Anal. Calcd for $Pt(B_{10}H_{12})[P(C_2H_5)_3]_2$: C, 26.1; H, 7.7; B, 19.6; P, 11.2; Pt, 35.4; mol wt, 552. Found: C, 26.1; H, 8.1; B, 19.7; P, 10.7; Pt, 36.1; mol wt (acetone) (ebullioscopic), 537. Ir spectrum (Nujol): 2535 (B–H) and 1940 cm^{-1} (BHB bridge); uv and visible maxima (CH_3CN): 220 (ϵ 21,180) and 245 mμ (ϵ 14,050); the ^{11}B nmr spectrum was broad and unresolved; ^1H nmr ($(CD_3)_2CO$): τ 8.86 (t, 3, CH_3CH_2) and 7.8 (q, 2, CH_3CH_2).

$Pt(B_{10}H_{12})[P(C_4H_9)_3]_2$.—A 50-ml solution of 0.005 mol of $NaB_{10}H_{13}$ was added to a slurry of 3.35 g (0.0025 mol) of *cis*-$[(C_4H_9)_3P]_2PtCl_2$ in tetrahydrofuran. The reaction was stirred for 30 min and filtered and the filtrate was evaporated to a yellow oil. Trituration with hexane gave a yellow solid. The crude product was recrystallized from benzene to give well-formed yellow crystals, mp 182–183°. The yield was 1.0 g (55%).

Anal. Calcd for $Pt(B_{10}H_{12})[P(C_4H_9)_3]_2$: C, 40.02; H, 9.24; B, 15.02. Found: C, 40.25; H, 9.09; B, 14.83. Ir spectrum (Nujol): 2530 (B–H) and 1430 cm^{-1} (BHB bridge); 19.3-MHz ^{11}B nmr ($BF_3O(C_2H_5)_2 = 0$) (acetone): δ −8.1 (b, 8) and 28.1 ppm (d, 2).

$Pd(B_{10}H_{12})[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$.—A suspension of 1.15 g (0.002 mol) of P,P,P′,P′-tetraphenylethylenediphosphine-palladium(II) chloride in 30 ml of tetrahydrofuran was treated with 0.004 mol of $NaB_{10}H_{13}$ in 20 ml of tetrahydrofuran. During a 3-hr period at 25°, the reaction mixture became yellow and then white. The mixture was filtered and the filtrate was evaporated. The off-white solid was recrystallized from acetone as light yellow needles, mp 230–240°.

Anal. Calcd for $Pd(B_{10}H_{12})[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$: C, 49.94; H, 5.80. Found: C, 50.53; H, 6.78. Ir spectrum (Nujol): 2535 (B–H) and 1940 cm^{-1} (BHB bridge).

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Hydrolysis of Tris(N-dibutylboryl-4-methyl-2-pyridylamino)borane

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The rate of hydrolysis of tris(N-dibutylboryl-4-methyl-2-pyridylamino)borane was investigated spectrophotometrically in aqueous dioxane. The reaction was affected by the addition of hydrochloric acid and was shown to be first order in the substrate. The hydrolysis proceeded more rapidly in a D_2O–dioxane solution than in a H_2O–dioxane solution by a factor of about 2.5 over a wide range of solvent composition. The rate changed with the solvent composition in a similar way as did the acidity function. The activation energy was obtained as 20.5 kcal/mol and the activation entropy as +18.1 eu at 300°K in 90 vol % aqueous dioxane. On the basis of these experimental results, the hydrolysis mechanism was concluded to be of the A-1 type which involves rapid preequilibrium between the reactants and a conjugate acid followed by a first-order rate-determining reaction of the conjugate acid.

Introduction

A preceding paper[1] has dealt with the mechanism of catalytic hydrolysis of borazine derivatives in aqueous dioxane media in the presence of hydrochloric acid or triethylamine. The present paper describes a kinetic and mechanistic study in which the rates of hydrolysis of tris(N-dibutylboryl-4-methyl-2-pyridylamino)borane [abbreviated hereafter as S] have been determined by measuring the rate of decreasing absorption of its aqueous dioxane solution. As shown in Figure 1, S has three kinds of B–N bonds, one of which is an N→B coordination bond. All of these B–N bonds are broken during the hydrolysis

$$S + 9H_2O \longrightarrow 3CH_3(C_5H_3N)NH_2 + 3C_4H_9B(OH)_2 + B(OH)_3 + 3C_4H_{10}$$

It is an important as well as an interesting point in this study to determine which bond is split at the rate-determining step. In order to clarify the mechanism and to determine the kinetic order, the rate of hydrolysis, the hydrogen isotope effect of solvent, and the activation parameters have been determined.

Experimental Section

Materials.—Dioxane was purified by the method of Fieser.[2] The mixed solvent of 90% dioxane–10% water was prepared by diluting one volume of water with nine volumes of dioxane. (This solvent will be abbreviated as 90% aqueous dioxane throughout this paper.) The catalyst was dissolved in water before mixing, and its concentration was corrected for the volume compression due to mixing. The sample of S was prepared by a method virtually identical with that described earlier using 4-methyl-2-aminopyridine instead of 2-aminopyridine.[3]

Kinetic Measurements.—The hydrolysis experiments were carried out in a glass-stoppered 1-cm quartz cuvette, and the progress of the hydrolysis was followed by reading the decrease in optical density of the sample solution on a Model EPU-2A photoelectric spectrophotometer from Hitachi Co., Ltd., the cell compartment of which was modified[1] so that the desired temperature could be maintained within ±0.02°. The sample gives rise to a strong absorption at 340 mμ and the measurements were

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[1] T. Yoshizaki, H. Watanabe, and T. Nakagawa, *Inorg. Chem.*, **7**, 422 (1968).

[2] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 284.

[3] H. Watanabe, K. Nagasawa, T. Totani, T. Yoshizaki, and T. Nakagawa, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 116; K. Nagasawa, T. Yoshizaki, and H. Watanabe, *Inorg. Chem.*, **4**, 275 (1965).

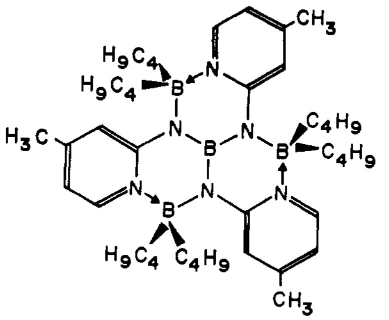

Figure 1.—Tris(N-dibutylboryl-4-methyl-2-pyridylamino)-borane.

made at 360 mμ where the reaction products show inappreciable absorption. The sample concentration was usually 3 × 10^{-5} *M*. Details of the procedure have been described elsewhere.[1]

Rate of Amine Production.—The reaction rate was also determined by measuring the amount of amine produced in the course of hydrolysis in order to compare it with that obtained spectrophotometrically under the same conditions.

In a typical run, the hydrolysis was carried out in 80% aqueous dioxane containing 10.2 × 10^{-5} mol/l. of the sample and 33.3 × 10^{-5} mol/l. of hydrochloric acid.[4] From time to time, two identical aliquots were taken out from the solution, one aliquot being diluted with the solvent and the other with water. The optical densities were measured with the former solutions and the electric conductivities were measured with the latter solutions. The amount of decomposition was estimated from the optical density and that of the produced amine was determined from the conductivity by using the calibration curve which had been obtained in the following way.

After the completion of hydrolysis, a known volume of the reaction mixture, x, was diluted with a $1 - x$ volume of 80% aqueous dioxane containing hydrochloric acid of the same concentration as above (33.3 × 10^{-5} *M*). A series of test solutions was prepared in the same manner with varying x. Their conductivities were measured after a proper dilution with water and plotted against x. Because the remaining reactant is deposited out from the solution by proper dilution with water, the composition of the solution must be the same as that of the test solution at the time of the conductivity measurement.

Results

The extinction ($-\log T$) observed at time t will be denoted hereafter by E for the sake of brevity. The notation E_∞ represents E at $t = \infty$ and, therefore, signifies the residual extinction after the reaction has run to completion.

Kinetic Order and Definition of k_{obsd}.—The logarithm of $E - E_\infty$ decreases linearly with time indicating the hydrolysis to be first order with respect to $E - E_\infty$. The quotient $-[\mathrm{d}(E - E_\infty)/\mathrm{d}t]/(E - E_\infty)$ gave a constant value in all of the experiments, because linearity was always maintained within the limit of experimental error over several half-lives. This pseudo-first-order constant is defined as k_{obsd}. The rate constants agreed within 2% or better.

Effect of Added Substances on k_{obsd}.—The effects of various substances on the hydrolysis rate have been examined. Hydrochloric acid showed prominent catalytic activity, whereas triethylamine, triethylammonium chloride, lithium chloride, and lithium hydroxide resulted in rates too slow to measure. The rate constant k_{obsd} increased in proportion to the analytical concentration of hydrochloric acid, $[\mathrm{HCl}]_{\text{anal}}$, up to 0.005 *M* as shown in Table I. Therefore, the reaction is apparently first-order with respect to $[\mathrm{HCl}]_{\text{anal}}$.

The common-ion salt effect on k_{obsd} of chloride ion was examined for the hydrolysis catalyzed by hydrochloric acid in 95% aqueous dioxane solution. A slight effect was observed on adding lithium chloride as shown in the last four lines of Table I.

Table I

Effects of Added Substances on the First-Order Rate Constant k_{obsd}

Solvent % $O_2C_4H_8$	$[\mathrm{HCl}]_{\text{anal}}$, *M*	$[\mathrm{LiCl}]_{\text{anal}}$, *M*	$10^4 k_{\text{obsd}}$, $\sec^{-1}$	Temp, °C
95	0	0	~0	Room temp
95	0	0–0.1	~0	Room temp
90	0	0	~0	6.4
90	0.000885	0	50.2	6.4
90	0.00118	0	64.3	6.4
84	0	0	~0	14.7
84	0.000956	0	149	14.7
84	0.00191	0	290	14.7
84	0.00478	0	707	14.7
95	0.00111	0	232	14.7
95	0.00111	0.00100	226	14.7
95	0.00111	0.00200	222	14.7
95	0.00111	0.00300	220	14.7

Effect of Solvent Composition on k_{obsd}.—The change of k_{obsd} was measured as a function of the solvent composition at a fixed catalyst concentration. The results are shown in the upper part of Table II.

Table II

Solvent Hydrogen Isotope Effect at 14.9° in the Presence of 0.00098 *M* HCl–DCl

	Solvent, % $O_2C_4H_8$ (mol % $O_2C_4H_8$)				
	95 (79)	90 (64)	84 (52)	79 (44)	69 (32)
$10^4 k^{\mathrm{H}}_{\text{obsd}}$, $\sec^{-1}$	220	149	147	166	293
$10^4 k^{\mathrm{D}}_{\text{obsd}}$, $\sec^{-1}$	567	356	360	401	624
$k^{\mathrm{H}}_{\text{obsd}}/k^{\mathrm{D}}_{\text{obsd}}$	0.39	0.42	0.41	0.41	0.47

Solvent Hydrogen Isotope Effect.—The kinetic effect of changing the solvent from H_2O–dioxane to D_2O-dioxane was studied at a constant concentration of catalyst. The results are presented in Table II, in which $k^{\mathrm{H}}_{\text{obsd}}/k^{\mathrm{D}}_{\text{obsd}}$ is given for various solvent compositions. The superscripts H and D refer to the H_2O–dioxane and D_2O–dioxane solutions, respectively. No significant effect of solvent composition on the ratio was observed. It is noteworthy that $k^{\mathrm{H}}_{\text{obsd}}/k^{\mathrm{D}}_{\text{obsd}}$ is less than unity.

Dependence of Rate on Temperature.—The logarithm of the rate constant, $\log (k_{\text{obsd}}/[\mathrm{HCl}]_{\text{anal}})$, increases in inverse proportion to temperature. The least-squares treatment of the data led to the activation energies $\Delta E^{\ddagger}$ and the activation entropies $\Delta S^{\ddagger}$ given in Table III, the transmission coefficient being set equal to unity. Their standard errors are also calculated.

Comparison of the Rate of Amine Production with That of Absorption Disappearance.—Figure 2 compares the decay of the reactant determined by the

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[4] Note that the concentration of the reactant is nearly equivalent to that of hydrochloric acid in this case.

TABLE III

ACTIVATION PARAMETERS

90% dioxane, $[HCl]_{anal}$ = 0.00118 M		95% dioxane, $[HCl]_{anal}$ = 0.00088 M	
Temp, °C	$k_{obsd}/[HCl]_{anal}$, sec^{-1} mol^{-1}	Temp, °C	$k_{obsd}/[HCl]_{anal}$, sec^{-1} mol^{-1}
6.42	5.45	6.30	8.06
11.32	10.00	14.45	22.80
11.97	10.76	18.80	37.27
18.25	23.45	18.95	37.04
27.30	46.70	25.00	80.00
$\Delta E^{\ddagger}$ = 20.5 ± 0.3 kcal/mol		$\Delta E^{\ddagger}$ = 20.1 ± 0.3 kcal/mol	
$\Delta S^{\ddagger}$ = 18.1 ± 0.9 eu (300°K)		$\Delta S^{\ddagger}$ = 17.5 ± 1.1 eu (300°K).	

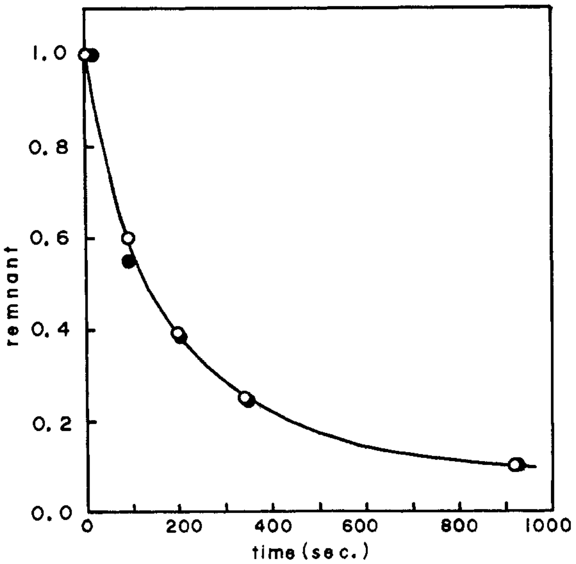

Figure 2.—Comparison of rates obtained by two methods: open circles, absorption disappearance; solid circles, amine production.

amine production with that of the absorption intensity decrease. The two curves completely coincide.

Ultraviolet Absorptions in Various Dioxane–Water Compositions.—If a complex is formed between S and water, the ultraviolet spectrum should undergo a change when the solvent composition is altered. All of the solutions ranging from 100 to 60% aqueous dioxane afforded the same spectra, and no evidence for a complex was observed.

Addition of hydrogen chloride did not affect the absorption for a moment indicating that complex formation between H^+ and S is of negligible concentration.

Discussion

All of the measurements under various conditions fit very well for a reaction which is first order in $(E - E_{\infty})$, and the rate of the decreasing absorption agrees with that of the increasing amine concentration. The satisfactory agreement between the rate of amine production and that of absorption decrease implies that one and only one slow process forms a bottleneck in the whole reaction course. The reaction was affected by the addition of hydrochloric acid and was apparently first order with respect to $[HCl]_{anal}$. On the other hand, the logarithm of k_{obsd} varied nonlinearly with solvent composition, passing through a minimum in the region of equimolar proportion of dioxane and water. This is in contrast to the behavior of tris(phenylethynyl)-borazines where the value of log k_{obsd} changes monotonically with solvent composition.[1] For comparison, log k_{obsd} in Table II is plotted against composition in Figure 3, along with H_0 which is determined for 0.1 M hydrochloric acid using p-nitroaniline as a proton acceptor.[5] Though there is a little discrepancy between the two curves, one can reasonably argue that log k_{obsd} varies linearly with the acidity function, because the maximum position of H_0 (the minimum position in Figure 3) has a tendency to shift to the right on diluting the hydrochloric acid concentration and the present experiments have been carried out at a concentration as low as 0.00098 M.

The linearity between k_{obsd} and h_0 ($H_0 = -\log h_0$) cannot be compatible with that between k_{obsd} and $[HCl]_{anal}$. However, it can easily be explained on the basis of data on the acidity function variation with solvent composition[6] that the variation in h_0 runs almost linearly with that in the acid concentration in aqueous methanol if the acid concentration is very low. Therefore, k_{obsd} is linear with h_0 but not with $[HCl]_{anal}$. Furthermore, the acidity function is plotted on the same scale as log k_{obsd} in Figure 3. The similarity in curvature suggests that, on plotting log k_{obsd} against the acidity function in a low acid concentration, the slope would be close to −1.

This correlation is to be expected if the hydrolysis mechanism involves a first-order rate-determining reaction of the conjugate acid formed in a preequilibrium step, on the analogy of the mechanism in aqueous solution pointed out by Hammett.[7] The most probable mechanism is the A-1 type[7b]

$$\mathrm{S} + \mathrm{H}^+ \overset{K_0}{\rightleftharpoons} \mathrm{SH}^+ \qquad \text{preequilibrium}$$

$$\mathrm{SH}^+ \xrightarrow{k} \mathrm{S_1}^+ \qquad \text{rate determining}$$

$$\mathrm{S_1}^+ + n\mathrm{H_2O} \longrightarrow \text{products} + \mathrm{H}^+ \qquad \text{fast}$$

The rate equation for this mechanism is

$$\text{rate} = -\frac{\mathrm{d}[\mathrm{S}]}{\mathrm{d}t} = k_{obsd}[\mathrm{S}] = \frac{kK_0h_0\left(\dfrac{f_{\mathrm{BH^+}}f_{\mathrm{S}}}{f_{\mathrm{B}}f_{\ddagger}}\right)}{1 + h_0K_0\left(\dfrac{f_{\mathrm{BH^+}}f_{\mathrm{S}}}{f_{\mathrm{B}}f_{\mathrm{SH^+}}}\right)}[\mathrm{S}]$$

The symbols used here have the meanings: H^+, a solvated proton in the medium; S_1, an unspecified kinetic intermediate; K_0, equilibrium constant, but not the dissociation constant of the conjugate acid SH^+; k, specific rate constant of the rate-determining step; f, activity coefficients of the species indicated; $\ddagger$, activated complex; B, p-nitroaniline. Brackets signify the concentrations of the materials enclosed. The concentration of S is low in the present experiments in comparison with that of the acid, and S is such a weak base that it is almost entirely in the uncharged basic form over the range of acidity investigated, as evidenced by the lack

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(5) E. A. Braude, *J. Chem. Soc.*, 1976 (1948).

(6) P. Salomaa, *Acta Chem. Scand.*, **11**, 125 (1957).

(7) (a) L. P. Hammett, *Chem. Rev.*, **16**, 67 (1934); "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940; (b) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

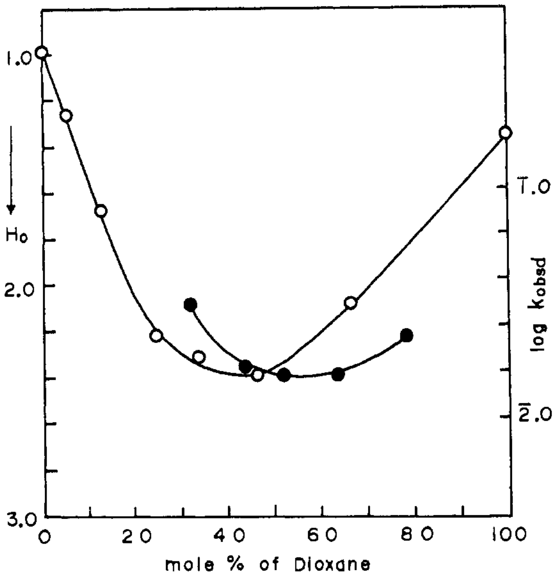

Figure 3.—Effect of acidity function on k_{obsd}: open circles, H_0 *vs.* mole per cent of dioxane; solid circles, log k_{obsd} *vs.* mole per cent of dioxane.

of absorption change by adding acid except that due to the hydrolysis. Then, [S] is practically the same as the over-all stoichiometric concentration, and the first-order rate coefficient k_{obsd} satisfies the equation

$$k_{obsd} = \frac{kK_0a_{H^+}f_S}{f_\ddagger} = \frac{kK_0h_0f_{BH^+}f_S}{f_Bf_\ddagger}$$

Here, one can reasonably assume that $f_\ddagger$ varies with changes in the medium in essentially the same way as f_{SH^+}, the activity coefficient of the conjugate acid of S, and that $f_S/f_\ddagger = f_B/f_{BH^+}$. It follows that the rate constant k_{obsd} is linear with h_0 so that

$$\log k_{obsd} = -H_0 + \log kK_0$$

Though the correlation[8] between Hammett's acidity function h_0 and rate has been thought to be valid only in aqueous solutions of sufficiently high acidity, it seems to be applicable to reactions in the mixed solvents used in this investigation because the acidity function differs appreciably from the hydrogen ion concentration. The extraordinary solvent isotope effect ($k^H{}_{obsd}/k^D{}_{obsd} \approx 0.41$) also suggests that the hydrolysis mechanism is quite different from those of amine borane derivatives,[9,10] for which $k^H{}_{obsd}/k^D{}_{obsd} = 1.9$, and from that of borazine derivatives,[1] for which $k^H{}_{obsd}/k^D{}_{obsd} = 2.11$.

The ratio $k^H{}_{obsd}/k^D{}_{obsd}$ in a fixed solvent composition may be written as

$$k^H{}_{obsd}/k^D{}_{obsd} = (K^H{}_0/K^D{}_0)(k^H/k^D)$$

The rate-determining step involves no proton transfer, and so the value of (k^H/k^D) can be set nearly equal to unity. The value of ($k^H{}_{obsd}/k^D{}_{obsd}$) depends on the ratio of [SH^+] in H_2O–dioxane to [SD^+] in D_2O–dioxane. Because the dissociation constants ($= 1/K_0$) of conjugate acids are usually smaller in heavy water than in light water as weak acids are,[11] the concentration of the conjugate acid is naturally expected to be larger in D_2O–dioxane. It follows that the reaction proceeds more rapidly in D_2O–dioxane solution. This consequence is consistent with the experimental result in a qualitative sense.

With use of the method proposed by Bunton and Shiner,[12] one can calculate a semiquantitative isotope effect. The relation between the acid–base equilibrium constant and the relevant hydrogen stretching frequencies is

$$K^H{}_0/K^D{}_0 = \text{antilog}\,\frac{\sum\nu_H - \sum\nu_{H'}}{12.53T}$$

where $\Sigma\nu_H$ and $\Sigma\nu_{H'}$ are the sums of hydrogen stretching frequencies (cm^{-1}) in the initial and final states, respectively, and T is the absolute temperature. The frequencies involving hydrogen atoms are assumed as:[1] 2900 cm^{-1} for the hydrated H_3O^+, 3400 cm^{-1} for hydrogen-bonded H_2O, and 2700 cm^{-1} in the conjugate acid. Then, the isotope effect for the first step of the A-1 mechanism is calculated as 0.6, which is considered in good agreement with the experimental value of 0.41. Thus, the A-1 mechanism can explain the solvent isotope effect and has received further support.

The positive activation entropy suggests an increase in freedom during the course from SH^+ to the transition state, though no completely satisfactory quantitative explanation can be given for the positive value as high as 18 eu. A possible explanation might be that the solvation sphere of the transition state was loosened relative to the ground-state SH^+ or possibly that the rotation of a pyridyl group was allowed in the transition state. The investigation of this possibility must be the subject of future research, although the present A-1 mechanism requests that a proton be covalently bound to one of the nitrogen atoms in the conjugate acid SH^+.

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