

CONTRIBUTION FROM THE SHIONOGI RESEARCH LABORATORY,
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Butanolysis of B-Tris(phenylethynyl)borazine in 1-Butanol-Dioxane Mixed Solvent

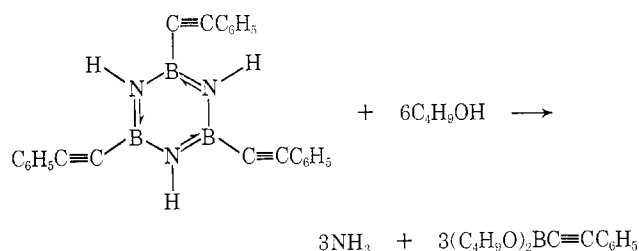
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Received January 22, 1968

The alcoholysis of B-tris(phenylethynyl)borazine was investigated in 1-butanol-dioxane mixed solvent in the presence of triethylamine as catalyst. The reaction was followed spectrophotometrically and was found to be first order with respect to the sample as well as the amine concentration. Distinct features were found in the activation parameters, the Arrhenius activation energy being 4.79 kcal/mol and the activation entropy being -45.3 eu. Solvent isotope effect and solvent composition effect on k_{obsd} were also examined. Analyses of these data led to the conclusion that butanol hydrogen-bonded to an amine or to a triethylammonium butylate ion pair attacks the borazine ring in the rate-determining step.

Introduction

Solvolytic or hydrolytic stability has been referred to in many preparative works of boron-containing compounds because they are usually unstable to solvolysis. However, it is only in recent years that detailed studies on the kinetics and mechanisms of hydrolysis reactions of boron hydride derivatives¹ and boron-nitrogen compounds² have been described. In a previous paper of this series,³ the kinetics and the mechanism of catalytic hydrolysis of borazine derivatives have been investigated leading to the findings that the amine-catalyzed hydrolysis proceeds through a one-step bimolecular mechanism in which a water molecule hydrogen-bonded to a triethylamine molecule, $\text{N}(\text{C}_2\text{H}_5)_3\text{H}^{\delta+}\cdot\text{OH}^{\delta-}$, attacks the borazine ring. It has been recognized that some borazines are solvolyzed by alcohols. The butanolysis of B-tris(phenylethynyl)borazine was established by analyzing the products to proceed according to the stoichiometry



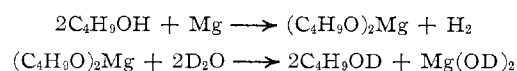
The present paper deals with the catalytic solvolysis of B-tris(phenylethynyl)borazine in a 1-butanol-dioxane mixed solvent in the presence of triethylamine to compare the kinetic data with those of the hydrolysis and to elucidate the mechanism.

Experimental Section and Results

Kinetic Measurements.—The rates of solvolysis were measured spectrophotometrically using the techniques and equipment described elsewhere.³

Materials.—The preparation of tris(phenylethynyl)borazine and the purification of solvents were performed in the same way as previously reported,³ except for butanol and butanol-*d*. 1-Butanol was purified by refluxing with magnesium butylate for

3 hr followed by distillation. 1-Butanol-*d* was prepared from the purified 1-butanol by the reaction



Although the excess butanol was removed by distillation under reduced pressure with application of heat, the deuterium content in butanol did not exceed 90% as determined by infrared intensity measurement.

Kinetic Order.—The amine concentration was several hundred times as large as the sample concentration in all experiments so that the change of concentration during the experiment was negligible. The extinction ($-\log T$) observed at time t and infinity is denoted by E and E_∞ , respectively. In all cases, plots of $\log(E - E_\infty)$ vs. time were linear over several half-lives; thus first-order kinetics were obeyed. The quotient $-[d(E - E_\infty)/dt]/(E - E_\infty)$ is defined as k_{obsd} .

Effect of Added Amine on k_{obsd} .—The rate constant k_{obsd} increased in proportion to the amine concentration, with a slope of $0.24 \text{ sec}^{-1} \text{ mol}^{-1} = k_{\text{obsd}}/[(\text{C}_2\text{H}_5)_3\text{N}]$ at 23.4° in 80 vol % dioxane-20 vol % butanol mixed solvent. (This solvent will be abbreviated as 20% butanol throughout this paper.) Without triethylamine, the rate was too slow to measure, and on adding the amine of 0.0161, 0.0322, and 0.0483 *M* concentration, k_{obsd} was increased to 0.00404, 0.00778, and 0.0116 sec^{-1} , respectively.

Effect of Solvent Composition on k_{obsd} .—The rate constant k_{obsd} was measured as a function of the solvent composition in the presence of 0.0343 *M* triethylamine. The results are shown in Table I.

TABLE I
EFFECT OF SOLVENT COMPOSITION ON k_{obsd} AT 24.0°

Concn of butanol		$10^4 k_{\text{obsd}}, \text{sec}^{-1}$
<i>M</i>	Vol %	
0.00	0	2.4
0.55	5	20.4
1.09	10	36.5
2.18	20	78.4
3.27	30	142

Solvent Isotope Effect on k_{obsd} .—Since the isotopic purity of butanol-*d* was about 90%, the value of k_{obsd} for pure butanol-*d* was obtained by extrapolating the values obtained in partially deuterated butanol-dioxane mixed solvents. The values of k_{obsd} were determined as 35.2, 30.9, 29.5, and $28.2 \times 10^{-4} \text{ sec}^{-1}$ for solvolyses at 23.4° catalyzed by 0.0155 *M* triethylamine in 20% butanol having protic deuterium contents of 0, 58, 72, and 87 mol %, respectively. The extrapolation of these data to 100 mol % deuterium content gave $27.1 \times 10^{-4} \text{ sec}^{-1}$ for k_{obsd} , leading to the isotope effect $k^{\text{H}}_{\text{obsd}}/k^{\text{D}}_{\text{obsd}} = 35.2/27.1 = 1.30$.

Dependence of Rate on Temperature.—The rate constant k_{obsd} was determined in 20% butanol in the presence of 0.0179 *M* triethylamine at 9.6, 17.2, 24.7, and 31.7° to examine the

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

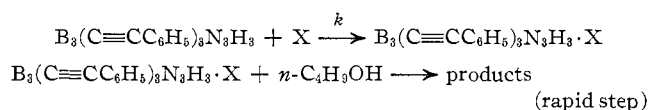
(2) M. F. Hawthorne and E. S. Lewis, *J. Am. Chem. Soc.*, **80**, 4296 (1958); G. E. Ryschkewitsch, *ibid.*, **82**, 3290 (1960); H. C. Kelly, F. R. Marchelli, and M. B. Giusto, *Inorg. Chem.*, **3**, 431 (1964).

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

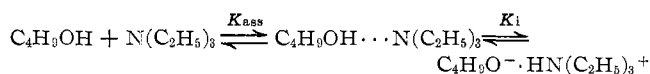
dependence of rate on temperature. The rates were 26.4, 33.2, 42.9, and $53.2 \times 10^{-4} \text{ sec}^{-1}$, respectively. The logarithm of the rate constant, $\log k_{\text{obsd}}$, increases in inverse proportion to temperature. The least-squares treatment of the data led to the activation energy ΔE^\ddagger of 4.79 kcal/mol for the solvolysis in 20% butanol catalyzed by 0.0179 *M* triethylamine. By setting the transmission coefficient equal to unity, the data gave an extremely large value of activation entropy, -45.3 eu , for the solvolysis at 300°K.

Discussion

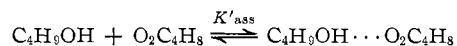
All of the data on solvolysis rate closely fit a rate law where the reaction is first order with respect to $E - E_{\infty}$, *i.e.*, borazine, as well as amine concentration, and this extends over at least 3 half-lives. No index of complex formation was found between borazine and amine under the conditions as mentioned above. These results may permit us to confine the present considerations to the following three types of mechanisms as discussed in more detail in a previous paper:³ (B-1) composed of a rapid preequilibrium step and a unimolecular rate-determining step followed by rapid reaction steps; (B-2) composed of a rapid preequilibrium step and a bimolecular rate-determining step followed by rapid reaction steps; and (B) composed of a rate-determining step followed by rapid reaction steps. Of these three types, qualitative similarities between the hydrolysis and alcoholysis in experimental results as well as in reagents suggest that alcoholysis proceeds through the B mechanism, although conclusive evidence for a single mechanism cannot be expected to be drawn from the present data alone.



The rate equation for this mechanism has already been given elsewhere,³ and it is greatly simplified for the present case because the activity coefficients of all of the molecular species can be set nearly equal to unity. Molecular species conceivable for X are $\text{N}(\text{C}_2\text{H}_5)_3$, $\text{C}_4\text{H}_9\text{OH} \cdots \text{N}(\text{C}_2\text{H}_5)_3$, and $\text{C}_4\text{H}_9\text{O}^- \cdots \text{HN}(\text{C}_2\text{H}_5)_3^+$, among which equilibria are established



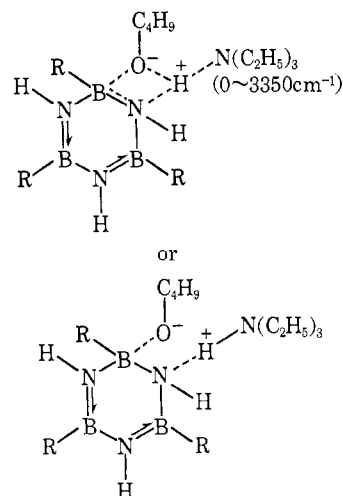
Butanol will also associate with dioxane through a hydrogen bond



The values of the equilibrium constants, K_{ass} , K_1 , and K'_{ass} , are not available at the moment but can be estimated to be in a range of 1–10 M^{-1} from the data for methanol–triethylamine in carbon tetrachloride⁴ ($K_{\text{ass}} = 6.4 M^{-1}$ at 20°) and for 1-heptanol–triethylamine in cyclohexane⁵ ($K_{\text{ass}} = 3.5 M^{-1}$ at 25°). The equilibrium constant for the butanol–dioxane system may be estimated to be of the same order as that for butanol–triethylamine from the same O–H stretching frequency

in both of the systems,³ water–dioxane and water–triethylamine. Assuming a set of proper values within the above-mentioned range for the two equilibrium constants, *i.e.*, $K_{\text{ass}} = 1$ and $K'_{\text{ass}} = 2$, the concentrations of $\text{C}_4\text{H}_9\text{OH} \cdots \text{N}(\text{C}_2\text{H}_5)_3$ and/or $\text{C}_4\text{H}_9\text{O}^- \cdots \text{HN}(\text{C}_2\text{H}_5)_3^+$ are calculated to increase along an upper concave curve in concert with the curve obtained by plotting k_{obsd} *vs.* butanol mole per cent. The coincidence between the two curves supports that alcoholysis proceeds through the B mechanism where X is $\text{C}_4\text{H}_9\text{OH} \cdots \text{N}(\text{C}_2\text{H}_5)_3$ and/or the ion pair. The effect of the dielectric constant of solvent must be taken into account, though no discussion can be made here, except that the effect of greater butanol concentration is to increase the extent of the ion pair or to assist the charge separation in the transition state.

This mechanism can explain the solvent deuterium isotope effect by assuming a proper transition state similar to that assumed for its hydrolysis.³ The probable models may be expressed as



A dilute solution of 1-butanol in triethylamine gives rise to a broad infrared absorption band attributable to OH stretching vibration at 3350 cm^{-1} where pure liquid 1-butanol shows an OH band. This fact implies, after the method of Bunton and Shiner,⁶ that the solvent isotope effect on K_{ass} is extremely small and the concentration of hydrogen-bonded amine–butanol is the same in both of the systems, butanol and butanol-*d*. Then the isotope effect is determined by the rate-determining step. The above-mentioned activated complex can take an OH or NH stretching frequency ranging from 0 to 3350 cm^{-1} , and hence calculations of $k^{\text{H}}_{\text{obsd}}/k^{\text{D}}_{\text{obsd}}$ similar to that of Bunton and Shiner⁶ give values ranging from 8 to 1 depending on the OH or NH frequency assumed. If the coordination of the oxygen atom of $\text{C}_4\text{H}_9\text{OH} \cdots \text{N}(\text{C}_2\text{H}_5)_3$ occurs first, the OH stretching frequency would not be greatly altered in the transition state and would give a small isotope effect consistent with the experimental result, 1.30.

The activation energy of 4.79 kcal/mol is extremely

(4) T. Gramstad, *Acta Chem. Scand.*, **16**, 807 (1962).

(5) R. L. Denyer, A. Gilchrist, J. A. Pegg, J. Smith, L. E. Sutton, and T. E. Tomlinson, *J. Chem. Soc.*, 3889 (1955).

(6) C. A. Bunton and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **83**, 42, 3207, 3214 (1961).

small and considerably different from those obtained for the hydrolysis.³ The inductive effect of the butyl group on the negative charge on oxygen can explain the decrease in activation energy as compared with the

value for hydrolysis. The activation entropy, -45.3 eu, is one of the largest negative values ever observed and may be attributed to a great deal of "freezing" of solvent into the transition state.

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Photochemistry of Borazine. Preparation and Characterization of Isotopically Substituted B-Monoaminoborazines¹

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Received December 29, 1967

A photochemical procedure for the preparation of B-monoaminoborazine has been extended to a series of deuterium and ¹⁵N isotopically labeled species. Infrared spectra of H₃N₃B₃H₂NH₂, H₃N₃B₃H₂¹⁵NH₂, and H₃N₃B₃D₂ND₂ have been obtained and frequencies assigned. Proton magnetic resonance spectra of H₃N₃B₃H₂NH₂, H₃N₃B₃H₂¹⁵NH₂, and H₃¹⁵N₃-B₃H₂¹⁵NH₂ have been obtained and discussed in relation to the analogous benzene derivatives.

Introduction

In the extensive literature on borazine chemistry most of the experimental work has been associated with B-trisubstituted or N-trisubstituted derivatives. Very little is known of the structure or chemical properties of the unsymmetrical mono- or disubstituted compounds. We have recently reported a photochemical procedure for the preparation of some B-monosubstituted borazines.³ Subsequently, as reported in this paper, the method has been extended to the preparation of deuterium and ¹⁵N-labeled B-monoaminoborazines suitable for infrared and nmr studies. It was anticipated that nmr studies on an unsymmetrical borazine derivative would reveal substituent effects, not observable in the symmetrical trisubstituted molecules.

Experimental Section

Borazine was prepared from LiBH₄ and NH₄Cl⁴ and the impurity, B₂H₅NH₂, was removed by adding ammonia and forming a nonvolatile adduct. A mixture of borazine and ammonia each at 10 mm pressure was irradiated for 20 min in a reaction vessel of about 1500 ml.³ The product, B-monoaminoborazine, was condensed in a trap at -65° , cooled in a slush bath of chloroform. B-Monoamino-¹⁵N-borazine was prepared starting with 95% ¹⁵NH₃ and borazine-¹⁵N₃ prepared from LiBH₄ and ¹⁵NH₄Cl (95%), and B-monoaminoborazine-*d*₃ was prepared starting with 95% B-trideuterioborazine and 99% ammonia-*d*₃. Since B-trideuterioborazine was prepared by a photochemical method not previously reported in the literature, the procedure will be described here. A mixture containing 75 mm of deuterium gas and 15 mm of borazine was irradiated for 10 min under the same conditions used for the preparation of aminoborazines. The partially deuterated borazine was then condensed with liquid nitrogen in the reaction vessel and the impure deuterium was pumped off. Pure deuterium was then added to the vessel in a

deuterium:borazine ratio of 5:1 and the mixture was again irradiated. This procedure was repeated three times to give a borazine sample over 95% deuterated on the B atom as determined mass spectrometrically. Some borazine is lost in the irradiation process and during the transfer of materials so that usually only about 60% of the original sample of borazine was recovered. Nuclear magnetic resonance spectra indicated the presence of H atoms bound only to nitrogen atoms.

Infrared spectra were obtained on a Perkin-Elmer Model 521 grating spectrophotometer calibrated against indene.⁵ The gas spectra were obtained in a 9-cm gas cell fitted with KBr windows and the spectra of solid films were obtained from samples deposited on a KBr window cooled by liquid nitrogen.³ For the ease of collecting samples for nmr studies, a U-tube trap sealed at the bottom to a long piece of 5-mm o.d. Pyrex tubing was used. Products of the ammonia-borazine reactions were condensed on the lower section of the U tube. When the samples liquefied at room temperature they were then transferred by gravity into the nmr tube. A small amount of a 5:1 CCl₄-TMS mixture was condensed into the tube for the internal standard. The tube was then sealed off at the top and a spectrum was taken at 37° with a Varian Model A-60 analytical nmr spectrometer. The noise level in the spectra obtained in the Pyrex sample tube did not present a serious problem in the analysis.

Results and Discussion

Nuclear Magnetic Resonance Spectra.—Proton nmr spectra of H₃N₃B₃H₂NH₂, H₃N₃B₃H₂¹⁵NH₂, and H₃¹⁵N₃-B₃H₂¹⁵NH₂ are shown in Figure 1. Chemical shifts based on TMS as internal reference are given in Table I. In general only the resonances associated with the H atom bound to nitrogen atoms were sufficiently intense for identification purposes. Spectra of the compound with the normal N isotopic abundances are very broad due to ¹⁴N quadrupole relaxation. Identification of the hydrogen groups was simplified by observing ¹⁵N isotopically substituted species. The intense broad peak at about 1.92 ppm in the normal compound, which splits into a doublet ($J = 79.1$ cps), is attributed to the

(1) Work supported by the Advanced Research Projects Agency and the Army Research Office, Durham, N. C.

(2) National Science Foundation Undergraduate Research Participant, summer 1967.

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