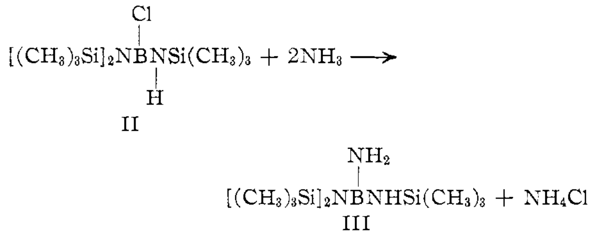
bis(trimethylsilyl)ammonium chloride, is unstable and will spontaneously decompose into hexamethyldisilazane, trimethylchlorosilane, and ammonia (eq 5). The

$$[(CH_3)_3Si]_2NH\cdot HCl \longrightarrow {}^1/_2[(CH_3)_3Si]_2NH + (CH_3)_3SiCl + {}^1/_2NH_3 \quad (5)$$

ammonia produced in reaction 5 is necessary for the next reaction. This step is the amination of the remaining boron–chlorine bond to form aminobis(trimethylsilyl)-aminotrimethylsilylaminoborane (III) and ammonium chloride (eq 6). The large amino groups on the boron probably prevent any condensation to form a diborylamine. The disappearance of the ammonium chloride[4] in the reaction in which the ratio of the hexamethyldisilazane to trichloroborane was 3:1 can best be explained by the final step in the reaction sequence. This is the reaction of hexamethyldisilazane with ammonium chloride to form trimethylchlorosilane and ammonia. This is the reverse of the reaction in which hexamethyldisilazane is normally prepared; however, the reaction between a silyl halide and an amine has been found to be reversible by Anderson.[18] Since the ammonia formed can be constantly used in the formation of III (eq 6), the reverse of this last reaction in this scheme cannot occur readily (eq 7). The necessity of having an excess of hexamethyldisilazane for the formation of the trisaminoborane (III) was demonstrated by a reaction between hexamethyldisilazane and boron trichloride in a 1:1 mole ratio in refluxing hexane. In this experiment there was no evidence for the formation of III.



$$[(CH_3)_3Si]_2N\overset{\overset{Cl}{|}}{B}\underset{\underset{H}{|}}{N}Si(CH_3)_3 + 2NH_3 \longrightarrow [(CH_3)_3Si]_2N\overset{\overset{NH_2}{|}}{B}NHSi(CH_3)_3 + NH_4Cl \quad (6)$$

II

III

$${}^1/_2[(CH_3)_3Si]_2NH + NH_4Cl \longrightarrow (CH_3)_3SiCl + {}^3/_2NH_3 \quad (7)$$

Acknowledgment.—This research was supported by the National Science Foundation, Grant No. GP 2932.

[18] H. H. Anderson, *J. Am. Chem. Soc.*, **73**, 5802 (1951).

CONTRIBUTION FROM SHIONOGI RESEARCH LABORATORY,
SHIONOGI & COMPANY, LTD., FUKUSHIMA-KU, OSAKA, JAPAN

The Kinetics and Mechanisms of Hydrolysis of Borazine Derivatives in Aqueous Dioxane

BY TAMOTSU YOSHIZAKI, HARUYUKI WATANABE, AND TOSHIO NAKAGAWA

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The hydrolysis rates of B-tris(phenylethynyl)borazine derivatives are increased by the addition of acids and bases. The reaction was found to be first order with respect to borazine as well as with respect to acid and base concentrations. The isotope effect and the solvent isotope effect on the hydrolysis rate were measured to elucidate the mechanism. The hydrolysis proceeds more rapidly in dioxane–H_2O than in dioxane–D_2O solution by a factor of 2.1 for hydrochloric acid catalyzed hydrolysis and by a factor of 1.70 for triethylamine-catalyzed hydrolysis. The activation energies $\Delta E^{\ddagger}$ for the acid- and amine-catalyzed hydrolyses are about 10 kcal/mole for all of the derivatives examined. On the basis of these data, a model of the transition state was proposed for the acid- and base-catalyzed hydrolyses, respectively.

Introduction

While considerable attention has been paid to the solvolysis reactions of boron compounds in recent years, the great majority of the work has dealt with boron compounds involving an sp^3-hybridized boron atom, *e.g.*, borohydrides and amine boranes.[1–3] Few studies of the solvolysis of sp^2 boron–nitrogen compounds have been described, and no mechanistic studies of the hydrolyses of borazines have been made probably owing to "the complexities involved in considering possible hydrolysis mechanisms of these compounds."[4] It is the purpose of the present and the following papers to elucidate the mechanism of borazine hydrolysis and to ascertain the factors determining hydrolysis stability.

The borazine derivatives dissolved in inert organic solvents react with water quantitatively to produce the corresponding amines and boronic acids according to the over-all equation

$$(BRNR')_3 + 6H_2O \longrightarrow 3RB(OH)_2 + 3R'NH_2$$

In preliminary experiments to determine the experimental conditions, it was found that the hydrolysis rate was greatly increased by the addition of base and

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

(2) G. E. Ryschkewitsch, *ibid.*, **82**, 3290 (1960).

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

(4) R. J. Brotherton and A. L. McCloskey, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 131.

acid, and that the rate without catalyst was low and the reproducibility of rate determination was poor. The fluctuation might originate in proton and hydroxyl ions of impurity, amine, and boronic acid of hydrolysis products, etc. The rate determinations were made mainly in the presence of excess acid or base as compared with the samples to eliminate the effects of the impurities and the reaction products. B-Tris(phenylethynyl)borazine, $B_3(C{\equiv}CC_6H_5)_3N_3H_3$, appears to be suitable for the present investigation because it hydrolyzes with an appropriate rate in a water–dioxane solvent system and the hydrolysis can be followed by the change in ultraviolet absorption.

The reaction was found to be first order with respect to borazine as well as with respect to acid and base concentration, the results being employed to exclude some of the various conceivable mechanisms. The remaining mechanisms were discussed on the basis of the kinetic parameters and the deuterium isotope effects.

Experimental Section

(1) **Compounds.**—Dioxane and triethylamine, initially guaranteed reagents, were refluxed over sodium metal for 15 hr followed by distillation. The hydrochloric acid was a guaranteed reagent grade from Wako Chemical Industries, Ltd. Lithium chloride and lithium hydroxide were also guaranteed reagents from Kanto Chemical Co., Inc., and from E. Merck, respectively. Commercial triethylamine hydrochloride was recrystallized three times from an alcohol–ether mixed solvent. Deuterium oxide was obtained from Showa Denko Co., Ltd. and was 99.75 mole % pure. B-Tris(phenylethynyl)borazines were prepared according to a previously described procedure.[5] B-Tris(phenylethynyl)-N-trideuterioborazine was prepared in the same way from B-trichloro-N-trideuterioborazine,[6] the deuterium content being estimated at about 98% from the infrared intensity measurement. The samples investigated are summarized in Table I.

TABLE I

COMPOUNDS AND WAVELENGTHS USED FOR KINETIC MEASUREMENTS

Compounds	HCl-catalyzed hydrolysis, mμ	$(C_2H_5)_3N$-catalyzed hydrolysis, mμ
$H_3N_3B_3(C{\equiv}CC_6H_5)_3$	273	273
$(C_6H_5)_3N_3B_3(C{\equiv}CC_6H_5)_3$	287	287
$(C_6H_5)_3N_3B_3(C{\equiv}CCH_3)_3$	226	280
$(C_6H_5)_3N_3B_3H_3$	235	280
$(C_6H_5)_3N_3B_3(CH_3)_3$	226	280

(2) **Solvent.**—Hydrolyses of borazines were carried out in aqueous dioxane to ensure complete solubility of the substrates. Solvents were prepared by adding an appropriate volume of water to dioxane so as to give the desired composition. Solvents involving catalysts were prepared by adding an aqueous solution of the appropriate substance instead of water. In this case, the volume due to compression by mixing was corrected for the calculation of the catalyst molar concentration. In the catalytic hydrolysis experiments, a large excess of catalyst was employed so that the change in catalyst concentration during solvolysis would be negligible as compared to the change in borazine concentration. The solvent composition, *e.g.*, 80 vol % dioxane–20 vol % water, will be abbreviated as 80% aqueous dioxane.

(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 ($E = -\log T$) of the solution on a photoelectric spectrophotometer, Model EPU-2A, from Hitachi Co., Ltd. In order to determine a suitable wavelength for the kinetics, the ultraviolet spectra of the reactant and the product of each reaction were measured in dioxane as well as in aqueous dioxane. The wavelengths of Table I were chosen for the kinetic studies, since the difference in molar absorptivity between the reactant and the product causes a large change during the kinetic run. The quartz cuvettes were held in the modified cell compartment as shown in Figure 1, so that the desired temperature could be maintained within ±0.02°.

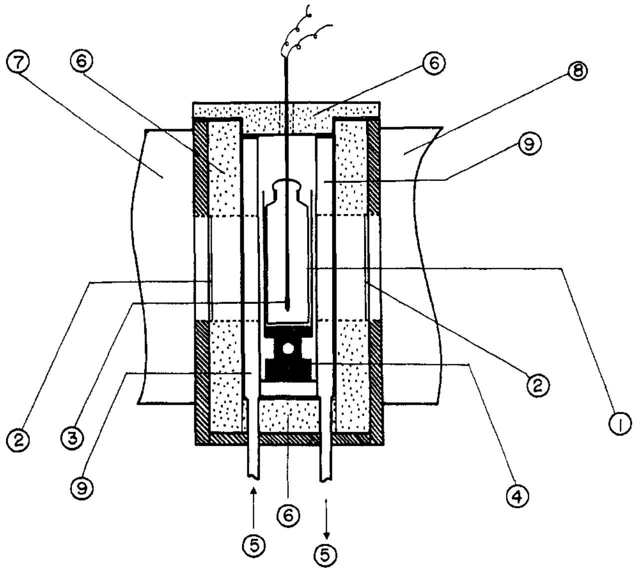

Figure 1.—Modified cell compartment: (1) glass-stoppered 1-cm quartz cuvette; (2) quartz window; (3) thermistor thermometer; (4) slider; (5) to and from thermostat; (6) insulator; (7) monochromater; (8) detector; (9) water jacket.

In a typical run, 3.3 ml of 90% aqueous dioxane involving hydrochloric acid was placed in each absorption cell. The temperature of the solvent was measured in one of the four cells with a thermistor thermometer, "Thermo-Finer," from Jintan Terumo Co., Ltd., Tokyo. B-Tris(phenylethynyl)borazine was dissolved in neutral 90% aqueous dioxane at a concentration of about 10^{-2} M, the concentration being chosen so as to give the highest accuracy on the spectrometer. When thermal equilibrium had been attained, 10 μl of the borazine solution at thermostat temperature was added by a microsyringe and the sample solution was immediately stirred for a few seconds with a small glass rod kept at the same temperature. After capping the cells quickly, the readings of absorbance were commenced and recorded on a tape recorder usually at 3-sec intervals. With two men working together, it was possible to prepare the reaction solution and to set up the reading within 15 sec. An infinity reading, $E_\infty = -\log T_\infty$, was made after about 10 half-lives. In all cases, plots of $\log E - E_\infty$ *vs.* time were linear; thus first-order kinetics were obeyed. The slope of the line was determined by the method of least squares to afford the total first-order rate constant, k_{obsd}, for decreasing absorption. The important constant, k_{obsd}, was defined as

$$k_{\text{obsd}} = \frac{-\mathrm{d}(E - E_\infty)}{\mathrm{d}t}/(E - E_\infty) \qquad (1)$$

In the above-mentioned procedure, it is unnecessary to know the initial concentration exactly and any convenient time is suitable as the starting time t_0.

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[5] H. Watanabe, T. Totani, and T. Yoshizaki, *Inorg. Chem.*, **4**, 657 (1965).

[6] H. Watanabe, T. Totani, T. Nakagawa, and M. Kubo, *Spectrochim. Acta*, **16**, 1076 (1960).

(4) **Effects of Added Substances on Rates in Aqueous Dioxane.**—The rate of hydrolysis was increased by the addition of acids, amines, and lithium hydroxide. The effects of various substances on the hydrolysis of B-tris(phenylethynyl)borazine are shown in Table II. These data demonstrate linear relationships between the observed rate constants, k_{obsd}, and the concentrations of the catalysts; *i.e.*, the reaction is first order with respect to the catalyst concentration. Lithium hydroxide markedly affects k_{obsd}, and its concentration cannot accurately be determined owing to its low concentration in the reaction having a rate observable with the present equipment.

TABLE II

EFFECTS OF CATALYSTS ON THE RATE CONSTANT k_{obsd} IN AQUEOUS DIOXANE

Solvent, vol % of dioxane	Catalyst	Concn of catalyst × 10^3, M	k_{obsd} × 10^4, sec^{-1}	Temp, °C
90	HCl	0.0	0.4	24.2
		5.0	22.5	
		20.0	88.3	
		39.9	169	
		59.9	244	
90	$N(C_2H_5)_3$	0.0	0.4	16.0
		7.3	20.2	
		20.4	54.8	
		35.6	92.6	
75	HCl	0.0	1.0	29.9
		7.1	109	
		13.5	189	
		18.9	255	
		27.0	352	
60	HCl	0.0	1.4	20.0
		2.6	61.5	
		7.1	156	
90	LiOH	0.0	0.4	24
		0.358	35.2	
		0.402	93.3	
		0.442	142	

(5) **Salt and Common-Ion Effect on Acid- and Base-Catalyzed Hydrolysis Rate.**—No significant salt effect was observed for the hydrolysis in neutral aqueous dioxane up to 0.05 M LiCl and $(C_2H_5)_3N \cdot HCl$. However, the addition of lithium chloride retarded the hydrolysis rate in hydrochloric acid catalyzed hydrolysis to a slight extent whereas triethylamine hydrochloride had no effect on triethylamine-catalyzed hydrolysis, as summarized in Table III.

TABLE III

SALT AND COMMON-ION EFFECTS ON k_{obsd} FOR HYDROLYSIS OF $H_3N_3B_3(C{\equiv}CC_6H_5)_3$ IN AQUEOUS DIOXANE[a]

Catalyst	concn × 10^5, M	Added subst	concn × 10^5, M	k_{obsd} × 10^4, sec^{-1}	Solvent $C_4H_8O_2$–H_2O vol %	Temp, °C
HCl	4990		0	209	90–10	24.2
HCl	4990	LiCl	5080	168	90–10	24.2
HCl	3860		0	259	80–20	24.9
HCl	3860	LiCl	3860	235	80–20	24.9
HCl	550		0	183	60–40	25.5
HCl	550	LiCl	560	176	60–40	25.5
TEA	506		0	235	60–40	29.9
TEA	506	TEAH	515	232	60–40	29.9
TEA	506	TEAH	1030	225	60–40	29.9

[a] TEA and TEAH mean triethylamine and triethylamine hydrochloride, respectively.

(6) **The Effect of Solvent Composition.**—An increase in the water content of the solvent causes an increase in the rate of acid- as well as amine-catalyzed hydrolysis. The value of k_{obsd} varied with the composition over a wide range and could not be determined at one catalyst concentration with the present technique. In order to overcome this difficulty, the rate constants k_{obsd} were measured at various concentrations of catalyst suitable for the measurements and divided by the catalyst concentration in order to compare them on the same scale. Here a linear correlation is assumed between the analytical concentration of catalyst and k_{obsd} in the range examined on the basis of the results in Figure 2. The results are shown in Table IV.

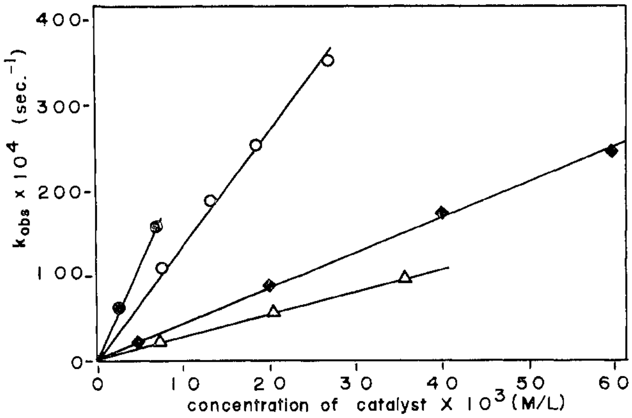

Figure 2.—Variation of the hydrolysis rate of $H_3B_3N_3(C{\equiv}CC_6H_5)_3$ with catalyst concentration: ◆, in 90% aqueous dioxane catalyzed by HCl at 24.2°; △, 90% $(C_2H_5)_3N$, 16.0°; ○, 75% HCl, 29.9°; ●, 60% HCl, 20.0°.

TABLE IV

SOLVENT COMPOSITION DEPENDENCE OF k_{obsd} FOR HYDROLYSIS OF $H_3N_3B_3(C{\equiv}CC_6H_5)_3$ IN ACIDIC AQUEOUS DIOXANE[a]

Solvent dioxane–H_2O vol %	Temp, °C	k_{obsd}/$[HCl]_{anal}$,[a] sec^{-1} M^{-1}	$10^5[HCl]_{anal}$,[a] M
60–40	30.3	4.35	690
75.0–25.0	29.9	1.54	710
80.0–20.0	30.4	0.99	1,960
90.0–10.0	29.0	0.52	12,000

[a] Brackets with suffix "anal" represent analytical concentration of the compound therein.

(7) **The Comparison of the Rate of Uv Absorption Disappearance with That of Amine Appearance.**—The rate of appearance of the amine produced by the hydrolysis of borazine was determined and compared with that of the disappearance in the ultraviolet absorption. The reaction solution was prepared in a thermostated volumetric flask by mixing an appropriate volume of a thermostated standard solution of hydrochloric acid with that of the borazine in 60% aqueous dioxane. The resulting initial concentrations were 400 × 10^{-5} M hydrochloric acid and 20 × 10^{-5} M B-tris(phenylethynyl)-N-triphenylborazine. The absorption and the amine contents in the reacting solution were determined at appropriate intervals. The produced amine was determined as follows. One part of the sample was diluted with five parts of water to deposit the unreacted starting material. After filtration, 1 ml of filtrate was mixed with 5 ml of *p*-dimethylaminobenzaldehyde solution in alcohol (3 g of crystals in 100 ml), and the optical density of the resulting solution was measured at 441 mμ to determine the amine produced. A good agreement was obtained between the rate of decrease of the absorption and that of the borazine concentration calculated from the amine appearance.

(8) **Complex Formations between the Sample and Catalyst.** (a) **Hydrochloric Acid.**—If a complex is formed between hydrochloric acid and borazine, the electric conductivity may be expected to be reduced. Measurements were made of the electric conductivities of the 66% aqueous dioxane solutions containing

TABLE V

ACTIVATION PARAMETERS FOR CATALYZED HYDROLYSIS OF BORAZINE DERIVATIVES $R'_3N_3B_3R_3$ IN AQUEOUS DIOXANE

Solvent C_4H_8–H_2O vol %	Substituent		HCl catalyzed			Amine catalyzed		
	R′	R	HCl concn × 10^5, *M*	$\Delta E^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu	Amine concn × 10^5, *M*	$\Delta E^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
80–20	C_6H_5	CH_3	28,000	10.1	−34.8	907[a]	12.6[a]	−19.3[a]
80–20	C_6H_5	H	116	9.4	−22.8		($k_{obsd} \approx 0$)	
80–20	C_6H_5	$C{\equiv}CC_6H_5$	8,410	10.4	−30.4	4700	8.7	−34.5
80–20	C_6H_5	$C{\equiv}CCH_3$	47,500	10.6	−32.2			
80–20	H	$C{\equiv}CC_6H_5$	3,360	12.0	−19.1			
80–20	H	$C{\equiv}CC_6H_5$	1,960	12.0	−19.1	1950	10.3	−24.1
60–40	H	$C{\equiv}CC_6H_5$	260	10.7	−20.3	368	9.0	−26.3
60–40	H	$C{\equiv}CC_6H_5$	690	10.8	−19.9	587	9.0	−26.3

[a] Lithium hydroxide catalyzed hydrolysis.

TABLE VI

COMPARISON OF HYDROLYSIS RATES OF BORAZINE DERIVATIVES IN 80 VOL % DIOXANE–20 VOL % WATER

Substituent		$10^5[HCl]_{anal}$, *M*	Temp, °C	$k_{obsd}/[HCl]_{anal}$, $sec^{-1}\ M^{-1}$	$10^5[(C_2H_5)_3N]_{anal}$, *M*	Temp, °C	$k_{obsd}/[(C_2H_5)_3N]_{anal}$, $sec^{-1}\ M^{-1}$
R′	R						
C_6H_5	CH_3	28,000	9.3	2.24×10^{-3}	Up to 1 *M*	8.7	~0
C_6H_5	H	116	9.4	3.34	Up to 1 *M*	8.7	~0
C_6H_5	$C{\equiv}CCH_3$	47,500	7.9	3.18×10^{-3}	10,200	8.6	2.64×10^{-3}
C_6H_5	$C{\equiv}CC_6H_5$	8,410	8.9	1.29×10^{-2}	4,700	9.7	3.24×10^{-2}
H	$C{\equiv}CC_6H_5$	3,360	8.1	1.98×10^{-1}	4,000	8.7	3.80×10^{-1}

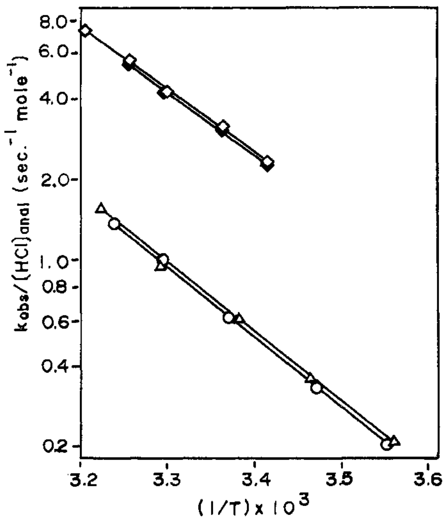

Figure 3.—Variation of hydrolysis rate of $H_3N_3B_3(C{\equiv}CC_6H_5)_3$ with temperature: in 60% aqueous dioxane: -■-■-, $[HCl]_{anal}$ = 690×10^{-5} *M*; -□-□-, $[HCl]_{anal}$ = 260×10^{-5} *M*; in 80% aqueous dioxane: -○-○-, $[HCl]_{anal}$ = 3360×10^{-5} *M*; -△-△-, $[HCl]_{anal}$ = 1960×10^{-5} *M*.

2.6 moles/l. of hydrochloric acid with and without adding 2.6 moles/l. of B-tris(phenylethynyl)-N-triphenylborazine and were then compared with each other. The results were 64.0 μmhos for both cases suggesting an inappreciable formation of the complex.

(b) **Triethylamine.**—Provided a complex is formed between the borazine and triethylamine, the ultraviolet spectrum of the sample solution should undergo a change by the addition of triethylamine. B-Tris(phenylethynyl)borazine afforded the same ultraviolet spectrum in the mixed solvent of 98% dioxane, 1% water, and 1% triethylamine as in pure dioxane.

(9) **The Variation of k_{obsd} with Temperature and Activation Parameters.**—The influence of temperature was investigated for the hydrolyses of several borazine derivatives. Some typical Arrhenius plots concerning the second-order rate constant, $k_{obsd}/[HCl]_{anal}$, are shown in Figure 3. The least-squares treatment of these data led to the activation energies $\Delta E^{\ddagger}$ and the activation entropies $\Delta S^{\ddagger}$ given in Table V, the transmission coefficient being set equal to unity.

(10) **Structural Effects.**—In order to examine the influence of substituents on the reaction rate, the values of $k_{obsd}/[HCl]_{anal}$ and $k_{obsd}/[(C_2H_5)_3N]_{anal}$ which have been obtained in the experiments of the above-mentioned temperature dependence are tabulated in Table VI for ease of comparison. Although the values depend on the catalyst concentrations to some extent, comparisons of the second-order rate constant are warranted.

(11) **Hydrogen Exchange between Borazine and Water.**—In order to examine the exchange reaction of the hydrogen attached to the ring nitrogen, B-tris(phenylethynyl)borazine-d_3 was dissolved in 60% aqueous dioxane without a catalyst and allowed to stand for about 10 min. After removing the solvent at room temperature under reduced pressure, the residue was recrystallized to purify the starting material. The absence of the NH stretching band at 3453 cm^{-1} indicated that the rate of exchange in the NH hydrogen is zero or negligible relative to the rate of solvolysis.

(12) **Hydrogen Isotope Effects.**—The kinetic effect of changing the protons attached to nitrogen to deuterium was studied for the hydrolysis of B-tris(phenylethynyl)borazine. No significant isotope effect was observed for the acid- and base-catalyzed hydrolysis in 60% aqueous dioxane, as shown in Table VII. This is presumably not due to the rapid exchange reaction between the N-trideuterioborazine and water as mentioned above.

TABLE VII

HYDROLYSIS RATES ($k_{obsd} \times 10^4$, SEC^{-1}) OF $H_3N_3B_3(C{\equiv}CC_6H_5)_3$ AND $D_3N_3B_3(C{\equiv}CC_6H_5)_3$ IN 60 VOL % DIOXANE–40 VOL % WATER AT 24.0°

Substrate	HCl catalyzed 170×10^{-5} *M*	$(C_2H_5)_3N$ catalyzed 109×10^{-5} *M*
$H_3N_3B_3(C{\equiv}CC_6H_5)_3$	50.4	34.6
$D_3N_3B_3(C{\equiv}CC_6H_5)_3$	50.0	32.7
Ratio	1.01	1.06

(13) **Solvent Isotope Effect.**—Solvolysis rates in dioxane–D_2O were compared with those in dioxane–H_2O to show distinct solvent isotope effects. Results are presented in Table VIII.

Discussion

In all of the experiments, the disappearance of the absorption $E - E_\infty$ of borazine solution as a function of time closely fits a rate law where the reaction is first

Table VIII

Solvent Deuterium Effects on Hydrolysis Rate ($k_{obsd} \times 10^4$, sec^{-1}) of $H_3N_3B_3(C{\equiv}CC_6H_5)_3$ in 60 Vol % Dioxane–40 Vol % Water at 24.0°[a]

Solvent	HCl, DCl catalyzed	$(C_2H_5)_3N$ catalyzed
Dioxane–H_2O	50.4	34.6
Dioxane–D_2O	23.9	20.3
Ratio	2.11	1.70

[a] The concentration of HCl or DCl was 170×10^{-5} *M*, and that of triethylamine was 109×10^{-5} *M*.

order with respect to $E - E_\infty$, at least over several half-lives. On the other hand, since the six boron–nitrogen bonds must be cleaved before completing its decomposition, the hydrolysis of borazine can be expected to involve several steps and hence intermediates which may not give rise to a first-order reaction. An apparent straight-line fit to a first-order plot may be obtained if the rate constants of the several steps are in a proper ratio. However, it is not probable that a fortuitous ratio of rate constants gives data which fit a first-order plot over the range of solvent composition, temperature, and wavelength studied, though there is some latitude in the determination of the absorption. Another condition giving the apparent straight line is that the reaction involves only one rate-determining step and the concentrations of all intermediates are quite low. The coincidence of the rate of absorption disappearance with that of the hydrolysis product formation also strongly supports the mechanism of one rate-determining step followed by some rapid steps in both acid- and amine-catalyzed hydrolysis.

Thus, among the possible mechanisms consistent with the experiments, types A-1, A-2, and B seem most likely, and other ones are unnecessary to consider. The symbols used in this paper have the following meanings: S_0 = sample borazine; S_1, S_2 = unspecified kinetic intermediate; X, Y = appropriate reactants, *e.g.*, H_3O^+, Cl^-, H_2O, etc.; K_0 = equilibrium constant of the rapid preequilibrium; k = specific rate constant of the rate-determining step; f_x, f_y = activity coefficients of X and Y; brackets signify the concentrations of the materials in them.

Mechanism A-1 is

$$\begin{aligned} &S_0 + X \overset{K_0}{\rightleftharpoons} S_1 && \text{rapid preequilibrium} \\ &S_1 \xrightarrow{k} S_2 && \text{rate-determining step} \\ &S_2 + nH_2O \longrightarrow \text{product} && \text{fast step} \end{aligned}$$

It will be convenient to express k_{obsd} in an explicit form in order to clarify the meaning of k_{obsd} in each mechanism. Mechanism A-1 leads to the well-known equation with neither a steady-state nor an equilibrium approximation

$$k_{obsd} = \frac{K_0 f_x[X]k}{1 + K_0 f_x[X]} \qquad (2)$$

where

$$K_0 \equiv \frac{[S_1]}{[S_0]f_x[X]}$$

If S_1 is much less than S_0, *i.e.*, if $K_0 f_x[X] \equiv [S_1]/[S_0] \ll 1$

$$k_{obsd} = K_0 f_x[X]k \qquad (3)$$

This condition may be satisfied by the experiments described in the section dealing with complex formations between the sample and catalyst.

Mechanism A-2 is

$$\begin{aligned} &S_0 + X \overset{K_0}{\rightleftharpoons} S_1 && \text{rapid preequilibrium} \\ &S_1 + Y \xrightarrow{k} S_2 && \text{rate-determining step} \\ &S_2 + nH_2O \longrightarrow \text{product} && \text{rapid reaction} \end{aligned}$$

which leads to

$$k_{obsd} = \frac{K_0 f_x[X]kf_y[Y]}{1 + K_0 f_x[X]} \qquad (4)$$

where

$$K_0 = \frac{[S_1]}{[S_0]f_x[X]}$$

When $K_0 f_x[X] \equiv [S_1]/[S_0] \ll 1$

$$k_{obsd} = K_0 f_x[X]kf_y[Y] \qquad (5)$$

Mechanism B is

$$\begin{aligned} &S_0 + Y \xrightarrow{k} S_1 && \text{rate-determining step} \\ &S_1 + nH_2O \longrightarrow \text{product} && \text{rapid reaction} \end{aligned}$$

which leads to

$$k_{obsd} = kf_y[Y] \qquad (6)$$

(1) Acid-Catalyzed Hydrolyses.—Molecule and ion species conceivable for X and Y are H_3O^+, Cl^-, H_3O^+-Cl^-, H_2O, and $H_3O^+ + H_3O^+Cl^-$, the last one signifying that H_3O^+ behaves in the same manner as the ion pair in affording catalytic effect. There are 25 sets of X and Y for mechanism A-2, 5 species of X for the A-1, and 5 species of Y for mechanism B. Most of these sets can be excluded by the following simple considerations.

Hydrochloric acid is almost completely ionized[7] to H_3O^+ and Cl^- at the concentration of 550×10^{-5} *M* in 60% aqueous dioxane indicated in Table III. Therefore, the concentration of H_3O^+ would not be significantly affected by the small variation of Cl^- concentration, whereas the ion pair $H_3O^+Cl^-$ of low concentration would increase in proportion to the increase of Cl^- ion concentration, as can easily be derived from the dissociation equilibrium equation. It follows that on adding lithium chloride or Cl^- ion, k_{obsd} should increase according to eq 3 and 5 if X or Y is Cl^- or $H_3O^+Cl^-$. The results in Table III indicate that k_{obsd} is independent of lithium chloride concentration and exclude sets involving Cl^- or $H_3O^+Cl^-$ as X or Y in mechanisms A-1, A-2, and B.

Some other sets may be ruled out by considering the relations between k_{obsd} and analytical hydrochloric acid concentration, $[HCl]_{anal}$. Since hydrochloric acid is almost completely dissociated in 60% aqueous dioxane, H_3O^+ concentration can be equated to $[HCl]_{anal}$. Then, with the set $X = H_3O^+ + H_3O^+Cl^-$ and Y =

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[7] H. P. Marshall and E. Grunwald, *J. Chem. Phys.*, **21**, 2143 (1953).

H_3O^+ in mechanism A-2, for example, we can rewrite eq 5 as

$$k_{obsd} = K_0\{f[H_3O^+] + [H_3O^+Cl^-]\}kf[H_3O^+] = K_0kf^2[HCl]_{anal}^2$$

where f is the activity coefficient for H_3O^+. That is, the hydrolysis should be second order with respect to $[HCl]_{anal}$, and this consequence is opposed to the results of the curves in Figure 2. Similar discussions apply to the following cases to exclude them: $X = Y = H_3O^+ + H_3O^+Cl^-$; $X = H_3O^+$, $Y = H_3O^+ + H_3O^+Cl^-$; and $X = Y = H_3O^+$.

In 90% aqueous dioxane, hydrochloric acid[7] is present mostly in the form of the ion pair $H_3O^+Cl^-$ in contrast to the 60% aqueous dioxane, and $[H_3O^+Cl^-]$ may be set equal to $[HCl]_{anal}$. By taking $[H_3O^+] \approx [Cl^-]$

$$f'[H_3O^+] = \sqrt{K[H_3O^+Cl^-]} \approx \sqrt{K[HCl]_{anal}}$$

where f' is the average activity coefficient for H_3O^+ and Cl^-. Then, it can readily be shown that for the set $X = H_3O^+$ and $Y = H_2O$ in mechanism A-2, k_{obsd} is related to $[HCl]_{anal}$ through the formula

$$k_{obsd} = K_0f'[H_3O^+]k[H_2O] = K_0k[H_2O]\sqrt{K[HCl]_{anal}}$$

This relation implies that the kinetic order is $^1/_2$ in $[HCl]_{anal}$ and is in discord with the results in Figure 2. Similar discussions can exclude the other three sets—$X = H_2O$ and $Y = H_3O^+$ in mechanism A-2, $X = H_3O^+$ in mechanism A-1, and $Y = H_3O^+$ in mechanism B.

One of the sets consistent with the above-mentioned experimental results is $X = H_2O$ and $Y = H_3O^+ + H_3O^+Cl^-$ of mechanism A-2. The complex formation between water and borazine could not be detected spectroscopically suggesting that the coordinated bond is extremely weak if present or the concentration of the complex is extremely low. This fact implies that the complex can be regarded as a kind of transient structure on the way from the initial to the transition state on the reaction coordinate. There is little point in setting up a distinction between mechanism A-2 involving a small amount of (or weak) complex formation and that with preequilibrium missing, *i.e.*, mechanism B, in which $Y = H_3O^+ + H_3O^+Cl^-$. The latter mechanism will be referred to later.

The following three sets fit the above-mentioned experimental results: $X = H_3O^+ + H_3O^+Cl^-$ and $Y = H_2O$ of mechanism A-2; $X = H_3O^+ + H_3O^+Cl^-$ of mechanism A-1; and $Y = H_3O^+ + H_3O^+Cl^-$ of mechanism B. These mechanisms will be examined by testing the deuterium isotope effect to deduce the most probable mechanism.

Deuterium Isotope Effect.—Let upper suffixes H and D represent the quantities in the normal aqueous dioxane solution and those in deuterium oxide–dioxane mixed solvent, respectively. Then the ratio k^H_{obsd}/k^D_{obsd} in the solvent of the same composition becomes

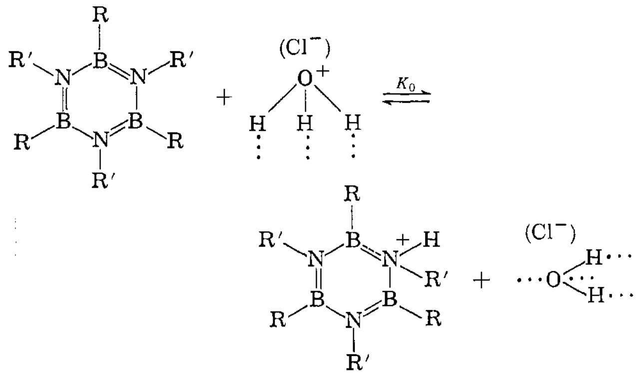
$$k^H_{obsd}/k^D_{obsd} = (K^H_0/K^D_0)(k^H/k^D)$$

for mechanisms A-1 and A-2 or

$$k^H_{obsd}/k^D_{obsd} = k^H/k^D$$

for mechanism B.

First, in order to estimate the solvent deuterium isotope effect on the preequilibrium constant K_0 in mechanisms A-1 and A-2, the following models were assumed for the initial and final states



where the dotted lines indicate hydrogen bonds donated to and accepted from other solvent molecules. The isotope effects were calculated using the method proposed by Bunton and Shiner,[8] in which the O–H and N–H bending frequencies[9] were reasonably assumed to be about 1600 cm^{-1} both in the initial and final state, thus leaving only the stretching vibrations to be taken into account. The O–H stretching frequencies[10] in H_2O and H_3O^+ are taken as 3400 and 2900 cm^{-1}, respectively, and the frequency of the hydrogen bonded to the ring nitrogen as 3263 cm^{-1} which is the average value of NH stretching frequencies of 1,3,5-trimethylcycloborazane,[11] 3278 and 3247 cm^{-1}. The isotope effect on the preequilibrium is then calculated as $K^H_0/K^D_0 = \text{antilog}\,[(\nu_H - \nu_{H'})/12.53T] = 0.43$. Second, in the rate-determining step, the reaction is assumed in mechanism A-2 to proceed through a transition state where a water molecule attacks the boron atom next to the ammonium ion formed in the preequilibrium step. The change in OH stretching frequency for this process is then nearly zero, leading to no isotope effect on k. Thus, the total isotope effect is calculated as 0.43. In the case of mechanism A-1, the N–H stretching frequency of the intermediate complex can reasonably be assumed to be maintained almost unchanged during its monomolecular decomposition process, and the same value of the isotope effect 0.43 is again obtained. Varying the N–H stretching frequencies over conceivable ranges, we made similar calculations to find a trend opposite to the observed value, 2.11, and ruled out the last mechanisms A-1 and A-2.

The exclusion can receive further support from the following consideration on the acidity function,[12,13] a measure of proton-donating power of the solvent. The present mechanism, therefore, requests that the intermediate complex is formed in proportion to the

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(8) C. A. Bunton and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **83**, 42 (1961).

(9) R. M. Silberstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

(10) M. Falk and P. A. Giguère, *Can. J. Chem.*, **35**, 1195 (1957).

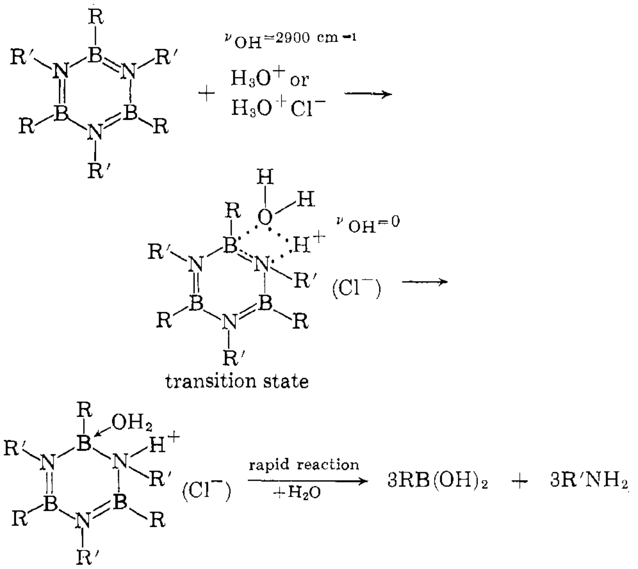
(11) D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **85**, 395 (1963).

(12) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter IX.

(13) L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932)

proton-donating power, *i.e.*, that $-\log k_{\text{obsd}}$ varies in proportion to the Hammett acidity function H_0. According to Braude,[14] the Hammett acidity function at a constant hydrochloric acid concentration varies through a minimum value at about 45 mole %, *i.e.*, about 80 vol % of dioxane, with increasing water content in the dioxane–water mixed solvent. Thus the rate constant k_{obsd} may be expected to vary with the solvent composition at a constant hydrochloric acid concentration through the minimum value at about 80 vol %. This expectation is again opposed to the results in Table IV, where k_{obsd} increases monotonically with the water content in the solvent. An example to show the minimum k_{obsd} value at about 80 vol % will be presented in a subsequent paper[15] dealing with the hydrolysis of tris(dialkylboryl-2-pyridylamino)borane. Thus none of the sets of X and Y for mechanisms A-2 and A-1 can explain all of the experimental results as mentioned above, leading to the conclusion that the hydrolysis mechanism does not include any preequilibrium step.

The mechanism consistent with all of the experimental results is $Y = H_3O^+ + H_3O^+Cl^-$ of mechanism B. The sum of $[H_3O^+Cl^-]$ and $[H_3O^+]$ is nearly equal to $[HCl]_{\text{anal}}$ and independent of the solvent composition as well as of the concentration of Cl^- ion added to the solution. Thus, assuming that H_3O^+ and $H_3O^+Cl^-$ may donate a proton with the same ease, one can explain the experimental results by the mechanism involving the concerted hydronium ion transfer



The stretching frequency of the proton moving from water to borazine may be set equal to zero at the stage of this transition state, as usual.[8] The frequency difference between the initial and the transition state gives the isotope effect,[16] $k^{\text{H}}_{\text{obsd}}/k^{\text{D}}_{\text{obsd}}$, of 3.2 in good agreement with the experimental value 2.11 in Table VIII, which supports mechanism B where $Y = H_3O^+ + H_3O^+Cl^-$.

(2) **Amine-Catalyzed Hydrolyses.**—The conceivable molecule or ion species for X and Y in mechanisms A-1, A-2, and B are H_2O, $N(C_2H_5)_3$, OH^-, $N(C_2H_5)_3H^+$, $N(C_2H_5)_3H^{\delta+}\cdot OH^{\delta-}$, and $N(C_2H_5)_3H^{\delta+}\cdot OH^{\delta-} + OH^-$, the last one signifying that the effect of the two species is similar. Most of these combinations can be excluded by a simple consideration of the facts that the reaction is first order with respect to borazine as well as $[N(C_2H_5)_3]_{\text{anal}}$. Addition of lithium chloride does not increase the hydrolysis rate, whereas lithium hydroxide increases, as shown in Table II, the slope $dk_{\text{obsd}}/d[\text{LiOH}]_{\text{anal}}$ being much larger than that of $dk_{\text{obsd}}/d[N(C_2H_5)_3]_{\text{anal}}$. This fact means that OH^- ion is much more effective in accelerating the hydrolysis of borazine and cannot be taken to afford an effect equivalent to $N(C_2H_5)_3H^{\delta+}\cdot OH^-$; *i.e.*, $(C_2H_5)_3NH^{\delta+}\cdot OH^{\delta-} + OH^-$ must be excluded.

The addition of triethylamine hydrochloride did not cause any significant effect on the rate of hydrolysis in water or any common-ion effect on the hydrolyses catalyzed by triethylamine. The ionization constant K of triethylamine is of the order of 10^{-4} in aqueous solution and is expected to be greatly decreased in aqueous dioxane solutions used in the present experiments. The concentration of OH^- ion is much lower than that of triethylamine hydrate, and OH^- catalyzes to an inappreciable extent in the amine-catalyzed hydrolysis experiments. Therefore, the increase of triethylamine hydrochloride concentration must decrease the hydrolysis rate in proportion to $[N(C_2H_5)_3\cdot HCl]_{\text{anal}}^{-1/2}$, if OH^- plays an important role in the mechanisms, except A-2 with $X = Y = OH^-$ where the reaction rate requires a proportional change with $1/[N(C_2H_5)_3\cdot HCl]_{\text{anal}}$. These consequences are all inconsistent with the experimental results and therefore the OH^- ion species is excluded.

The absence of the isotope effect in Table VII excludes the mechanisms involving addition onto the ring nitrogen in the preequilibrium step.

The mechanisms compatible with the above-mentioned results and discussions are: (a) $X = H_2O$ and $Y = N(C_2H_5)_3$ or its hydrate for A-2; (b) $X = N(C_2H_5)_3$ or its hydrate and $Y = H_2O$ for A-2; (c) $X = N(C_2H_5)_3$ hydrate for A-1; (d) $Y = N(C_2H_5)_3$ hydrate for B. Although conclusive evidence cannot be found to exclude some of them, it is not plausible to form complex or adduct in the preliminary equilibrium step. No change could be observed in the ultraviolet spectra on adding triethylamine to borazine solution as mentioned in experiment 8. Therefore, the most probable mechanism is (d); *i.e.*, triethylamine hydrate attacks borazine in one step. This mechanism may explain the solvent (deuterium) isotope effect by assuming a proper transition state and proper hydrogen stretching frequencies. Two probable models may be expressed as follows: the first (a) attacking through the amine nitrogen and the second (b) through the water molecule associated with triethyl-

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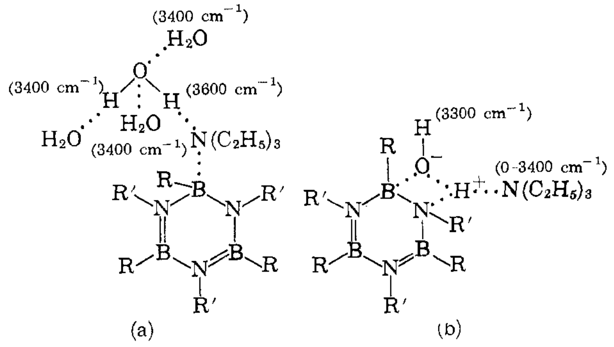
[14] E. A. Braude, *J. Chem. Soc.*, 1971, 1976 (1948).

[15] T. Yoshizaki, H. Watanabe, and T. Nakagawa, the second paper of this series, submitted for publication.

[16] C. A. Bunton and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **83**, 3207, 3214 (1961).

amine. The estimated stretching frequencies are indicated in parentheses



transition state

In the course of formation of the activated complex (a), the O–H···N stretching frequency may be assumed to increase from 3400 cm^{-1} for the initial state up to 3600 cm^{-1}. Calculations of $k^{H}{}_{obsd}/k^{D}{}_{obsd}$ similar to that of Bunton and Shiner[16] give values less than unity contrary to the experimental value of 1.7. On the other hand, the activated complex of model (b) gives the isotope effect ranging from 1.0 to 10 depending on the OH stretching frequency assumed.

Thus, the amine-catalyzed hydrolysis is concluded to proceed through a route where the hydrated amine attacks the borazine molecule in one step through a transition state of model (b).

Isotope Effects.—The relatively small solvent isotope effects (2.11 and 1.70) in acid- and amine-catalyzed hydrolyses suggest that the O–H stretching vibration is not greatly altered in the transition state and also that hydride-transfer mechanisms are involved in the rate-determining steps.[17] This suggestion is consistent with the mechanisms proposed above.

The small effects of isotopic substitution on nitrogen ($k^{NH}{}_{obsd}/k^{ND}{}_{obsd}$ = 1.01 in acid-catalyzed hydrolysis and 1.07 in amine-catalyzed hydrolysis) suggest that these may be secondary isotope effects and arise from the differences between hydrogen vibrational frequencies in the initial and the transition state.

Activation Parameters.—Relatively small activation energies of about 10 kcal/mole were obtained for various borazine derivatives as shown in Table V, scattering over a small range of values. The magnitude is considerably different from those reported for amine boranes,[2,3] 25.7 kcal/mole. The influence of substituents on the Arrhenius activation energies is considerably small as can be seen in Table V, whereas that on the rate constant is larger, leading to larger differences in the preexponential factor A. In acid-catalyzed hydrolysis, the ratio of $k_{obsd}/[HCl]_{anal}$ for N-triphenylborazine to that for N-triphenyl-B-trimethylborazine is about 1500, only $^1/_{500}$ of which can be ascribed to the difference in activation energy. The remaining 500 must arise from the frequency factor. The difference in the frequency factor may be ascribed to the difference in the steric shielding of the substituents.

The results in Table IV indicate that k_{obsd} increases with an increase in the water content in the reaction solvent. The proposed mechanisms request that k_{obsd} is independent of the water concentration in the solvent and appear to be inconsistent with the change in k_{obsd}. This apparent inconsistency can be explained by the solvent effect on the activation energy. For instance, calculations show that the acid-catalyzed hydrolysis of B-trisphenylethynylborazine proceeds in 60% aqueous dioxane 8 times as rapidly as in 80% aqueous dioxane, and that of the amine-catalyzed hydrolysis is 15 times as rapid. The observed increments are within these factors.

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(17) F. Hawthorne and E. S. Lewis, *J. Am. Chem. Soc.*, **80**, 4296 (1958).