegoleva, V. D. Sheludyakov, and B. M. Mikhailov, *Zh. Obshch. Khim.*, **35**, 1066 (1965); *J. Gen. Chem. USSR*, **35**, 1070 (1965).

placement of amine governs the rate. Such solvent attack does not obtain in the hydrolysis of I, where carboxylate and then hydroxide are the attacking species.

The steric restrictions to approach for cations of primary and secondary amine are usually less than that for tertiary amines (except for π bases like pyridine) and may account for the observed differences in lability. The facile loss of trimethylamine from Z, which is not sterically much different from inert $[(CH_3)_3N]_2BH_2^+$, would then require explanation. An attractive possibility is that the linkage of the attacking carboxylate to the substrate in Z permits a configuration with close oxygen–boron approach in the absence of solvent cage. Simple aquated ions and water, in this view, are inoperative because of large size or insufficient nucleophilicity to displace amine from the cations. One would expect attack only by small anions with good nucleophilic power and weak solvation. Some supportive evidence is found in the pyrolysis of $[(CH_3)_3N]_2BH_2^+X^-$ salts.[11] Whereas the halide ions require temperatures near 200° for amine replacement, the more nucleophilic azide and carbonate react at 100° or below.

A structural factor also of importance in hydrolysis of I is the location of the carboxylate group such that cyclization can proceed to give a five-membered ring. The similar cation $(CH_3)_3NBH_2CH_2N(CH_3)_2CH_2CO_2C_2H_5^+$ [12] loses the ester moiety in base but is not hydrolyzed. A cyclization *via* the carboxylate did not occur either because of a different electronic environment at boron, or more likely because of the additional strain that the six-membered ring closure would produce.

The results of this study of the first hydrolytically unstable bistertiary amine–borane cation, then, implicate steric effects as the primary source of the chemical inertness of bistertiary amine–borane cations.

Acknowledgment. Support by a grant from the National Science Foundation is gratefully acknowledged. Assistance in calculation of trial exponential functions from Mr. Lanny Hoffman is also appreciated.

---

[11] N. E. Miller, B. L. Chamberland, and E. L. Muetterties, *Inorg. Chem.*, 3, 1064 (1964).

[12] N. E. Miller and D. L. Reznicek, *ibid.*, 8, 275 (1969).

Boron Insertion Reactions. II. The Preparation of μ-Dimethylborylpentaborane(9) and 4,5-Dimethylhexaborane(10)[1]

Donald F. Gaines and Terry V. Iorns

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received February 17, 1970

Abstract: Lithium octahydropentaborate(1−), LiB_5H_8, reacts with dimethylboron chloride at low temperatures to produce μ-dimethylborylpentaborane(9), in which the dimethylboryl moiety appears to occupy a bridging position between two boron atoms in the base of the pentaborane(9) tetragonal pyramid. This unusual compound is considered to be a stable intermediate in the formation of a B_6 pentagonal pyramid structure from a B_5 tetragonal pyramid precursor *via* a rational boron insertion reaction. This hypothesis is supported by the observation that μ-dimethylborylpentaborane(9) isomerizes in the presence of diethyl ether to 4,5-dimethylhexaborane(10).

The preparation of the octahydropentaborate(1−) anion, $B_5H_8^-$, and several group IV derivatives of pentaborane(9) has been described in previous papers.[2] In related research, other workers have reported that the octahydropentaborate(1−) anion reacts with dialkylchlorophosphines to form phosphinopentaborane(9)'s[3] and with diborane(6) to yield hexaborane(10) as the end product.[4]

Several explicit examples of boron insertion reactions have been reported in which phenylboron dichloride reacts with the (3)-1,2-dicarbollide ion to form 3-phenyl-1,2-dicarba-*closo*-dodecaborane(12)[5]

$$C_6H_5BCl_2 + Na_2B_9C_2H_{11} \longrightarrow 2NaCl + C_6H_5B_{10}C_2H_{11}$$

and with $B_{10}H_{10}S^{2-}$ to form the icosahedral species $C_6H_5B_{11}H_{10}S$.[6] The recently reported preparation of 1,1-dimethyldiborane(6) and 2,2-dimethyltetraborane(10) from the reaction of dimethylboron chloride with sodium borohydride and sodium triborohydride, respectively, represents another type of boron insertion reaction.[1] We wish to describe here a boron insertion reaction involving the octahydropentaborate(1−) anion and the subsequent characterization and some chemical properties of the product of this reaction.

Results and Discussion

Lithium octahydropentaborate(1−) reacts readily with dimethylboron chloride to form a bridge-substituted pentaborane(9) derivative

---

[1] For the previous paper see D. F. Gaines, *J. Amer. Chem. Soc.*, 91, 6503 (1969).

[2] D. F. Gaines and T. V. Iorns, *ibid.*, 90, 6617 (1968), and references therein.

[3] A. B. Burg and H. Heinen, *Inorg. Chem.*, 7, 1021 (1968).

[4] R. A. Geanangel and S. G. Shore, *J. Amer. Chem. Soc.*, 89, 6771 (1967).

[5] M. F. Hawthorne and P. A. Wegner, *ibid.*, 90, 896 (1968).

[6] W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, 6, 1696 (1967).