

and  $-3.50$  ppm in the spectrum of  $1,2,3,4\text{-B}_{10}\text{H}_{10}\text{D}_4$  and the collapse to area 1 of the quartet at  $-0.55$  ppm in the spectrum of  $2\text{-BrB}_{10}\text{H}_{13}$  allow the unambiguous assignment of the 1,3 and 2,4 positions in the spectrum of  $\text{B}_{10}\text{H}_{14}$ . The quartet of area 4 must arise from the 5,7,8,10 positions. The remaining quartet at  $-3.6$  ppm may now be assigned to the 6,9 positions.

The order of chemical shifts in the  $^1\text{H}$  nmr parallels that of the  $^{11}\text{B}$  nmr, with the exception of a small

inversion of the 1,3 and 6,9 positions, and is in agreement with the order postulated by Williams, *et al.*<sup>4</sup>

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## The Kinetics and Mechanism of Trimethylamine-Haloborane Hydrolysis<sup>1,2</sup>

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The rates of solvolysis of trimethylamine-mono-haloboranes in aqueous dioxane at  $25^\circ$  increase in the series  $(\text{CH}_3)_3\text{NBH}_2\text{Cl} < (\text{CH}_3)_3\text{NBH}_2\text{Br} < (\text{CH}_3)_3\text{NBH}_2\text{I}$ . The diiodoborane adduct reacts more slowly than the monoiodo compound but faster than trimethylamine-borane. Only a very slight retardation in rate is observed on substitution of deuterium for hydrogen on boron in the diiodo derivative ( $k_{\text{H}}/k_{\text{D}} = 1.1$ ); however, a noticeable solvent isotope effect ( $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 1.8$ ) is observed for hydrolysis of both the mono- and diiodoborane adducts in 67% aqueous dioxane at  $25^\circ$ . Rates increase with increasing water content of the aqueous dioxane solvent system. No significant effect on rate of acidity is seen for hydrogen ion concentrations as high as  $0.3 M$  or hydroxide ion concentrations up to  $0.1 M$ , nor is the rate appreciably affected by the addition of potassium chloride or potassium iodide up to  $0.3 M$ . The results indicate a mechanism for hydrolysis of the halo compounds quite different from that postulated for amine- $\text{BH}_3$  adducts. It is proposed that a rate-determining cleavage of a boron-halogen bond is followed by rapid collapse of an incipient boron( $1+$ ) ion. An analogy to nucleophilic substitution reactions in haloborane-amines leading to kinetically stable boronium ions is suggested.

### Introduction

Various effects of B and N substitution on the rates and mechanism of hydrolysis of amine-boranes have been reported.<sup>4-9</sup> Reaction paths proposed include rate-determining cleavage of a boron-hydrogen bond for solvolysis of certain B-phenyl-substituted boranes,<sup>4-6</sup> the boron-nitrogen bond for solvolysis of  $-\text{BH}_3$  adducts of amines,<sup>7,8</sup> and a boron-halogen bond for the decomposition of tertiary amine-trichloroboranes in aqueous ethanol.<sup>9</sup> The development, in recent years, of convenient routes to the synthesis of mono- and dihaloborane adducts of amines<sup>10-13</sup> now allows the

study of these substrates as a means of elucidating specific effects of B-halo substitution on the mechanism of reactions of hydride-containing amine-borane addition compounds.

### Experimental Section

**Materials.**—Sources of chemicals were as follows: trimethylamine-borane (99.1%) and boron trichloride, Matheson Coleman and Bell; deuterium oxide (99.8% isotopic purity), New England Nuclear Corp.; lithium tetrahydroaluminate and boron tribromide, Alfa Inorganics. Tetrahydrofuran (MCB) was distilled from  $\text{LiAlH}_4$  prior to use (*caution should be exercised in the distillation of tetrahydrofuran*).<sup>14</sup> The *p*-dioxane was obtained from Eastman and was treated according to the procedure described by Vogel<sup>15</sup> and then boiled under reflux with  $\text{LiAlH}_4$  and distilled. Benzene (MCB) was distilled from sodium.

**Spectra and Analysis.**—Infrared spectra were obtained on samples contained in KBr wafers using a Perkin-Elmer Model 237 infrared spectrophotometer. Proton nmr were obtained using a Varian A-60A spectrometer and are referred to tetramethylsilane as external standard. The  $^{11}\text{B}$  nmr were obtained using a Varian Model HA100 spectrometer with a  $^{11}\text{B}$  probe (32.1 Mc) and are referred to trimethyl borate as external standard. Chemical analyses for C, H, N, and halogen as well as molecular weight data were obtained by M-H-W Laboratories, Garden City, Mich. Hydridic hydrogen was determined by measurement of the hydrogen evolved on acid hydrolysis of known

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samples of haloborane-amine, and boron was determined by the subsequent titration of the hydrolysates as previously described for the analysis of amine-boranes.<sup>16</sup>

**Preparation of Compounds.**—Haloborane-amine addition compounds were prepared by the methods described by Nöth and Beyer<sup>11</sup> or by slight modifications thereof. Some data on yields and compound characterization are given below.

**(CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>I.**—A 25-g (91% theory) yield was obtained from the reaction of 10 g (0.14 mol) of (CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub> with 17.5 g (0.07 mol) of I<sub>2</sub> in 250 ml of benzene. The compound was purified by sublimation *in vacuo* at 50°; mp 73° (lit.<sup>11</sup> mp 72°).

**(CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>Br.**—A 21.7-g (91% theory) yield was obtained from 11.5 g (0.157 mol) of (CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub> and 13.5 g (0.053 mol) of BBr<sub>3</sub> in 140 ml of benzene under dry N<sub>2</sub>; B<sub>2</sub>H<sub>6</sub> was trapped in an equimolar mixture of THF and methanol. *Anal.* Calcd for (CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>Br (151.85): H(hydridic), 1.33. Found: H(hydridic), 1.28, 1.29; mp 67° (lit.<sup>11</sup> mp 67°).

**(CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>Cl.**—A yield of 27.2 g (92% theory) was obtained from the reaction of 20.1 g (0.275 mol) of (CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub> in 500 ml of benzene and gaseous hydrogen chloride (dried over P<sub>2</sub>O<sub>5</sub> and bubbled through the benzene solution of borane). The product was recrystallized from a mixture of benzene and petroleum ether. *Anal.* Calcd for (CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>Cl (107.4): C, 33.6; H, 10.3; N, 13.0; B, 10.1; H(hydridic), 1.87. Found: C, 33.3; H, 10.3; N, 13.1; B, 10.2; H(hydridic), 2.05; mp 82–84° (lit.<sup>11</sup> mp 85°).

**(CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>I<sub>2</sub>.**—A yield of 26 g (58% theory) of white crystals was obtained from the reaction of 10 g of (CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub> with 35 g (0.14 mol) of I<sub>2</sub> in 250 ml of refluxing benzene (12 hr). The product was purified by sublimation *in vacuo* at 50°. *Anal.* Calcd for (CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>I<sub>2</sub> (324.8): C, 11.10; H, 3.10; N, 4.31; B, 3.33; I, 78.16; H(hydridic), 0.31. Found: C, 11.10; H, 3.05; N, 4.02; B, 3.26; I, 78.76; H(hydridic), 0.32; mol wt 328; mp 111.5–112°. The infrared spectrum shows a sharp singlet in the B–H stretching region at 2500 cm<sup>-1</sup>. The proton nmr exhibits a singlet at –1.99 ppm relative to (CH<sub>3</sub>)<sub>4</sub>Si and the <sup>11</sup>B spectrum consists of a symmetrical doublet at 41.6 ppm relative to trimethyl borate with J<sub>B–H</sub> = 140 cps.

**(CH<sub>3</sub>)<sub>3</sub>NBD<sub>2</sub>.**—A yield of 4.52 g (85% theory) was obtained *via* hydride exchange through reaction of 5.11 g (0.070 mol) of (CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub> with D<sub>2</sub>O in the presence of sulfuric chloride according to the method of Davis and coworkers.<sup>17</sup>

**(CH<sub>3</sub>)<sub>3</sub>NBDI<sub>2</sub>.**—A yield of 5.75 g (53% theory) was obtained from the reaction of 2.53 g (0.033 mol) of (CH<sub>3</sub>)<sub>3</sub>NBD<sub>3</sub> with 8.87 g of I<sub>2</sub> in benzene by the method used for the preparation of the corresponding hydrido derivative. *Anal.* Calcd for (CH<sub>3</sub>)<sub>3</sub>NBDI<sub>2</sub> (325.7): C, 11.06; H + D, 3.41; N, 4.30; I, 77.92. Found: C, 11.06; H + D, 3.25; N, 4.22; I, 77.83; mp 112°. The infrared spectrum exhibited strong absorption in the B–D stretching region at 1875 cm<sup>-1</sup> and negligible absorption in the B–D stretching region.

**(CH<sub>3</sub>)<sub>3</sub>NBHBBr<sub>2</sub>.**—A yield of 10.4 g (77% theory) was obtained from the reaction of 4.2 g (0.058 mol) of (CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub> with 9.6 g (0.038 mol) of BBr<sub>3</sub> in 180 ml of refluxing benzene. The product was purified by recrystallization from a mixture of benzene and petroleum ether. *Anal.* Calcd for (CH<sub>3</sub>)<sub>3</sub>NBHBBr<sub>2</sub> (230.8): C, 15.6; H, 4.4; N, 6.1. Found: C, 15.4; H, 4.5; N, 6.1; mol wt, 230; mp 126–127° (lit.<sup>11</sup> mp 126–127°).

**(CH<sub>3</sub>)<sub>3</sub>NBHCl<sub>2</sub>.**—A solution of 2.93 g (0.040 mol) of (CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub> in 75 ml of benzene was deaerated in the high-vacuum line by four freeze-pump-thaw cycles following which 621 ml (STP) of boron trichloride was condensed into the borane solution and the reaction mixture warmed to room temperature. From time to time material that had volatilized was recondensed into the reaction bulb and the mixture was again warmed. The solution was stirred at room temperature for 12 hr. Volatile material was removed by evaporation *in vacuo* and the evolved diborane was solvolyzed in a mixture of THF-methanol. A white solid

residue was obtained; yield 5.30 g (93% theory). *Anal.* Calcd for (CH<sub>3</sub>)<sub>3</sub>NBHCl<sub>2</sub> (141.8): C, 25.40; H, 7.11; N, 9.88; Cl, 49.99. Found: C, 25.07; H, 7.25; N, 9.63; Cl, 49.47; mp 150 (lit.<sup>10</sup> mp 151°).<sup>10</sup> The compound exhibits a sharp singlet at 2465 cm<sup>-1</sup> in the infrared.

**Kinetic Experiments.**—Aqueous dioxane solutions were prepared by mixing freshly distilled dioxane with appropriate volumes of water, deuterium oxide, standard aqueous HCl, or standard aqueous NaOH, and the concentration of solvated hydrogen ion or hydroxide ion was calculated from dilution. For studies at constant ionic strength, reagent grade KCl was used when the total ionic strength was not due solely to the contained acid or alkali. The temperature was controlled through the use of a Sargent Thermometer controlled water bath or with a Wilkins-Anderson constant-temperature bath. Kinetic studies on the diiodo compound were carried out by the iodometric determination of soluble hydride at various periods of time as previously described for the study of the solvolysis of amine-borane adducts.<sup>7a</sup> For the relatively rapidly reacting monobromo and monoiodo adducts, measured samples of the hydrolysate were periodically discharged directly into prepared acidified I<sub>3</sub><sup>-</sup> solutions to diminish the uncertainty in the time of sampling. The reaction of the monochloroborane adduct with iodine was too slow for the determination of substrate concentration by this method, but its reaction with Br<sub>2</sub> was sufficiently fast to permit the use of a modified procedure involving generation of Br<sub>2</sub> from standard KBrO<sub>3</sub> and excess KBr in acid solution and an iodometric determination of the Br<sub>2</sub> which was present in excess of that required to react with soluble hydride.<sup>18</sup> Reactions of the dibromo- and dichloroboranes with halogen were slow and rate constants for the hydrolysis of these substrates were not measured. Slow hydrolysis rates relative to the monobromo and monochloro adducts were evidenced, however, by negligible evolution of hydrogen from 67% aqueous dioxane solutions of these substrates over a period of several days at 25°. Except for the dibromo- and dichloroboranes, all hydrolyses were carried to greater than 50% completion of reaction and that of the monobromo adduct was carried to greater than 3 half-lives. Initial concentrations of haloborane-amine ranged from 10<sup>-3</sup> to 0.031 M. In all cases linear relationships of log [amine-borane] *vs.* time were observed over all time intervals. A linear regression analysis of the data was performed for the determination of activation parameters and most rate constants.

For the determination of solvent isotope effects, separate measurements of the rates of solvolysis of the appropriate iodoborane-amines were made at 25° in 67% dioxane-33% H<sub>2</sub>O and 67% dioxane-33% D<sub>2</sub>O. For the study of substrate isotope effects, the rates of hydrolysis of (CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>I and (CH<sub>3</sub>)<sub>3</sub>NBDI<sub>2</sub> (initial concentrations 0.0002–0.0004 M) were measured independently in 67% dioxane-33% H<sub>2</sub>O at 25°.

## Results and Discussion

Data obtained for the solvolysis of several amine-haloboranes (Table I) clearly indicate a dissimilarity in mechanism from those proposed for the hydrolysis of amine-BH<sub>3</sub> adducts and amine-B-aryl derivatives. In contrast to the behavior of trimethylamine-borane which undergoes hydrolysis at a significant rate only *via* an acid-catalyzed path, the solvolysis rates of the monohaloborane adducts of trimethylamine are appreciable in neutral aqueous dioxane and show a first-order dependence on substrate (eq 1) which is not appreciably affected by the addition of hydrogen ion up to concentrations of 0.3 M. This behavior also con-

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TABLE I

RATES OF SOLVOLYSIS OF TRIMETHYLAMINE-HALOBORANES

Solvent % dioxane-% water <sup>a</sup>	Temp, °C	10 <sup>3</sup> k <sub>obsd</sub> , sec <sup>-1</sup>	μ <sup>b</sup>
(CH <sub>3</sub> ) <sub>3</sub> NBH <sub>2</sub> I Substrate			
67-33	25.0	4.09	
67-33	25.0	4.02	0.3
67-33	25.0	2.25 <sup>c</sup>	0.3
67-33	25.0	3.00	0.2
67-33	25.0	1.54	0.1
67-33	25.0	1.28	0.3 <sup>d</sup>
67-33	25.0	1.55	0.3 <sup>e</sup>
67-33	25.0	1.34	0.3 <sup>f</sup>
67-33	10.0	0.82	0.3
67-33	17.5	1.93	0.3
60-40	25.0	4.32	0.3
50-50	25.0	6.41	0.3
(CH <sub>3</sub> ) <sub>3</sub> NBHI <sub>2</sub> Substrate			
67-33	25.0	0.0847	0.3
67-33	25.0	0.0480 <sup>c</sup>	0.3
67-33	25.0	0.0725	0.3 <sup>e</sup>
67-33	25.0	0.0626	0.3 <sup>h</sup>
67-33	25.0	0.0712	
67-33	25.0	0.0741	0.2
67-33	25.0	0.0818	0.1
67-33	32.4	0.172	0.3
67-33	40.0	0.436	0.3
67-33	47.5	0.802	0.3
50-50	25.0	0.456	0.3
60-40	25.0	0.189	
80-20	25.0	0.0162	
(CH <sub>3</sub> ) <sub>3</sub> NBH <sub>2</sub> Br Substrate			
67-33	6.1	0.0612	
67-33	15.0	0.171	
67-33	25.0	0.506	
67-33	35.0	1.31	
50-50	25.3	2.11	
60-40	25.3	1.02	
70-30	25.3	0.347	
80-20	25.3	0.108	
90-10	25.3	0.023	
95-5	25.3	0.0003	
60-40	25.3	1.01	0.3
67-33	25.3	0.41	0.3 <sup>f</sup>
60-40	25.3	1.06	0.05 <sup>i</sup>
(CH <sub>3</sub> ) <sub>3</sub> NBH <sub>2</sub> Cl Substrate			
67-33	25.0	0.00129	
67-33	35.0	0.00411	
67-33	45.1	0.0110	
67-33	55.6	0.0326	

<sup>a</sup> Denotes volume per cent. <sup>b</sup> Concentration of added electrolyte (KCl unless specified otherwise). No entry means no added salt. <sup>c</sup> Solvent: 67% dioxane-33% D<sub>2</sub>O. <sup>d</sup> 0.15 M HCl, 0.15 M KCl. <sup>e</sup> 0.23 M HCl, 0.07 M KCl. <sup>f</sup> 0.3 M HCl. <sup>g</sup> 0.3 M KI. <sup>h</sup> 0.1 M NaOH, 0.2 M KCl. <sup>i</sup> 0.05 M NaOH.

trasts to that of the -BH<sub>3</sub> adducts of arylamines which have been shown to hydrolyze by both uncatalyzed and acid-dependent paths. Further, a comparison of first-order rate constants for the hydrolysis of trimethylamine adducts of -BH<sub>3</sub> and the mono- and diiodoboranes in aqueous dioxane shows  $k_{\text{BH}_2\text{I}} > k_{\text{BHI}_2} \gg k_{\text{BH}_3}$  which seems incompatible with a suggestion that such a series reflects the effect of successive substitution of halide for hydride in reactions occurring by a similar pathway. It is, however, consistent with the proposal

that substitution of iodide for hydride ion in the -BH<sub>3</sub> adduct leads to a change in mechanism and that substitution of a second iodide exerts a retarding effect on the hydrolysis occurring by this different pathway. This is further supported by the fact that rates are greatly enhanced as the water content of the aqueous-dioxane solvent system is increased, a solvent effect opposite to that observed for the solvolysis, in neutral solution, of arylamine-boranes.<sup>7a</sup> Such an effect, however, is similar to that reported for trimethylamine-trichloroborane solvolysis in aqueous ethanol.<sup>9</sup>

TABLE II

SOLVENT AND SUBSTRATE ISOTOPE EFFECTS FOR THE SOLVOLYSIS OF TRIMETHYLAMINE-IODOBORANES IN 67% DIOXANE-33% WATER AT 25°

Substrate	Solvent component	10 <sup>3</sup> k <sub>obsd</sub> , sec <sup>-1</sup>	k <sub>H<sub>2</sub>O</sub> / k <sub>D<sub>2</sub>O</sub>	k <sub>H</sub> /k <sub>D</sub>
(CH <sub>3</sub> ) <sub>3</sub> NBH <sub>2</sub> I	H <sub>2</sub> O <sup>a</sup>	4.0 ± 0.2	1.8	
	D <sub>2</sub> O <sup>a</sup>	2.3 ± 0.1		
(CH <sub>3</sub> ) <sub>3</sub> NBHI <sub>2</sub>	H <sub>2</sub> O <sup>a</sup>	0.085 ± 0.001	1.8	
	D <sub>2</sub> O <sup>a</sup>	0.048 ± 0.001		
(CH <sub>3</sub> ) <sub>3</sub> NBHI <sub>2</sub>	H <sub>2</sub> O	0.0712 <sup>b</sup>		1.09
(CH <sub>3</sub> ) <sub>3</sub> NBDI <sub>2</sub>	H <sub>2</sub> O	0.0656 <sup>c</sup>		

<sup>a</sup> Solution contained 0.3 M KCl. <sup>b</sup> Average of three determinations: 0.0714, 0.0710, 0.0713. <sup>c</sup> Average of three determinations: 0.0680, 0.0658, 0.0629.

Solvent isotope effects  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 1.8$  are obtained for the solvolysis of both the mono- and diiodoborane adducts in 67% dioxane-33% water at 25° (Table II). This also contrasts with the acid-independent solvolysis of arylamine-boranes in which this ratio is found to be unity<sup>7a</sup> and with the hydrolysis of pyridine-diarylboranes in which much larger isotope effects, attributed to rate-determining solvent proton transfer,<sup>4</sup> are observed. The low substrate isotope effect observed for the hydrolysis of trimethylamine-diiodoborane ( $k_{\text{H}}/k_{\text{D}} = 1.1$ ) also suggests that extensive B-H bond cleavage is not occurring in the transition state. Activation parameters are given in Table III.

TABLE III

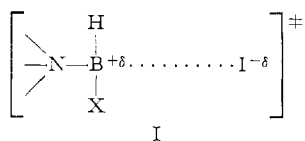
ACTIVATION PARAMETERS FOR SOLVOLYSIS OF HALOBORANE-AMINES IN 67% DIOXANE-33% WATER

Substrate	ΔH <sup>‡</sup> , <sup>a</sup> kcal/mol	r <sup>b</sup>	ΔS <sup>‡</sup> <sub>298</sub> , <sup>c</sup> eu
(CH <sub>3</sub> ) <sub>3</sub> NBH <sub>2</sub> I <sup>d</sup>	17.2	-0.999	-11.9
(CH <sub>3</sub> ) <sub>3</sub> NBHI <sub>2</sub> <sup>d</sup>	18.8	-0.997	-14.0
(CH <sub>3</sub> ) <sub>3</sub> NBH <sub>2</sub> Br	17.6	-0.999	-14.5
(CH <sub>3</sub> ) <sub>3</sub> NBH <sub>2</sub> Cl	19.8	-0.999	-19.2

<sup>a</sup> Obtained by linear regression analysis of data (Table I). <sup>b</sup> Correlation coefficient for line obtained from plot of log k<sub>obsd</sub> vs. 1/T. <sup>c</sup> Calculated from k<sub>298</sub> and ΔH<sup>‡</sup>. <sup>d</sup> Solution contained 0.3 M KCl.

We believe the kinetic data are consistent with a model for hydrolysis of the haloborane-amines which involves the rate-determining cleavage of a boron-halogen bond. The transition state is viewed as one of

incipient boronium ion formation with some question remaining as to the precise role of solvent water.

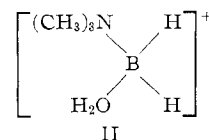


The enhancement of rate with increasing water content of the solvent occurs in the solvolyses of all the haloboranes studied. No demonstration of order in water is apparent from a plot of  $[\text{H}_2\text{O}]$  vs.  $k_{\text{obsd}}$ , which is nonlinear, but this may be complicated by a solvent effect due to the formation of a relatively highly polar activated complex. In an effort to establish whether  $k_{\text{obsd}}$  might best be regarded as a genuine first-order rate constant or as a pseudo-first-order constant (implying a concerted displacement of halide ion by  $\text{H}_2\text{O}$ ), plots of logarithms of both  $k_{\text{obsd}}$  and an "apparent second-order constant" ( $k_2 = k_{\text{obsd}}/[\text{H}_2\text{O}]$ ) against the Kirkwood parameter,  $(D - 1)/(2D + 1)$ ,<sup>19</sup> and against Winstein–Grunwald  $Y$  values<sup>20,21</sup> for various water–dioxane mixtures were made for the solvolyses of the monoiodo-, diiodo-, and monobromoborane adducts. Pronounced curvature was observed in plots of  $\log k$  vs. the Kirkwood parameter, but a generally linear correlation is obtained when  $\log k_{\text{obsd}}$  is plotted vs.  $Y$  for the solvolysis of the monobromoborane over the range 50–90% aqueous dioxane. The slope,  $m = +0.59$  (correlation coefficient  $+0.999$ ), argues for a rate-determining ionization of substrate but does not rule out the possibility of water serving in the capacity of a nucleophile.<sup>21,22</sup> A plot of  $\log k_2$  vs.  $Y$  also is linear over the same range of solvent composition,  $m = +0.38$  (correlation coefficient  $+0.997$ ).

The magnitude of the solvent isotope effect does not seem out of line for consideration as a secondary effect in view of the general predictions of Bigeleisen and Wolfsberg for probable upper limits of secondary isotope effects involving O–H bonds.<sup>23</sup> Such an interpretation is consistent with a concerted displacement of halide ion from boron by  $\text{H}_2\text{O}$ ; however, if only secondary effects are important, a smaller rate in deuterium oxide is predicted for a reaction proceeding from reactants to a more highly solvated activated complex, as would be the case for a process of ionization, even without simultaneous nucleophilic attack by water. Thus, measured  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$  values greater than unity for numerous organic solvolytic reactions have been attributed by Laughton and Robertson<sup>24,25</sup> to differences in bonding in  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  in ordered water around reactants and, in separate studies, by Pritchard and Long<sup>26</sup> to differ-

ences in  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  in the solvation of ions. The mechanistic uncertainty associated with such an isotope effect is emphasized in the neutral solvolysis of ethylene oxide where  $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$  values less than 1 (observed  $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 0.8\text{--}0.9$ ) are predicted both for a mechanism involving a rate-determining unimolecular ring opening and for a bimolecular pathway in which water serves as a displacing nucleophile.<sup>26</sup>

It is interesting to consider the solvolysis of the mono-haloboranes in the light of the general susceptibility of such substrates to substitution reactions wherein halide ion is replaced by a neutral nucleophile to give a positively charged boronium ion. Thus, trimethylamine–monoiodoborane is a useful precursor for ions of the type  $\text{LL}'\text{BH}_2^+$  where L is trimethylamine and L' is some other neutral electron donor coordinating to boron through an atom such as nitrogen, phosphorus, arsenic, or sulfur.<sup>27,28</sup> The kinetic hydrolytic stability of the resultant boron(1+) ion is a sensitive function of the nature of L', the greatest kinetic stability resulting when L' is a trialkylamine with stability generally decreasing as L' varies through the series trialkylphosphine > trialkylarsine > dialkyl sulfide.<sup>29</sup> It may be that hydrolysis of a trimethylamine–haloborane represents another example of the replacement of halide ion by a neutral nucleophile (water) but where the product aquoboron(1+) ion (II below) is relatively short-lived with respect to hydrolytic decomposition. Whether attack by solvent is concerted or not, it seems reasonable that a molecule of water would tend to occupy a coordination site on boron made available by departure of the halide ion, and although there is presently no kinetic evidence for an aquoboron(1+) ion in this system, such an intermediate, though probably highly reactive, seems quite reasonable.



The insensitivity of rate to hydroxide ion concentrations as high as 0.1 M suggests the absence of a strong  $\text{S}_{\text{N}}2$  reaction particularly in view of the apparent importance of the basicity of the reagent in nucleophilic attack at four-coordinate boron.<sup>30</sup> Thus, the kinetic data seem generally consistent with a predominantly dissociative mechanism. The reaction is somewhat reminiscent of the aquation of certain coordination compounds such as the chloropentaamminecobalt(III) ion in which the energetic importance of cleavage of the metal–halogen bond in the rate-determining step seems well substantiated but where the role of  $\text{H}_2\text{O}$  in the transition state is less well defined (it is of interest that a solvent isotope effect  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 1.4$  has been reported by Pearson and coworkers<sup>31</sup> for the aquation of

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(30) J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962).

(31) R. G. Pearson, N. C. Stellwagon, and F. Basolo, *ibid.*, **82**, 1077 (1960).

the Co(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup> ion at 49.4°). By analogy to the hydrolysis of such cobalt(III) complexes and since an S<sub>N</sub>1 classification may imply too limited a role for water in the transition state, it is suggested that haloborane-amine hydrolysis be designated mechanistically as an I<sub>d</sub> process<sup>32</sup> to underscore the dissociative character of the reaction with respect to the boron-halogen bond.

The trend in rate for the monohaloboranes,  $k_{\text{BH}_2\text{I}} > k_{\text{BH}_2\text{Br}} > k_{\text{BH}_2\text{Cl}}$ , presumably reflects the relative leaving-group tendencies of the respective halide ions. This is similar to the trend generally observed in nucleophilic substitution reactions of alkyl halides, wherein the ease of displacement of halide ion (I<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup>) correlates inversely with the basicity of the leaving group.<sup>33,34</sup> Since the degree of solvation of halide ions by water lies in the order Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup>,<sup>35,36</sup> the relative degree of solvation of halide in the respective transition states may to a large extent account for the observed trend in  $\Delta S^\ddagger$  values for the monohaloboranes.

The relative rates of reaction of the mono- and di-

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(33) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp 258-263.

(34) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 81, 82.

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iodoboranes can be explained quite reasonably in terms of the substituent effect of X in I. Electronic inductive effects of iodide and hydride are such that stabilization of the incipient boronium ion should be greater when X = H as in the monoiodoborane adduct.

In considering possible pathways for haloborane-amine hydrolysis, it is worth noting that the monohaloborane adducts of trimethylamine are isoelectronic with neopentyl halides which exhibit severe steric inhibition to displacement *via* back-side attack but for which many examples of unimolecular dissociation have been cited.<sup>37</sup> Due to many factors including the highly polar character of the boron-nitrogen bond, analogies between amine-boranes and isoelectronic carbon-carbon compounds are necessarily limited. Nevertheless, a study of the comparative kinetics of selected reactions, such as the hydrolysis of progressively less hindered substrates as, for example, -BH<sub>2</sub>X adducts of dimethyl- and monomethylamine, may provide a useful approach to further understanding of the route of nucleophilic displacement in such borane-donor addition compounds.

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## Reaction of Boron-Hydrogen Compounds with Dimethylchloramine

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Dimethylchloramine has been shown to react with amine-boranes to give amine-chloroboranes as the first product. Thus, trimethylamine-borane gives trimethylamine-monochloroborane. In the reaction with dimethylamine-borane and pyridine-boranes, the chloroboranes react further to give boron cations. The reactions with sodium borohydride and diborane were also investigated.

Dimethylchloramine is usually thought of as an aminating agent. Thus, with tertiary phosphines or arsines,<sup>1</sup> it forms aminophosphonium or aminoarsonium compounds. It has also been used for amination of aromatic compounds.<sup>2</sup> We have allowed it to react with several boron-hydrogen-containing compounds and have found that it behaves as a chlorinating agent. Although this is unusual, it is not unknown. Thus, it has been found to chlorinate *n*-heptane in concentrated sulfuric acid.<sup>3</sup> In the reaction with primary and secondary phosphines, dimethylchloramine has been postulated to form first the chlorophosphine.

This then reacts with more phosphine to give a phosphorus-phosphorus bond.<sup>4</sup> A similar reaction has been observed for arsines.<sup>5</sup> Another compound containing a nitrogen-chlorine bond, N-chlorosuccinimide, has also been reported to chlorinate amine-boranes.<sup>6</sup>

### Experimental Section

**Reaction of Dimethylchloramine with Trimethylamine.**—A solution in CCl<sub>4</sub> of 2.08 g (28.5 mmol) of (CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub> and 2.27 g (28.5 mmol) of (CH<sub>3</sub>)<sub>2</sub>NCl was heated at 35-40° for 40 hr. After filtering, the solution was evaporated to give a 75% yield (2.27 g) of (CH<sub>3</sub>)<sub>3</sub>NBH<sub>2</sub>Cl, mp 80°. The identity was confirmed by the ir and nmr spectra and sublimation gave a sample melting at 84° (lit.<sup>7</sup> mp 84-85°). The nmr spectra of other reaction mix-

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