pletion of the X-ray study which is currently in progress.

Whereas the incorrect formulation[2b] of these adducts could accommodate more than two ligands, when sterically possible, our structure for $B_{20}H_{16}(NCCH_3)_2 \cdot CH_3CN$ is clearly a diligand molecular compound. If this result is general, the compound $B_{20}H_{16} \cdot 3.5C_2H_5OH$[2b] should be formulated as $B_{20}H_{16}(C_2H_5OH)_2 \cdot 1.5C_2H_5OH$.

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Electronic Effects of the NH_2BH_3 Group. The Hydrolysis of Diamine Bisboranes

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The hydrolysis of *m*- or *p*-phenylenediamine bisborane occurs by two consecutive first-order processes in neutral aqueous dioxane and exhibits consecutive pseudo-first-order kinetics in the same solvent containing a relatively high concentration of hydrogen ion. In neutral solution the first step is faster than the second, while the reverse is true in acid solution. These results are interpreted in terms of the substituent effects of the *m*- and *p*-NH_2BH_2, -NH_2, and -NH_3^+ groups on hydrolysis of the second and originally equivalent NH_2BH_3 function. The acid-catalyzed hydrolysis of ethylenediamine bisborane also occurs in consecutive pseudo-first-order reactions in the region pH 2.4–3.1. Rate constants were evaluated by a graphical method and their relative values are consistent with previously proposed mechanisms for amine borane hydrolysis.

Introduction

Various studies of substituent effects on amine borane solvolysis have been reported,[1–5] including the effect of aryl substituents on the rates of hydrolysis of substituted aniline boranes in aqueous dioxane[6] In the latter study, Hammett relationships were established for the acid-independent and acid-catalyzed hydrolyses. These relationships suggested that some information on the electronic effect of the phenyl-substituted NH_2BH_3 linkage itself might be obtained by studying the solvolysis rates of *m*- and *p*-phenylenediamine bisboranes, that is, by determining the influence of the NH_2BH_3 substituent on the rate of hydrolysis of an identical functional group in the same molecule. This paper describes the preparation of *m*- and *p*-phenylenediamine bisboranes and their hydrolysis kinetics in aqueous dioxane. Also reported is a study of the acid-catalyzed hydrolysis of ethylenediamine bisborane, $H_3BH_2NCH_2CH_2NH_2BH_3$, in which effects of the $H_3BH_2NCH_2CH_2$ and $H_3\overset{\oplus}{N}CH_2CH_2$ groups are compared to those of various N-alkyl substituents.

Experimental Section

Materials.—Samples of *m*- and *p*-phenylenediamine dihydrochloride were used as obtained from Eastman without further purification. Lithium borohydride was obtained from Ventron Corp. Diethyl ether (USI) was dried by distillation from lithium aluminum hydride. Purification of 1,4-dioxane and the preparation of aqueous dioxane solutions for rate studies have been previously described.[6] The acidified water–dioxane solutions were all brought to about 0.5 *M* in total monovalent ionic species by adding appropriate amounts of Baker reagent potassium chloride. Ethylenediamine bisborane was prepared from ethylenediamine (Eastman 98%) and the tetrahydrofuran–borane complex by the method previously used in preparing arylamine boranes[6] and purified by treatment with cold water.[7] Buffer solutions were prepared using $KHC_8H_4O_4$–HCl and KH_2PO_4–HCl mixtures.

Preparation of *m*-Phenylenediamine Bisborane.—A 500-ml, round-bottom, three-neck flask equipped with a mercury-seal stirrer, dropping funnel, and cold-water condenser was purged with gaseous N_2 and charged with 12.0 g (0.06 mole) of *m*-phenylenediamine dihydrochloride. The flask was cooled in ice water and 115 ml of a clear diethyl ether solution containing 0.15 mole of lithium borohydride added dropwise with stirring over a period of 20 min. The separatory funnel was washed three times with dry ether and the washings (40 ml) were added to the flask. Gas evloved (H_2) was passed through the cold-water condenser, a $CaCl_2$ drying tube, and a wet-test meter. Stirring was continued for 3.5 hr or until no further evolution was observed for a period of 1 hr (total evolution 4.0 l.). The reaction mixture was allowed to stand at 0° overnight. The solid was collected by filtration under flowing nitrogen through a coarse fritted-glass filter, washed with dry ether, and dried under streaming nitrogen. This solid was added slowly with stirring to about 100 ml of water at about 5°, slight evolution occurring during this time. The product was again collected by filtration under nitrogen, washed with several small portions of cold water, and dried *in*

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

[2] G. E. Ryschkewitsch, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, pp 53–58.

[3] G. E. Ryschkewitsch and E. R. Birnbaum, *Inorg. Chem.*, **4**, 575 (1965).

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

[5] L. T. Murray, Ph.D. Thesis, Purdue University, Aug 1963.

[6] H. C. Kelly, F. R. Marchelli, and M. B. Giusto, *Inorg. Chem.*, **3**, 431 (1964).

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

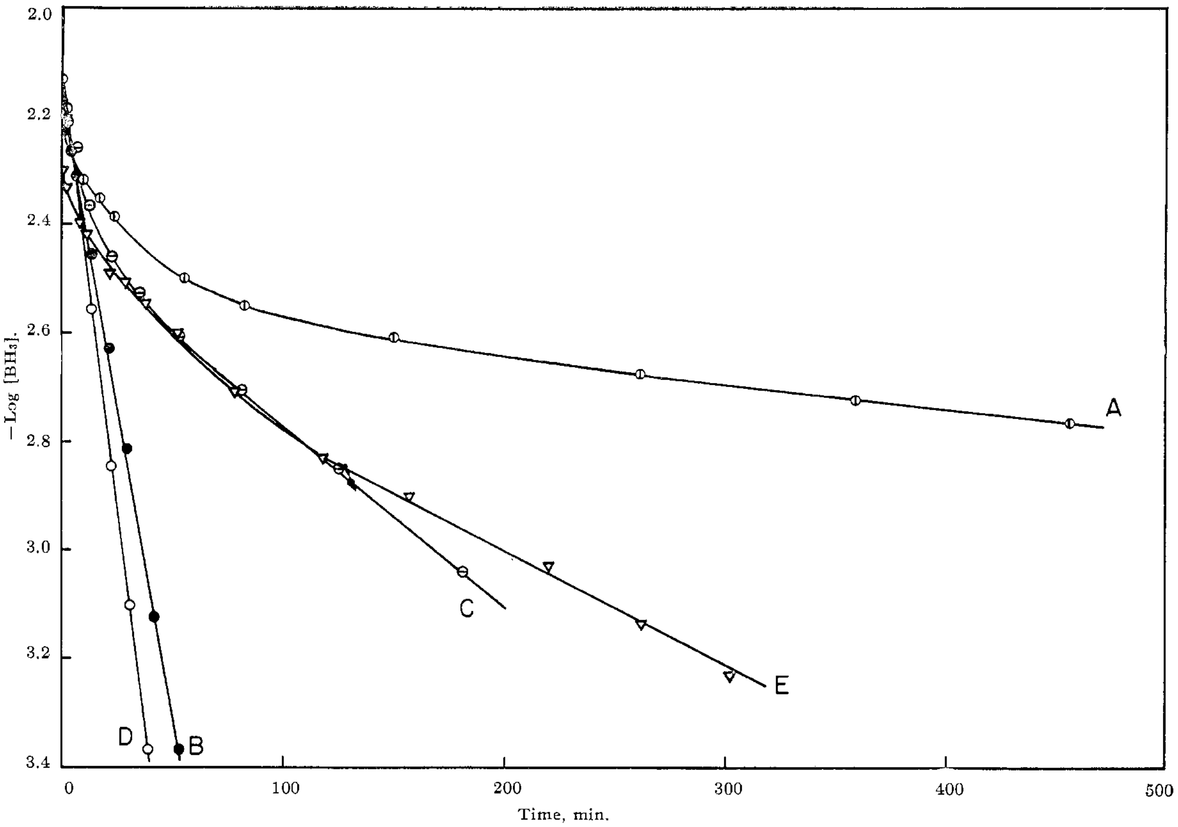

Figure 1.—Solvolysis of diamine bisboranes at 25°: A, p-$H_3BH_2NC_6H_4NH_2BH_3$ in 50% aqueous dioxane; B, p-$H_3BH_2NC_6H_4NH_2BH_3$ in 50% aqueous dioxane, $[H^+] = 0.29$ M, [KCl] = 0.21 M; C, m-$H_3BH_2NC_6H_4NH_2BH_3$ in 50% aqueous dioxane; D, m-$H_3BH_2NC_6H_4NH_2BH_3$ in 50% aqueous dioxane, $[H^+] = 0.29$ M, [KCl] = 0.21 M; E, $H_3BH_2NCH_2CH_2NH_2BH_3$ in water, pH 2.37, $\mu = 0.5$.

vacuo. A total of 5.5 g (61% theory) of a white crystalline solid was recovered. *Anal.* Calcd for $C_6H_4(NH_2BH_3)_2$: H (hydridic), 4.45; B, 15.9; N, 20.6. Found: H (hydridic), 4.34; B, 15.5; N, 20.5. The analysis for hydridic hydrogen was carried out by measuring the hydrogen evolved on acid hydrolysis. The boron and nitrogen analyses were obtained from a titration of the hydrolysate with standard base. A pK value of 5.04 for the second ionization of the m-phenylenediammonium ion was determined from the titration curve. A pK value of 5.0 was obtained by titrating a separate solution of m-phenylenediamine dihydrochloride. The infrared spectrum was obtained on a KBr wafer of the compound using a Beckman IR-10 spectrophotometer. Strong absorption was observed at 681, 790, 1128, 1141, 1245, 1260, 1592, 1620, 2240, 2260–2400, 3140, and 3240–3260 cm^{-1}, and somewhat less intense absorption at 945, 1005, 1020, 1085, 1170, 1180, 1200, 1210, 1475–1500, and 2140 cm^{-1}.

Preparation of p-Phenylenediamine Bisborane.—In a procedure similar to that used in preparing the *meta* compound, 7.7 g (85.6% theory) of a white crystalline solid was recovered after an aqueous wash of the product obtained from the reaction of 12.0 g (0.066 mole) of p-phenylenediamine dihydrochloride and 180 ml of an ethereal solution containing 3.8 g (0.17 mole) of lithium borohydride. *Anal.* Calcd for $C_6H_4(NH_2BH_3)_2$: H (hydridic), 4.45; B, 15.9; N, 20.6. Found: H (hydridic), 4.20, 4.17; B, 15.3; N, 20.1; pK(p-$H_2NC_6H_4NH_3^+$), 6.18; pK (p-$H_2NC_6H_4NH_3^+$) from titration of a solution of p-$C_6H_4(NH_2)_2 \cdot 2HCl$, 6.2. The infrared spectrum obtained with a KBr wafer showed strong bands at 527, 828, 1136, 1256, 1508–1522, 1565, 2310–2400, 3200, and 3260 cm^{-1} and less intense bands at 765, 945, 985, 1110, 1175, 1180, 1490, and 2250–2260 cm^{-1}.

Kinetic Studies.—All kinetic measurement was made at 25° using an E. H. Sargent Thermonitor controlled water bath. The temperature variation was less than 0.01°. Weighed samples of m- or p-phenylenediamine bisborane were treated with appropriate volumes of aqueous dioxane which had been equilibrated at the same temperature, the time of addition being taken as t_0. Initial concentrations of contained borane $[BH_3]_0$ were calculated from the known quantity of starting materials. Neutral aqueous solutions of ethylenediamine bisborane, which hydrolyze at a negligible rate compared to rates at high acidity, were prepared, analyzed, and diluted with equal volumes of buffer solution at t_0. In these solutions, the ionic strength was adjusted to 0.5 by adding KCl. In all cases, the quantity of soluble hydride at different times was determined iodometrically as previously described.[6,8] The pH measurements were made on a Beckman Expandomatic pH meter.

Results and Discussion

When the hydrolysis of m- or p-phenylenediamine bisborane is carried out in neutral aqueous dioxane, a plot of the logarithm of the calculated BH_3 content of the solution *vs.* time results in a curve in which the slope becomes progressively less negative with increasing time until a limiting slope (straight line) is obtained (see curves A and C in Figure 1). This indicates that hydrolysis proceeds by two irreversible consecutive first-order processes,[9] as shown in eq 1 and 2 for the *para* isomer, and that k_1 is greater than k_2. These

$$p\text{-}H_3BH_2NC_6H_4NH_2BH_3 \xrightarrow{k_1} p\text{-}H_2NC_6H_4NH_2BH_3 \qquad (1)$$

$$p\text{-}H_2NC_6H_4NH_2BH_3 \xrightarrow{k_2} p\text{-}H_2NC_6H_4NH_2 \qquad (2)$$

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

[9] For a discussion of consecutive first-order reactions see: A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 8; S. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, Chapter III.

equations represent only the starting material, an intermediate product, and final product and designate species involved in consecutive rate-determining steps. They do not account for the rapid hydrolysis of BH_3 or a BH_3-containing intermediate which is thought to follow the rate-determining step in the hydrolysis of a NH_2BH_3 group. Since each step in the above sequence represents the irreversible hydrolytic decomposition of a BH_3 group, the over-all extent of reaction can be followed by measuring the quantity of soluble hydride in solution at various time intervals. Values of k_1 and k_2 (Table I) were obtained by determining the times corresponding to 15, 35, and 70% total reaction and using a graphical method of analysis described by Swain.[10] The value of k_2 obtained in this way compares favorably with that obtained from the limiting slope (the linear portion) of the log $[BH_3]$ *vs.* time plot at large values of t (this slope is equal to $k_2/2.3$ at t_∞ when $k_1 > k_2$).

Studies of the hydrolysis of *m*- and *p*-phenylenediamine bisboranes were also carried out in acidified water–dioxane solutions in the range 0.08–0.53 M hydrogen ion. Under these conditions for the *para* compound, a plot of log $[BH_3]$ *vs.* time was linear from t_0 to the conclusion of the run (4–5 half-lives with respect to soluble hydride). The *meta* compound showed some initial curvature with an increasing negative slope with increasing time until (usually at about 20–30% reaction) a limiting slope was obtained. The data suggest that the relative magnitudes of the consecutive first-order rate constants (which in acid solution we will call k_1^A and k_2^A) are reversed from those in neutral solution. Since $k_2^A > k_1^A$, this limiting slope should be equal to $k_1^A/2.3$. Values of k_1^A calculated at various acidities are reported in Table I.

These results are consistent with previously reported effects of ring substituents on the two different paths observed for amine borane solvolysis in aqueous dioxane. Thus, in neutral water–dioxane, acid catalysis is negligible and the mechanism is considered to involve the rate-determining unimolecular decomposition of the NH_2BH_3 linkage. For a given diamine bisborane, both NH_2BH_3 groups are identical and should exhibit the same tendency to hydrolyze, but when one of these groups has decomposed, the resultant NH_2 group has a retarding effect on the hydrolysis of the remaining NH_2BH_3 group. Values of log k_2 for the *meta*- and *para*-substituted compounds show a reasonable correlation with $\sigma_{m\text{-}NH_2}$ and $\sigma_{p\text{-}NH_2}$ values[11,12] in terms of the Hammett relationship observed with other substituents[6] for this reaction.

TABLE I

RATES OF SOLVOLYSIS OF PHENYLENEDIAMINE BISBORANES IN 50% AQUEOUS DIOXANE AT 25°

	m-H_3BH_2N-$C_6H_4NH_2BH_3$	*p*-H_3BH_2N-$C_6H_4NH_2BH_3$
10^4k_1, sec^{-1} [a]	15.6	7.1[b]
10^4k_2, sec^{-1} [a]	1.25	0.23
10^4k_2, sec^{-1} [c]	1.27	0.22[d]
$[H^+]$, M [e]	$10^4k_1^A$, sec^{-1}	
0.078	11.5	6.33
0.12	12.3	6.83
0.17	12.5	7.17
0.29	13.0	9.33
0.32	14.7	
0.40	15.3	
0.53	15.7	13.5
10^4k_1, sec^{-1} (extrapolated)[f]	11.0	5.0
$10^4k_{1(H^+)}$, M^{-1} sec^{-1} [g]	10.3	15.7

[a] From graphical analysis of data on kinetic runs in neutral aqueous dioxane. [b] Average of four runs. [c] Obtained from limiting slope of log $[BH_3]$ *vs.* time curve on runs in neutral aqueous dioxane. [d] Limiting slope defined by five points in region t = 200–1250 min. [e] $\mu \sim 0.5$. [f] Value of k_1^A obtained from the relation $k_1^A = k_1 + k_{1(H^+)}[H^+]$ by extrapolating to very low $[H^+]$. [g] Obtained from the relation $k_1^A = k_1 + k_{(H^+)}[H^+]$.

In acidified water–dioxane, the intermediate, owing to rapid proton transfer, will be the corresponding *meta*- or *para*-substituted ammonium ion, $H_3BH_2NC_6H_4NH_3^+$. Under conditions of essentially constant hydrogen ion concentration, k_1^A and k_2^A are pseudo-first-order rate constants and each step in the sequence is a result of both acid-independent and acid-catalyzed modes of hydrolysis. Thus, for the sequence

$$p\text{-}H_3BH_2NC_6H_4NH_2BH_3 \xrightarrow{k_1^A} p\text{-}H_3NC_6H_4NH_2BH_3^+ \quad (3)$$

$$p\text{-}H_3NC_6H_4NH_2BH_3^+ \xrightarrow{k_2^A} p\text{-}H_3NC_6H_4NH_3^{2+} \quad (4)$$

$$k_1^A = k_1 + k_{1(H^+)}[H^+] \quad (5)$$

and

$$k_2^A = k_2' + k_{2(H^+)}[H^+] \quad (6)$$

where k_1 and k_2' are the first-order rate constants for the acid-independent hydrolysis of the diamine bisborane and the ammonium-substituted monoamine borane, respectively, and $k_{1(H^+)}$ and $k_{2(H^+)}$ are the second-order rate constants for the acid-catalyzed reactions of these compounds. Again, considering substituent effects, NH_3^+ would be expected to retard the acid-catalyzed solvolysis and enhance the acid-independent rate relative to NH_2. Presumably, the reversal in magnitude of the consecutive first-order rate constants is a result of the importance of this latter substituent effect.

A plot of k_1^A *vs.* $[H^+]$ gives a straight line of slope $k_{1(H^+)}$ and y intercept k_1. Values of k_1 thus obtained are somewhat lower than those obtained by the graphical method. Owing to the steepness of the log $[BH_3]$ *vs.* time curve in the early stages of the reaction in neutral water–dioxane there may be a little more uncertainty in the graphically obtained value of k_1. For both *meta* and *para* compounds, however, the values of k_1 obtained by the two methods agree within 30%.

Considering substituent effects further, it is tempting to try to assign approximate values of Hammett σ

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[10] C. G. Swain, *J. Am. Chem. Soc.*, **66**, 1696 (1944).

[11] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

[12] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

TABLE II

RATES OF HYDROLYSIS OF ETHYLENEDIAMINE BISBORANE IN WATER AT 25°[a]

Run	$[\mathrm{H}^+]$, M	10^3k_1,[b] sec^{-1}	10^3k_2,[b] sec^{-1}	$k_{1(\mathrm{H}^+)}$,[c] M^{-1} sec^{-1}	$k_{2(\mathrm{H}^+)}$,[c] M^{-1} sec^{-1}	$k_{2(\mathrm{H}^+)}$[d](slope), M^{-1} sec^{-1}
66	8.30×10^{-4}	0.14	0.015	0.17	0.018	
67	9.13×10^{-4}	0.13	0.016	0.14	0.018	0.021
71	7.77×10^{-4}	0.10	0.012	0.13	0.015	0.016
73	4.40×10^{-3}	0.860	0.0880	0.195	0.020	0.018
78	3.00×10^{-3}	0.522	0.0572	0.174	0.019	
			Av	0.16	0.018	0.018

[a] $\mu = 0.5$. [b] Obtained from graphical analysis of data. [c] $k_1 = k_{(\mathrm{H}^+)}[\mathrm{H}^+]$; $k_2 = k_{2(\mathrm{H}^+)}[\mathrm{H}^+]$. [d] Obtained from limiting slope of log $[\mathrm{BH_3}]$ *vs.* time curve.

constants to the *m*- and *p*-$\mathrm{NH_2BH_3}$ groups. Based on the effect of other substituents on the hydrolysis rates of substituted aniline boranes, ρ values of $+2.32$ and -1.32 were previously obtained for the acid-independent and acid-catalyzed reactions, respectively.[6] For a given diamine bisborane, each $\mathrm{NH_2BH_3}$ linkage exerts an effect on the rate of hydrolysis of the other $\mathrm{NH_2BH_3}$ group. Thus, k_1 (or $k_{1(\mathrm{H}^+)}$) measures the influence of both $\mathrm{NH_2BH_3}$ groups on the reactivity at the other site. Since the two amine borane groups are identical, k_1 (or $k_{1(\mathrm{H}^+)}$) should be halved to obtain a measure of the substituent effect of a single $\mathrm{NH_2BH_3}$ group. Estimated values of σ for the $\mathrm{NH_2BH_3}$ group, therefore, are obtained by correlating log $(k/2)$ with previously established Hammett plots. From values of k_1 obtained graphically (Table I, line 1) and the Hammett relationship for acid-independent solvolysis, $\sigma_{m\text{-}\mathrm{NH_2BH_3}} = +0.25$ and $\sigma_{p\text{-}\mathrm{NH_2BH_3}} = +0.10$. From values of k_1 obtained by extrapolation (Table I, line 11), $\sigma_{m\text{-}\mathrm{NH_2BH_3}} = +0.19$ and $\sigma_{p\text{-}\mathrm{NH_2BH_3}} = +0.04$. From a correlation of log $[k_{1(\mathrm{H}^+)}/2]$ and the relationship for acid-catalyzed solvolysis, $\sigma_{m\text{-}\mathrm{NH_2BH_3}} = +0.35$ and $\sigma_{p\text{-}\mathrm{NH_2BH_3}} = +0.22$. This treatment is subject to uncertainties not only in the values of rate constants determined in this study but also in the Hammett relations established for these reactions. Also, since σ constants are defined in terms of the ionization constants of substituted benzoic acids and not by means of correlations of reactions, these values should be viewed only as a qualitative indication of the substituent effects of the respective groups.

In a separate investigation, the acid-catalyzed hydrolysis of ethylenediamine bisborane (ethane-1,2-diamine borane) ($\mathrm{H_3BH_2NCH_2CH_2NH_2BH_3}$) was studied in aqueous solution in the region pH 2.37–3.11. As with many other alkylamine boranes under these conditions, the rate of any acid-independent reaction is negligible compared to the acid-catalyzed path which is for the general case described by the rate expression

$$\frac{-\mathrm{d}(\mathrm{RNH_2BH_3})}{\mathrm{d}t} = k[\mathrm{RNH_2BH_3}][\mathrm{H}^+] \qquad (7)$$

Again, the extent of total reaction was followed by measuring the quantity of soluble hydride in solution over a period of time (Figure 1). At constant pH two irreversible consecutive first-order reactions are indicated

$$\mathrm{H_3BH_2NCH_2CH_2NH_2BH_3} \xrightarrow{k_1} \mathrm{H_3BH_2NCH_2CH_2NH_3}^+ \qquad (8)$$

$$\mathrm{H_3BH_2NCH_2CH_2NH_3}^+ \xrightarrow{k_2} \mathrm{H_3NCH_2CH_2NH_3}^{2+} \qquad (9)$$

where k_1 and k_2 are pseudo-first-order rate constants each equal to the product of a second-order constant and the concentration of hydronium ion (en = $\mathrm{H_2NCH_2CH_2NH_2}$).

$$\frac{-\mathrm{d}[\mathrm{en(BH_3)_2}]}{\mathrm{d}t} = k_{1(\mathrm{H}^+)}[\mathrm{en(BH_3)_2}][\mathrm{H}^+] \qquad (10)$$

$$\frac{-\mathrm{d}[\mathrm{en(BH_3)H}^+]}{\mathrm{d}t} = k_{2(\mathrm{H}^+)}[\mathrm{en(BH_3)H}^+][\mathrm{H}^+] \qquad (11)$$

Thus, $k_1 = k_{1(\mathrm{H}^+)}[\mathrm{H}^+]$ and $k_2 = k_{2(\mathrm{H}^+)}[\mathrm{H}^+]$.

Values of k_1 and k_2 at various acidities were obtained by the graphical method of Swain[10] and are listed in Table II along with calculated values of the corresponding second-order rate constants. In three runs, k_2 was determined from the slope of the linear portion of the log $[\mathrm{BH_3}]$ *vs.* time curve at large values of *t*. The degree of agreement between values of $k_{2(\mathrm{H}^+)}$ obtained in this way and by the graphical method is shown in Table II. The fact that $k_1 > k_2$ is consistent with the previously proposed mechanism involving a rate-determining electrophilic attack of H^+ on nitrogen with displacement of $\mathrm{BH_3}$. From a consideration of field and σ-inductive effects,[13,14] the conversion of a $\mathrm{NH_2BH_3}$ group to $\mathrm{NH_3}^+$ would be expected to decrease the rate of hydrolysis of the amine borane group at the other end of the molecule. The effect of the $\mathrm{H_3BH_2NCH_2CH_2}$ group is to retard the hydrolysis rate of the other amine borane function relative to the effect of N-alkyl substituents (Table III).

TABLE III

RATES OF ACID-CATALYZED HYDROLYSIS OF PRIMARY ALKYLAMINE BORANES ($\mathrm{RNH_2BH_3}$) IN WATER AT 25° ($\mu = 0.5$)

Substrate	R	k_{H^+}, M^{-1} sec^{-1}
$\mathrm{CH_3NH_2BH_3}$	$\mathrm{CH_3}$	0.45[a]
$\mathrm{CH_3CH_2NH_2BH_3}$	$\mathrm{CH_3CH_2}$	0.58[a]
$\mathrm{CH_3CH_2CH_2NH_2BH_3}$	$\mathrm{CH_3CH_2CH_2}$	0.61[b]
$\mathrm{(CH_3)_2CHNH_2BH_3}$	$\mathrm{(CH_3)_2CH}$	0.67[a]
$\mathrm{(CH_3)_3CNH_2BH_3}$	$\mathrm{(CH_3)_3C}$	0.87[a]
$\mathrm{H_3BH_2NCH_2CH_2NH_2BH_3}$	$\mathrm{H_3BH_2NCH_2CH_2}$	0.16[b]
$\mathrm{H_3NCH_2CH_2NH_2BH_3}^+$	$\mathrm{H_3NCH_2CH_2}^+$	0.018[b]

[a] Previously reported.[6] [b] Obtained for this study.

The logarithms of second-order rate constants for the acid-catalyzed hydrolysis of several primary alkylamine boranes ($\mathrm{RNH_2BH_3}$) are linearly related to

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(13) M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3539, 3541, 3546, 3548 (1962).

(14) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt-Dryden, New York, N. Y., 1959, Chapter 7.