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# The Kinetics and Mechanism of Solvolysis of Amineboranes

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The rates of solvolysis of substituted phenylamineboranes in aqueous dioxane are described by the expression $-d[AB]/dt = (k_1 + k_2[H^+])$, where [AB] = concentration of amineborane. The acid-independent solvolysis rate is accelerated and the acid-dependent rate retarded by electron-withdrawing *para* and *meta* ring substituents, by increasing N-alkyl substitution, and by increasing dioxane content of the solvent. No primary hydrogen isotope effects were observed for either mode of solvolysis. For the acid-independent reaction, the rate of disappearance of amineborane equals the rate of appearance of free amine. This rate is not significantly influenced by the addition of moderate amounts of free amine or neutral salt and is essentially the same in dioxane–$D_2O$ as in dioxane–$H_2O$. The acid-dependent rate is subject to general acid catalysis and $k_2$ exhibits a slight positive salt effect. Mechanisms for both modes of solvolysis are proposed. Data for the hydrolysis of selected alkyl and heterocyclic amineboranes, including the effect of variations in structure on rate, indicate that these substrates hydrolyze by a mechanism similar to that proposed for the acid-dependent solvolysis of arylamineboranes.

## Introduction

It is only in recent years that detailed studies on the mechanism of solvolysis reactions of boron hydride derivatives have been described. This includes work on alkali metal tetrahydroborates[1–8] and a few studies on the solvolysis of boron–nitrogen substrates. In the latter category, Hawthorne and Lewis[9] have investigated the hydrolysis of pyridine diarylboranes and concluded that the rate-determining step involves "attack of a water proton on the electrons of the boron–hydrogen bond."

In regard to $BH_3$ addition compounds, examples of the relative kinetic stability of certain amineboranes in hydroxylic solvents have been reported.[10,11] In general, the borane adducts of tertiary amines have been found to be more stable than those derived from secondary and primary amines, but quantitative data are rare. The investigation of Ryschkewitsch[12] on the kinetics of hydrolysis of trimethylamineborane, $(CH_3)_3NBH_3$, is among the more comprehensive studies on this type of substrate. Two models for the mechanism of hydrolysis were found to be consistent with the reported data, one involving a breaking of the boron–nitrogen bond in the rate-determining step, and the other involving a breaking of a boron–hydrogen bond. More recent results obtained on the hydrolysis of dimethylamineborane and on the solvolysis of substituted pyridineboranes in 1-propanol have been interpreted to favor, for each system, boron–nitrogen bond breakage in the rate-determining step.[13,14]

It was the purpose of the present study to attempt to elucidate the mechanism of amineborane solvolysis and determine the effect of variations in structure on solvolysis rate. Results and conclusions derived from studies of the solvolysis of arylamineboranes in aqueous dioxane and of the hydrolysis of selected alkyl and heterocyclic amineboranes are described.

## Experimental

**Materials.**—The arylamines were obtained from Eastman and Matheson Coleman and Bell and used without further purification. The hydrochlorides of methylamine and ethylamine (Eastman) were dried *in vacuo* at 60–80° for several hours. Sodium borohydride (98%) and lithium aluminum deuteride (isotopic purity, 99.5%) were obtained from Metal Hydrides Inc. Tetrahydrofuran (THF) was distilled from $LiAlH_4$, b.p. 65°, and *p*-dioxane was boiled under reflux with KOH pellets and distilled from $LiAlH_4$, b.p. 101.5°. Dimethylamineborane and *t*-butylamineborane were obtained from Callery and Eastman, respectively. Isopropylamine (Pennsalt) was distilled from calcium hydride, b.p. 32°. Boron trifluoride–diethyl ether complex ($BF_3 \cdot (C_2H_5)_2O$) was distilled *in vacuo*, b.p. 54° (25–26 mm.). Deuterium oxide (99.5 mole %) was obtained from Matheson Coleman and Bell. Solutions of DCl were prepared by the addition of $SiCl_4$ to $D_2O$ followed by distillation of volatile material *in vacuo*.

**Preparation of Arylamineboranes.**—The following preparation of *p*-toluidineborane is typical for the synthesis of the arylamineboranes. A suspension of 20 g. (0.52 mole) of $NaBH_4$ in 400 ml. of THF was stirred vigorously under dry nitrogen at 0° while 80 g. (0.56 mole) of $BF_3 \cdot (C_2H_5)_2O$ was added dropwise over a period of 15 min. A solution of 35 g. (0.33 mole) of *p*-toluidine in 100 ml. of THF was added slowly to the resultant tetrahydrofuran–borane solution and the mixture stirred for 15 min. Insoluble salts were removed by filtration and 33 g. of solid amineborane was recovered by evaporation of the solvent *in vacuo* at 0°. *Anal.* H (hydridic), 2.15. The crude product was washed with 200 ml. of 33% *p*-dioxane–67% water (by volume) at about 5°, and the solid was collected by filtration, washed repeatedly with

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[1] M. Kilpatrick and C. D. McKinney, Jr., *J. Am. Chem. Soc.*, **72**, 5474 (1950).

[2] R. L. Pecsok, *ibid.*, **75**, 2862 (1953).

[3] J. B. Brown and M. Svensson, *ibid.*, **79**, 4241 (1957).

[4] T. Freund, *J. Inorg. Nucl. Chem.*, **9**, 246 (1959).

[5] R. E. Davis and C. G. Swain, *J. Am. Chem. Soc.*, **82**, 5949 (1960); R. E. Davis, C. L. Kibby, and C. G. Swain, *ibid.*, **82**, 5950 (1960); R. E. Davis, E. Bromels, and C. L. Kibby, *ibid.*, **84**, 885 (1962); R. E. Davis, *ibid.*, **84**, 892 (1962); R. E. Davis and J. A. Gottbrath, *ibid.*, **84**, 895 (1962).

[6] R. E. Dessy and E. Grannen, Jr., *ibid.*, **83**, 3953 (1961).

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

[8] R. E. Mesmer and W. L. Jolly, *Inorg. Chem.*, **1**, 608 (1962).

[9] M. F. Hawthorne and E. S. Lewis, *J. Am. Chem. Soc.*, **80**, 4296 (1958).

[10] H. C. Kelly and J. O. Edwards, *Inorg. Chem.*, **2**, 39 (1963).

[11] L. T. Murray, Ph.D. Thesis, Purdue University, Jan., 1963.

[12] G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **82**, 3290 (1960).

[13] G. E. Ryschkewitsch and E. R. Birnbaum, *J. Phys. Chem.*, **65**, 1087 (1961).

[14] G. E. Ryschkewitsch, paper presented before International Symposium on Boron–Nitrogen Chemistry, Durham, N. C., April 23–25, 1963; personal communications, May, 1963.

20–30-ml. portions of water (5°), and dried *in vacuo* at 25°. The yield was 23 g. (58% of theory). *Anal.* H (hydridic), 2.42.

The aqueous dioxane wash was effective for the purification of all the arylamineboranes except N,N-dimethyl-*p*-toluidineborane and N,N-dimethylanilineborane, which were purified by recrystallization from diethyl ether. All the arylamineboranes were obtained as crystalline solids. All were white except *p*-anisidineborane (pale violet) and *m*-anisidineborane (pale yellow). When heated in capillary tubes at 1 atm., each compound decomposed with evolution of hydrogen. General ranges for decomposition temperatures were 68–78° for the borane adducts of aniline, N-methylaniline, *m*-toluidine, and *m*-anisidine and 90–100° for the adducts of *p*-toluidine, *p*-anisidine, and *p*-bromoaniline. Decomposition of *p*-chloroanilineborane was observed at 80–85°.

**Preparation of *p*-Toluidineborane-$d_3$.**—A stirred suspension of 2.5 g. (0.06 mole) of $LiAlD_4$ in 100 ml. of dry diethyl ether was treated under dry nitrogen with a solution of 14 g. (0.1 mole) of $BF_3 \cdot (C_2H_5)_2O$ in 30 ml. of ether, and the resultant deuteriodiborane, $B_2D_6$, was passed in a stream of nitrogen through a cold finger condenser (−80°) into 100 ml. of THF at 0°. A solution of 7.2 g. (0.07 mole) of *p*-toluidine in 36 ml. of THF was slowly added to the stirred THF solution. Exit gases were passed through a moist acetone trap. The product was recovered by vacuum evaporation of the solvent. Purification was carried out as described for the $BH_3$ adduct of *p*-toluidine. The yield was 6 g. (72% of theory). *Anal.* Calcd. for *p*-$CH_3C_6H_4NH_2BD_3$ (123.97): D, 4.8. Found: D, 4.3. The infrared spectrum showed strong absorption in the B–D stretching region (1715–1795 cm.$^{-1}$) and negligible absorption in the B–H stretching region (2300–2400 cm.$^{-1}$).

**Alkyl and Heterocyclic Amineboranes.**—Isopropylamineborane, morpholineborane, and N-methylmorpholineborane were prepared from the corresponding amines, $NaBH_4$, and $BF_3 \cdot (C_2H_5)_2O$, as described for *p*-toluidineborane. The heterocyclic compounds were purified by recrystallization from water. Isopropylamineborane was purified by washing the crude solid with cold water and drying *in vacuo*.

Methylamineborane and ethylamineborane were obtained by the reaction of the corresponding amine hydrochlorides with sodium borohydride suspended in tetrahydrofuran as described for the preparation of other amineboranes.[15,16]

**Chemical Analysis and Infrared.**—Hydridic hydrogen was determined by measurement of the gas evolved on acid hydrolysis. Titration of the aqueous hydrolysate with standard NaOH using a Beckman Model GS pH meter gave a point of inflection at the p$K_a$ of the amine salt and a sharp break at the anilinium ion end point. Continued titration resulted in a gradual break at the boric acid end point. A typical analysis for *p*-toluidineborane is as follows. *Anal.* Calcd. for *p*-$CH_3C_6H_4NH_2BH_3$ (120.99): H (hydridic), 2.50; B, 8.94; N, 11.58. Found: H (hydridic), 2.40; B, 8.98; N, 11.90.

Infrared spectra were obtained on compressed KCl wafers containing the particular samples using a Perkin-Elmer Model 221 infrared spectrophotometer.

**Kinetic Experiments.**—Solvolyses of arylamineboranes were carried out in aqueous dioxane to ensure complete solubility of the substrates. Solvents were prepared by the addition of a given amount of water or standard aqueous hydrochloric acid to an appropriate volume of dioxane, and the concentration of solvated hydrogen ion was calculated from dilution. Rates were measured over the concentration range of about $5 \times 10^{-4}$ to 0.094 *M* amineborane and from about $10^{-10}$ to 0.23 *M* hydrogen ion. In solutions of $[H^+] > 0.01$ *M*, a large excess of hydrochloric acid was employed so that the change in hydrogen ion concentration during solvolysis would be negligible compared to the change in amineborane concentration. These acid solutions were adjusted to constant ionic strength ($\mu \simeq 0.5$) by adding inert salt (KCl).

For a given run, a 250-ml. iodine flask containing a weighed sample of the amineborane was placed in a constant temperature water bath (Precision Scientific Co.). The temperature was maintained within ±0.04°. The time, $t_0$, was taken on addition of solvent (which had been equilibrated at the same temperature) to the amineborane. The concentration of amineborane at various times was determined iodometrically.[17] Ten-ml. samples of solution were added to known quantities of standard $KIO_3$ followed immediately by the addition of excess KI and 6 *N* $H_2SO_4$. The time was recorded at the appearance of the brown iodine color. Excess $I_3^-$ was titrated with standard $Na_2S_2O_3$. For all the amineboranes, equiv. wt. = mol. wt./6.

In several experiments, the rate of formation of free amine in the hydrolysate was determined by absorption in the ultraviolet region. Samples were periodically withdrawn from the bath and transferred to Beckman short-path cells (0.1-mm. length). Absorbances were obtained with a Bausch and Lomb Spectronic 505 spectrophotometer. For *p*-toluidine, $\lambda_{max}$ 237 m$\mu$ ($\epsilon$ 10,600); aniline, $\lambda_{max}$ 235 m$\mu$ ($\epsilon$ 9600); *p*-chloroaniline, $\lambda_{max}$ 243 m$\mu$ ($\epsilon$ 13,300).

The rate of solvolysis of *p*-toluidineborane in 50% aqueous dioxane at 25° was studied as a function of the concentration of chloroacetic acid over the range 0 to 1.6 *M* acid, and of dichloroacetic acid over the range 0 to about 0.6 *M* acid at concentrations of about 0.2 *M* of the corresponding acetate ions. For each study, the contribution of chloroacetic or dichloroacetic acid to the rate was obtained by subtracting the contribution due to hydrogen ion from the over-all rate.

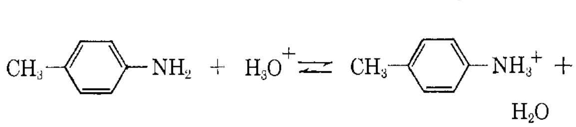
For the hydrolysis of alkyl and heterocyclic amineboranes, the concentration ranges were $10^{-3}$ to 0.047 *M* substrate and $10^{-5}$ to 0.28 *M* hydronium ion. At pH > 2.5, phthalate buffers containing 0.025 to 0.15 *M* hydrogen phthalate ion were employed to maintain constant $a_{H_3O^+}$.

**Isolation of Unsolvolyzed Material. (A) In 50% Dioxane–50% $H_2O$.**—A total of 0.6 g. (5 mmoles) of *p*-toluidineborane-$d_3$ was dissolved in 100 ml. of 50% dioxane–50% water (by volume) at 25°. After 138 min. (50% solvolysis), the solution was removed from the constant temperature bath and treated with 12.5 g. of NaCl. Two layers were formed. The upper (dioxane-rich) layer was separated and the solvent removed *in vacuo* to give a white crystalline solid. The infrared spectrum of the product was identical with that of *p*-toluidineborane-$d_3$.

**(B) In Acidic Aqueous Dioxane.**—A typical experiment is described. A 0.34-g. (2.7 mmoles) sample of *p*-toluidineborane-$d_3$ was dissolved at 25° in 74 ml. of a 50% aqueous dioxane solution which was 0.36 *M* in KCl and 0.14 *M* in hydrogen ion. At *t* = 18.5 min. (35% solvolysis), a 25-ml. portion of the solution was removed and added to 25 ml. of dry diethyl ether. Two layers were formed; the upper layer was separated and cooled in an ice–water bath as the ether was removed by vacuum evaporation to give a white crystalline product. The infrared spectrum showed absorption in both the B–H and B–D stretching regions.

## Results

**Stoichiometry.**—Hydrolysis of the substrates occurs according to the stoichiometry shown for *p*-toluidineborane.



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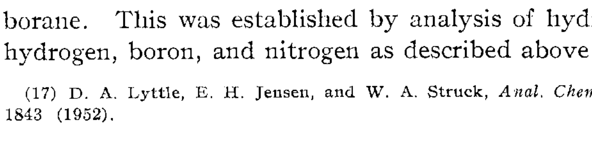

(2)

This was established by analysis of hydridic hydrogen, boron, and nitrogen as described above and

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[15] G. W. Schaeffer and E. R. Anderson, *J. Am. Chem. Soc.*, **71**, 2143 (1949).

[16] J. Goubeau and H. Schneider, *Ber.*, **94**, 816 (1961).

[17] D. A. Lyttle, E. H. Jensen, and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).

TABLE I

RATES OF SOLVOLYSIS OF ARYLAMINEBORANES IN 50% DIOXANE–50% WATER AT 25°

| | $k_1 \times 10^3$, sec.$^{-1a}$ | $k_{obsd} \times 10^3$, sec.$^{-1b}$ | | | | | | $k_2 \times 10^3$,$^b$ l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| | | [H$^+$], $M$ | | | | | | |
| | | 0.057 | 0.114 | 0.142 | 0.171 | 0.200 | 0.227 | |
| $p$-$CH_3OC_6H_4NH_2BH_3$ | 0.047 | 0.202 | 0.378 | | 0.548 | | 0.773 | 3.02 |
| $p$-$CH_3OC_6H_4NH_2BD_3$ | 0.047 | | 0.372 | | 0.542 | | | 3.0 |
| $p$-$CH_3C_6H_4NH_2BH_3$ | 0.083 | 0.212 | 0.360 | | 0.528 | | 0.695 | 2.71 |
| | 0.075$^c$ | 0.152$^f$ | | | 0.31$^g$ | | | 1.45$^c$ |
| $p$-$CH_3C_6H_4NH_2BD_3$ | 0.085 | | 0.360 | 0.437 | | | 0.678 | 2.71 |
| $m$-$CH_3C_6H_4NH_2BH_3$ | 0.158 | 0.262 | 0.362 | | 0.477 | | 0.587 | 1.90 |
| $C_6H_5NH_2BH_3$ | 0.188 | 0.293 | 0.387 | | 0.473 | | 0.587 | 1.74 |
| $m$-$CH_3OC_6H_4NH_2BH_3$ | 0.322 | 0.378 | | 0.492 | | 0.582 | 0.593 | 1.22 |
| $p$-$ClC_6H_4NH_2BH_3$ | 0.65 | 0.705 | 0.757 | | 0.785 | | 0.823 | 0.712 |
| $p$-$BrC_6H_4NH_2BH_3$ | 0.828 | 0.877 | 0.892 | | 0.940 | | 0.985 | 0.667 |
| $C_6H_5NH(CH_3)BH_3$ | 0.272 | | | 0.287 | | 0.297 | | ~0.13 |
| $C_6H_5N(CH_3)_2BH_3$ | 3.8 | | | | | ~3.8 | | ≪0.13 |
| | 3.8$^c$ | | | | | | | |
| $p$-$CH_3C_6H_4N(CH_3)_2BH_3$ | 1.62 | | | | | | | |
| | 1.0$^d$ | | | | | | | |
| | 1.0$^e$ | | | | | | | |

[a] $\mu \simeq 0$. [b] $\mu = 0.5$. [c] 50% dioxane–50% $D_2O$. [d] 40% dioxane–60% $H_2O$. [e] 40% dioxane–60% $D_2O$. [f] 50% dioxane–50% $D_2O$, 0.046 $M$ $D^+$. [g] 50% dioxane–50% $D_2O$, 0.16 $M$ $D^+$.

as previously described for other amineboranes.[18]

**Kinetic Order in Amineborane and Acid.**—Data for numerous kinetic experiments are given in Table I. In all of the solvolyses, the disappearance of amineborane as a function of time is first order in the concentration of amineborane. Unlike the hydrolysis of many other hydrides, *the observed rates of solvolysis of the phenylamineboranes are independent of the concentration of solvated hydrogen ion in the investigated region of* $[H^+] < 10^{-3}$ $M$. Thus, in 50% dioxane–50% water, a plot of the logarithm of amineborane concentration *vs.* time is linear over several half-lives, even though the hydrogen ion concentration may change by more than a factor of ten during this time. At $[H^+] > 10^{-3}$ $M$, the observed rate increases markedly with increasing hydrogen ion concentration (Fig. 1). The variation of the pseudo-first-order rate constant, $k_{obsd}$, with $[H^+]$ for various substituted phenylamineboranes is shown in Fig. 2.

These data lead to the rate expression given in eq. 3 for the solvolysis of a given amineborane, AB. The

$$\frac{-d[AB]}{dt} = [AB](k_1 + k_2[H^+]) \qquad (3)$$

value of $k_1$ is obtained from the $y$-intercept of a given line and is a measure of the rate of the *acid-independent solvolysis* for that substrate. The slope, $k_2$, is a measure of the *acid-dependent solvolysis* rate. It is noteworthy that the observed scale of relative stabilities of the substituted phenylamineboranes in solution depends on the acidity, and at $[H^+] > 0.01$ $M$, a small change in $[H^+]$ can result in a drastic change in relative solvolysis rates.

The rate of $p$-toluidineborane solvolysis in 50% aqueous dioxane increases linearly with increasing concentration of certain Brönsted acids, and catalysis constants for $ClCH_2COOH$ and $Cl_2CHCOOH$ are $1.5 \times 10^{-5}$ and $5.6 \times 10^{-5}$ l. mole$^{-1}$ sec.$^{-1}$, respectively.

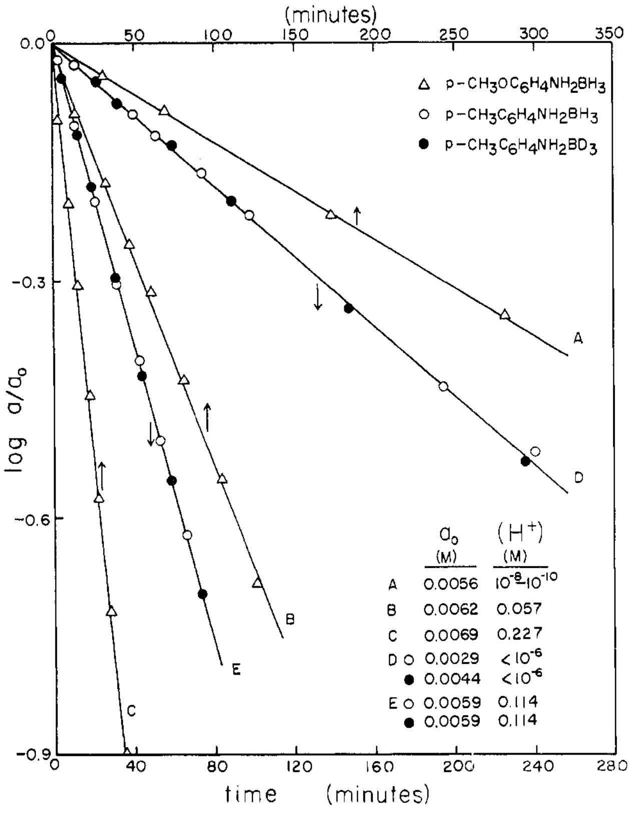

Fig. 1.—Solvolysis of $p$-anisidineborane, $p$-toluidineborane, and $p$-toluidineborane-$d_3$ in 50% dioxane–50% water at 25°.

The acid-dependent reaction, therefore, is *general acid catalyzed* and the rate expression is more appropriately written

$$\frac{-d[AB]}{dt} = [AB](k_1 + \sum_i k_i[HA_i]) \qquad (4)$$

where $[HA_i]$ is the concentration of a given Brönsted acid. Thus, in eq. 3, $k_2$ is the catalysis constant for the solvated hydrogen ion. Subsequent discussion of factors which influence the rate of the acid-dependent

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(18) H. C. Kelly and J. O. Edwards, *J. Am. Chem. Soc.*, **82**, 4842 (1960).

solvolysis of amineboranes is based on effects observed on the magnitude of $k_2$ under conditions where the contribution of acidic species other than the solvated proton is negligible.

**Structural Effects.**—The acid-independent rate of solvolysis of the phenylamineboranes is enhanced by electron-withdrawing *para* and *meta* substituents in the ring and retarded by electron-donating substituents (Fig. 2). For the acid-dependent reaction, the opposite is true; electron-donating substituents enhance the rate while electron-withdrawing substituents have a retarding effect. A correlation of solvolysis rates with Hammett $\sigma$ constants is shown in Fig. 3. For the acid-independent solvolysis, $\rho = +2.32$; for the acid-dependent reaction, $\rho = -1.32$.

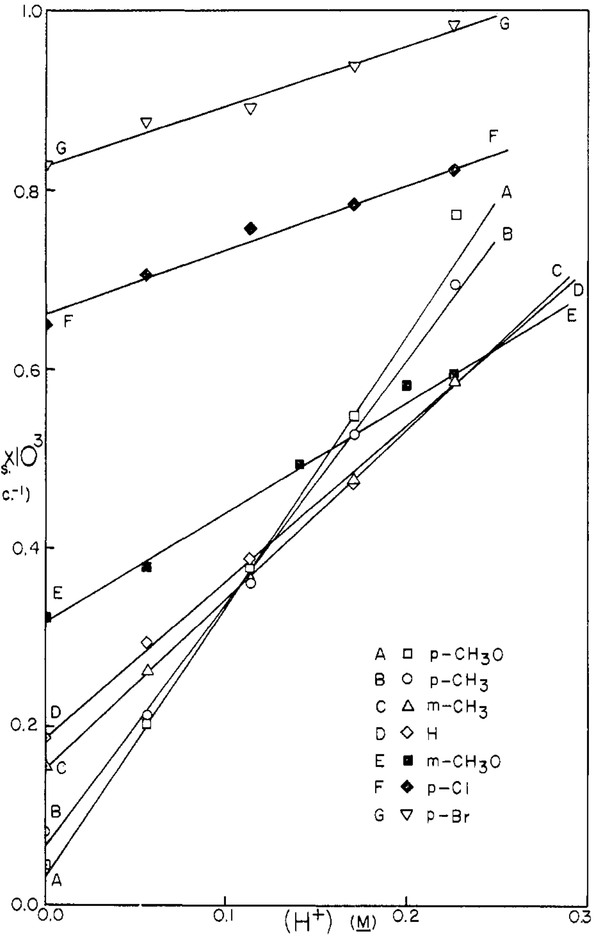

Fig. 2.—Variation of the rates of solvolysis of substituted phenylamineboranes with hydrogen ion concentration in 50% aqueous dioxane at 25°.

Data for N-substituted anilineboranes and $p$-toluidineboranes show that an increase in alkyl substitution on nitrogen increases the acid-independent rate and retards the acid-dependent solvolysis (Table I).

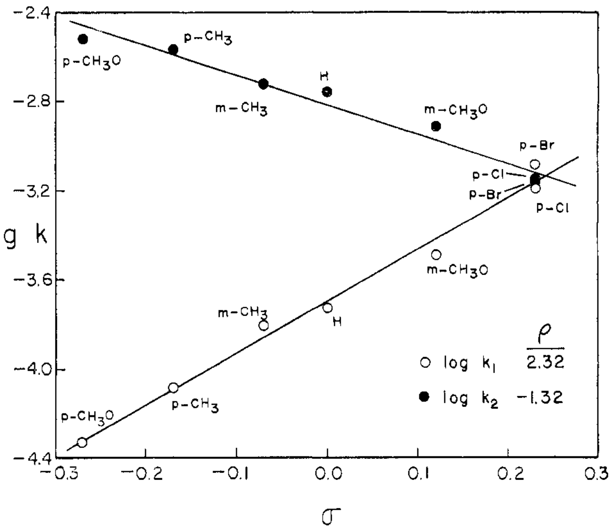

Fig. 3.—Correlation of solvolysis rates of substituted phenylamineboranes with Hammett $\sigma$ values.

Table II

Effect of Solvent Composition on Solvolysis Rate at 25°

| Solvent dioxane–$H_2O$ (vol. %) | $D^a$ | $Y^b$ | $k_1 \times 10^3$, sec.$^{-1}$ | $k_2 \times 10^3$,$^c$ l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|---|---|
| | | *p*-Toluidineborane | | |
| 33.3–66.7 | 49 | | 0.045 | 6.00 |
| 40–60 | 43 | 1.945 | 0.057 | 4.20 |
| 50–50 | 34.5 | 1.361 | 0.083 | 2.71 |
| 60–40 | 25.5 | 0.715 | 0.113 | 1.90 |
| 70–30 | 17.7 | 0.013 | 0.167 | |
| 80–20 | ~10.5 | −0.833 | 0.260 | |
| | | N,N-Dimethylanilineborane | | |
| 33.3–66.7 | 49 | | 1.61 | |
| 40–60 | 43 | 1.945 | 2.33 | |
| 50–50 | 34.5 | 1.361 | 3.8 | |

[a] Dielectric constant. Values extrapolated from S. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, Chapter XV, p. 539. [b] Reference 20. [c] $\mu = 0.5$.

**Solvent and Salt Effects.**—An increase in the dioxane content of the solvent (decrease in dielectric constant) causes an increase in the rate of the acid-independent reaction and a decrease in the acid-dependent rate as shown in Table II. Figure 4 shows the inverse linear relationship between log $k_1$ for $p$-toluidineborane and Grunwald–Winstein $Y$ values[19,20] for various dioxane–water mixtures at 25°.

No significant salt effect was observed for the acid-independent solvolysis of $p$-toluidineborane up to 0.5 $M$ KCl. The acid-dependent reaction, however, is subject to a slight positive salt effect. For $p$-toluidineborane and $p$-anisidineborane, values of $k_2$ are about 10–15% lower at $\mu = 0.2$, and about 20% lower at $\mu = 0.05$–$0.1$, than those obtained at $\mu = 0.5$.

**Effect of Free Amine and Amine Salt.**—In 50% dioxane–50% water, the amine produced by solvolysis of $p$-toluidineborane exists in solution predominantly in the form of the base (negligible amount of $p$-toluidinium ion). The rate of appearance of the amine, determined spectrophotometrically, is equal to the rate of disappearance of the amineborane calculated from loss of soluble hydride, *i.e.*, 6 mequiv. of hydridic hydrogen disappear for each mmole of amine formed. Com-

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(19) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

(20) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 297–300.

parable results were obtained for anilineborane and *p*-chloroanilineborane. The accumulation of amine in solution had no effect on the rate as shown by the linearity of a log [amineborane] *vs.* time plot over the entire reaction time. Also, when the solvolysis of *p*-toluidineborane (initial concentration 0.004 *M*) was studied in the presence of 0.07 *M* *p*-toluidine, the rate of disappearance of the amineborane was the same as in the absence of added amine. When the reaction was carried out in a strong acid medium, the accumulation of the *p*-toluidinium ion had no effect on the solvolysis rate, nor was the rate significantly influenced by the presence of 0.077 *M* *p*-toluidine hydrochloride in a solution of initial *p*-toluidineborane concentration of 0.005 *M* at $[H^+] = 0.12\ M$ and $\mu = 0.5$.

**Deuterium Isotope Effects and Deuterium-Hydrogen Exchange.**—The rate of solvolysis of *p*-toluidineborane-$d_3$ is identical with that of *p*-toluidineborane over the entire range of acidity that was investigated (Table I and Fig. 1). The rate of exchange of deuterium of the deuteride with solvent protons is catalyzed by hydrogen ion.[21]

$$\text{amine } BD_3 \xrightarrow{H^+} \text{amine } BH_3 \qquad (5)$$

In 50% dioxane–50% $H_2O$, with no added hydronium ion, the rate of exchange in the *p*-toluidineborane system is negligible relative to the rate of solvolysis. Thus, on solvolysis of *p*-toluidineborane-$d_3$, the starting material, isolated after about 50% reaction, shows strong absorption in the B–D stretching region of the infrared and no absorption in the B–H stretching region.

At high acid concentrations the rate of exchange increases. If *p*-toluidineborane-$d_3$ is dissolved in a strong acid medium, the unsolvolyzed material isolated from solution shows an increase in intensity of absorption in the B–H region relative to that in the B–D region with increasing time of exposure to the solution. For example, at initial concentrations of 0.037 *M* *p*-toluidineborane-$d_3$ and 0.14 *M* $H^+$ at 25° and $\mu = 0.5$, the ratio of hydride to deuteride in the unsolvolyzed amineborane is about 0.8 after about 35% solvolysis, and exchange is virtually complete after about 53% solvolysis (Table III). The rate of solvolysis observed in this system was identical with that of the nondeuterated species under the same experimental conditions; hence, the solvolysis rate is not dependent on the B–H:B–D ratio, but is proportional to the total concentration of amineborane whether in the form of hydride or deuteride. *Thus, under the conditions described, there is no deuterium isotope effect in the solvolysis of p-toluidineborane.*[22]

TABLE III

HYDROGEN–DEUTERIUM EXCHANGE DURING SOLVOLYSIS OF *p*-TOLUIDINEBORANE-$d_3$ IN 50% AQUEOUS DIOXANE AT 25°

| Run | $[S]_0$,[a] *M* | Exposure time, min. | $[H^+]_0$, *M* | % solvolysis | $\frac{I\nu_{B-H}}{I\nu_{B-D}}$ (infrared) |
|---|---|---|---|---|---|
| 1 | 0.094 | 138 | $\sim 10^{-7}$ | 50 | 0 |
| 4 | 0.097 | 4.75 | 0.277 | | ~1 |
| | | 16.75 | | | ~2.5 |
| 6 | 0.036 | 28.1 | 0.142 | 48 | ~4–5 |
| 7 | 0.037 | 18.5 | 0.142 | 35 | ~0.8 |
| | | 31.7 | 0.142 | 53 | Very large |

[a] Initial concentration of substrate, *p*-toluidineborane-$d_3$.

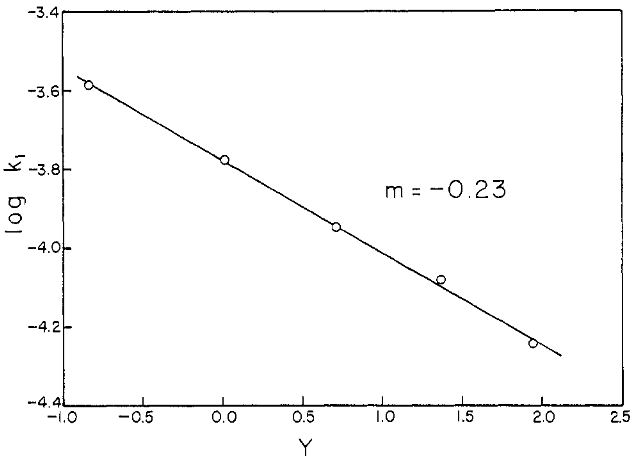

Fig. 4.—Variation of the acid-independent solvolysis rate of *p*-toluidineborane with Grunwald–Winstein *Y* values for dioxane–water mixtures at 25°.

**Activation Parameters.**—The variation of $k_1$ and $k_2$ with temperature for the solvolysis of *p*-toluidineborane in 50% aqueous dioxane is shown in Fig. 5. Activation parameters for the acid-independent solvolysis are $\Delta H^* = 21.8$ kcal. mole$^{-1}$ and $\Delta S^* = -0.8$ cal. mole$^{-1}$ deg.$^{-1}$. For the acid-dependent reaction, $\Delta H^* = 21.7$ kcal. mole$^{-1}$ and $\Delta S^* = +0.6$ cal. mole$^{-1}$ deg.$^{-1}$.

**Solvent Isotope Effects.**—Solvolysis rates in dioxane–$D_2O$ mixtures are shown in Table I. No significant solvent isotope effect was observed for the acid-independent solvolysis of *p*-toluidineborane, N,N-dimethyl-*p*-toluidineborane, and N,N-dimethylanilineborane, but a distinct solvent isotope effect prevails in the acid-dependent solvolysis of *p*-toluidineborane ($k_{H_2O}/k_{D_2O} = 1.9$). Exchange of the protons on nitrogen with deuterium of the solvent was found to occur in acidic dioxane–$D_2O$ solution, but the rate was not extremely fast compared to solvolysis. After about 56% solvolysis, a sample of unreacted *p*-toluidineborane-$d_3$ was isolated from a 50% dioxane–50% $D_2O$ solution containing about 0.05 *M* substrate and about 0.1 *M* $D^+$. The infrared spectrum showed strong absorption in both the N–H (~3200 cm.$^{-1}$) and N–D (~2400 cm.$^{-1}$) stretching regions with the intensity in the N–H region somewhat the stronger. The slower rate of the acid-dependent solvolysis in $D_2O$ is, therefore, attributed to a true solvent isotope effect (as expected for a reaction subject to general acid catalysis) rather than a secondary substrate effect.

**Structural Effects with Alkyl and Heterocyclic Amineboranes.**—The hydrolyses of various alkyl and heterocyclic amineboranes exhibited second-order kinetics, first order each in amineborane concentration and

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[21] Hydride exchange with solvent in the trimethylamineborane system has been described: R. E. Davis, A. E. Brown, R. Hopmann, and C. L. Kibby, *J. Am. Chem. Soc.*, **85**, 487 (1963).

[22] A referee has suggested that perhaps a normal primary isotope effect is being overcome by a secondary inverse isotope effect. This is possible but the authors consider it unlikely.

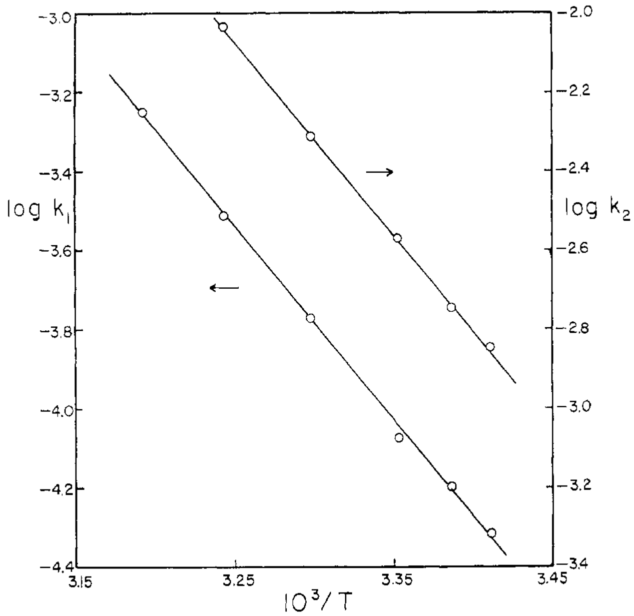
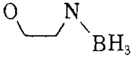
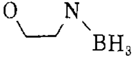


Fig. 5.—Temperature dependence of the rate of solvolysis of *p*-toluidineborane in 50% aqueous dioxane.

hydronium ion activity. No acid-independent solvolysis reaction was observed under the conditions employed. In the methylamine and morpholine series, rates decrease with increasing N-alkyl substitution. In the series of primary alkylamineboranes (methyl, ethyl, isopropyl, and *t*-butyl), a small increase in hydrolysis rate occurs with successive substitution of methyl for hydrogen on the $\alpha$-carbon atom (Table IV). Salt and solvent effects observed in the hydrolysis of morpholineborane are in the same direction as those described for the acid-dependent solvolysis of arylamineboranes and those reported by Ryschkewitsch[12] for the acid hydrolysis of trimethylamineborane.

TABLE IV
HYDROLYSIS OF SELECTED AMINEBORANES IN WATER AT 25°

| Substrate | $\mu$ | $k_2 \times 10^2$,[a] l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|
| $CH_3NH_2BH_3$ | 0.1 | 35 |
| | 0.5 | 45 |
| $CH_3CH_2NH_2BH_3$ | 0.1 | 43 |
| | 0.5 | 58 |
| $(CH_3)_2CHNH_2BH_3$ | 0.5 | 67 |
| $(CH_3)_3CNH_2BH_3$ | 0.5 | 87 |
| $(CH_3)_2NHBH_3$ | 0.08 | 0.97 |
| | 0.02 | 0.83 |
|  | 0.03 | 0.053 |
| | 0.14 | 0.057 |
| | 0.2 | 0.060 |
| | 0.38 | 0.063 |
| | 0.5 | 0.072 |
| | 0.5 | 0.042[b] |
| | 0.5 | 0.035[c] |
|  | 0.5 | $7.7 \times 10^{-4}$ |

[a] $k_2 = \frac{-d[\text{amineborane}]}{dt}/[\text{amineborane}]a_{H_3O^+}$. [b] 20% dioxane–80% $H_2O$. [c] 25% dioxane–75% $H_2O$.

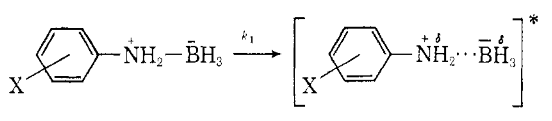
## Discussion

Any statement of mechanism of amineborane solvolysis must be consistent with the following facts. Arylamineboranes undergo solvolysis in aqueous dioxane by two mechanisms. Both reactions show first-order dependence on amineborane concentration. One is independent of hydrogen ion and the other is first order in hydrogen ion and satisfies criteria for general acid catalysis.

The acid-independent reaction is not significantly affected by changes in ionic strength, is unaffected by the addition of free amine over the concentration range specified, but is enhanced by an increase in the dioxane content of the solvent. It is accelerated by electron-withdrawing *meta* and *para* substituents in the ring and by an increase in N-alkyl substitution. The rate of appearance of free amine is equal to the rate of disappearance of amineborane. The rate of solvolysis of the amine–$BD_3$ complex is equal to the rate of solvolysis of the amine–$BH_3$ complex, and the exchange of deuterium in the amineborane-$d_3$ with solvent protons is negligible compared to the rate of solvolysis. The rate is essentially the same in dioxane–$H_2O$ as in dioxane–$D_2O$.

The acid-dependent reaction shows a slight positive salt effect, but is not otherwise affected by adding moderate amounts of amine salt. The rate is enhanced by electron-releasing ring substituents and retarded by N-alkyl substitution. The rate of solvolysis of the amineborane-$d_3$ is equal to that of the undeuterated amineborane. An increase in rate occurs with an increase in the water content of the solvent.

The proposed mechanism for the acid-independent solvolysis of arylamineboranes involves a rate-determining heterolytic cleavage of the boron–nitrogen bond of the amineborane followed by a rapid solvolysis of the $BH_3$ fragment. Presumably the boron–nitrogen bond is being broken in the transition state.



(6)

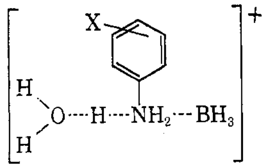
Such a model is consistent with the influence of ring substituents. As the boron–nitrogen bond is broken, nitrogen is converted from four to three coordination. Electron-withdrawing substituents in the ring stabilize the incipient amine (activated complex) relative to the amineborane (ground state), with consequent enhancement of the solvolysis rate.

The independence of rate on the concentration of free amine is contrary to a mechanism involving equilibration of the amineborane, amine, and a solvated $BH_3$ fragment followed by a rate-determining decomposition of the borane group. The loss of 6 mequiv. of soluble hydride for each mmole of amine formed also argues against an equilibrium of this type and indicates that no long-lived partially dehydrogenated intermediate is formed. The absence of a boron–hydrogen isotope effect indicates that boron–hydrogen bond breakage is not occurring in the transition state.

The observed variation of rate with changes in the dioxane–water content of the solvent is consistent with the proposed mechanism involving the collapse of a strong dipole in the rate-determining step. In regard to the formation and destruction of charged species, this is the reverse of the proposed rate-determining step for the ionization of a neutral molecule such as *t*-butyl chloride. In the latter case, bond breaking results in the *formation* of oppositely charged species. For solvolysis reactions, the Grunwald–Winstein *Y* parameter gives a qualitative description of "the ionizing power of the medium."[20] An inverse relation, therefore, between the acid-independent rates of solvolysis of *p*-toluidineborane and *Y* values for aqueous dioxane mixtures is not surprising. The absence of a significant solvent isotope effect is also consistent with the proposed mechanism.

Considering only the inductive effects of alkyl substituents, an increase in N-alkyl substitution would be expected to stabilize the ground state relative to the transition state. The fact that increasing N-alkyl substitution results in increased rates suggests that the predominant effect of the substituent on nitrogen is steric and that a release in strain occurs in the transition of nitrogen from four to three coordination.

A proposed mechanism for the acid-dependent solvolysis involves a rate-determining attack of the solvated hydrogen ion on the amineborane in which a proton is being transferred to nitrogen concurrent with a breaking of the boron–nitrogen bond, again followed by rapid solvolysis of the borane fragment. A possible configuration for the activated complex is shown below.



This model is intended to suggest, mainly, the formation and breaking of bonds in the transition state. No evidence of linearity or other geometric orientation of species is available at this time. A comparable mechanism has been suggested by Ryschkewitsch for the protolysis of methylamineboranes in water.[12]

The proposed model is consistent with the fact that electron-releasing *para* and *meta* substituents in the ring enhance the rate, for such substituents stabilize the incipient anilinium ion (activated complex) relative to the polar but neutral amineborane molecule (ground state). The independence of the rate on amine salt concentration is consistent with the above model (as opposed to an equilibrium of amineborane, amine salt, and a solvated $BH_3$ entity), and the absence of a boron–hydrogen isotope effect again argues against the breaking of a boron–hydrogen bond in the transition state. This solvolysis is pictured as the attack of a positively charged ion at the positive end of a strong dipole (a repulsive ion–dipole interaction). The observed increase in rate with an increase in dielectric constant of the solvent and the observed positive salt effect are consistent with solvent and salt effects predicted for certain electrostatic models that have been proposed for repulsive ion–dipole interactions.[23]

The observed solvent isotope effect and demonstration of general acid catalysis indicates that a *proton is being transferred* from the acid moiety to the substrate in the rate-determining step. This is consistent with the proposed mechanism and precludes a mechanism involving a rapid pre-equilibrium protonation of the substrate followed by a rate-determining reaction of this protonated species.

Similarities in reaction order, solvent and salt effects, and effects of changes in structure on rate suggest that the hydrolyses of the alkyl and heterocyclic substrates proceed by a mechanism similar to that proposed for the acid-dependent solvolysis of the arylamineboranes. The trend in rate for primary alkylamineborane hydrolysis with alkyl substitution at the $\alpha$-carbon atom is probably due to an increase in stabilization of an activated complex (involving the formation of an ammonium ion) relative to the ground state with an increase in electron-donating character of the alkyl substituent. The influence of N-alkyl substituents on the acid-dependent reactions indicates that the predominant effect here is steric and that increasing N-alkyl substitution results in an increase in steric hindrance to the attack of the solvated hydrogen ion on the nitrogen atom of the amineborane.

The rate-determining steps in the acid-independent and acid-dependent solvolyses of *p*-toluidineborane are proposed to involve cleavage of the boron–nitrogen bond *without* concurrent breakage of a boron–hydrogen bond. Previous publications have noted the absence of a deuterium isotope effect in the hydrolysis of trimethylamineborane[5] and in rapid exchange of hydridic hydrogen with solvent hydrogen for this substrate.[21] If the acid hydrolysis of trimethylamineborane occurs by the same mechanism as the acid-dependent solvolysis of *p*-toluidineborane, then no isotope effect would be expected even in the absence of such exchange. Further, although reports of electrophilic attack at unsaturated centers are common, the reported attack of an electrophile at a saturated tetrahedrally coordinated center, such as proposed for the acid-dependent solvolysis mechanism, is relatively rare.

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[23] S. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, Chapter XV, pp. 534–537.