

TABLE VI
INFRARED VIBRATIONAL FREQUENCIES OF METHYLTIN HALIDES IN THE REGION 400-1500 CM.⁻¹: POSITIONS OF BANDS (IN CM.⁻¹)

X =	(CH ₃) ₃ SnX			(CH ₃) ₂ SnX ₂			CH ₃ SnX ₃			(CH ₃) ₄ Sn	
	F k ^a	Cl n	Br l	Cl k	Br k,n	I n	Cl k	Br k,n	I k,n	b	c
..		513m	512m	515s	514s	511m					
555s		545s	543s	567s	563s	547m	540s	539s	527s	524	528
782s		722m	723w	745w	743sh	735sh					
		782s	781s	786s	779s	772s	788s	780s	770s	764	770
					790sh	789sh					
1194m	1200w	1198w	1194w	1204w	1198w	1198w	1204w	1197m	1188m	1190	1198
1216w			1204w								
1412w	1410w	1400w	1400w	1410w	1410w	1404w	1402w	1406w	1402w	1445	1443

^a Nujol mull (n), KBr pressed disc (k) or a liquid film (l) was used in the KBr region. ^b W. F. Edgell and C. H. Ward, *This Journal*, **77**, 6486 (1955). ^c E. R. Lippincott and M. C. Tobin, *ibid.*, **75**, 4141 (1953).

tion near 780 cm.⁻¹ is strong and can be found in all of the methyltin compounds, this vibration is considered characteristic of methyltin compounds. The symmetric deformation vibration of methyl groups attached to silicon and to germanium⁹ produces sharp bands near 1260 and 1230 cm.⁻¹, respectively; the former band has been considered characteristic of all methylsilicon compounds. In the methyltin compounds the band is sometimes weak, but it is helpful for identification.

Another characteristic band, attributable to the asymmetric deformation vibration of the methyl group attached to tin, is hidden in the carboxylates but is found as a weak band, near 1400 cm.⁻¹, in the halides shown in Table VI. Two other weak bands associated with C-H stretching vibration of the CH₃(-Sn) group are found near 3000 cm.⁻¹.

Valuable information is obtained from the spectra of the methyltin compounds in the KBr region. All the compounds shown in Table VI have one or two strong absorptions in the range 500-600 cm.⁻¹. In the trimethyltin and dimethyltin chlorides, bromides and iodides, which all have been known to have a tetrahedral structure,¹⁰ the band near 512 cm.⁻¹ and the band at 540-570 cm.⁻¹ can be assigned as the Sn-C symmetric and asymmetric stretching vibrations, respectively.

(9) M. P. Brown, R. Okawara and E. G. Rochow, submitted to *Spectrochim. Acta*.

(10) H. A. Skinner and A. D. Sutton, *Trans. Faraday Soc.*, **40**, 164 (1944).

Earlier we have shown from the spectra in the NaCl region that trimethyltin formate and dimethyltin diformate are ionic, the spectra being interpreted as due to the superposition of absorptions of the methyltin cation and the formate anion. Since the formate anion shows no bands below 700 cm.⁻¹, the band found in the spectra of the tin formates must be due to the methyltin cation. The spectra of these compounds have only one band in the KBr region, as shown in Fig. 3. If we assume the configuration of the trimethyltin cation to be planar and that of the dimethyltin cation to be linear, then the Sn-C symmetric stretching vibrations are infrared inactive, and we can expect only the Sn-C asymmetric stretching vibration in this region. This assumption is further supported by the frequency of the band.

For the trimethyltin acetate, chloroacetates and propionate the strong absorption found at 552 ± 3 cm.⁻¹ is also assigned to Sn-C vibration, and all other bands can be assigned to the COO deformation vibrations of the acid anion.

Trimethyltin fluoride is found to have only one band at 555 cm.⁻¹ in the KBr region, due to the planar trimethyltin cation. This confirms the conclusion from chemical evidence that this compound is ionic.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA]

Amine Boranes. I. Kinetics of Acid Hydrolysis of Trimethylamine Borane

BY GEORGE E. RYSCHKEWITSCH

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The rates of the reaction of trimethylamineborane with aqueous HCl and with HCl in 20% dioxane-water mixtures have been studied at 0.1 < [H₃O⁺] < 0.6 and in the temperature range 35 to 44°. The reaction is first order with respect to amine borane and with respect to acid concentration and increases with the ionic strength of solution; the experimental results are very well represented by: $d[(CH_3)_3NBH_3]/dt = -k'[(CH_3)_3NBH_3]$; $k' = k[H_3O^+] \exp b[H_3O^+]$; $k = A \exp(-\Delta E/RT)$. The apparent activation energy in either solvent was 25.73 ± 0.13 kcal./mole.

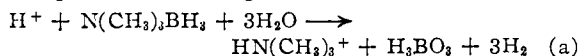
In most compounds containing a boron-hydrogen bond, removal of hydrogen can be achieved by the attack of protonic reagents. The reactivity of such compounds in homogeneous media varies

widely ranging, e.g., from extremely rapid attack of alcohols on some boron hydrides to the extreme resistance of phosphinoboranes even to hot mineral acids. Even though a good deal of qualitative and

semi-quantitative information has been published relatively few papers have dealt with precise studies of reaction kinetics; fewer data yet are available that permit inferences as to reaction mechanism and the relation between structural parameters and reactivity.^{1,2}

The addition compounds of amines with borane, BH_3 , appear to be of particular interest in the investigation of reaction kinetics of the B-H linkage for the following reasons: they are structurally relatively simple, reactivities vary over a wide range, and they are easily accessible experimentally. The present study was undertaken as part of a more comprehensive investigation into the reactivity of the boron-hydrogen bond in borane addition compounds.

Concentration Dependence.—The reaction of trimethylamineborane in acidic solution proceeds to completion according to the over-all equation

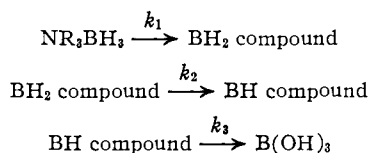


The progress of the reaction can be followed by determining the loss of reducing power of the solution. This method could be expected also to measure any oxidizable intermediates in the system and would give an accurate analysis for amine borane only if the ambient concentrations of reducible intermediates are quite low.

In this investigation reaction with excess potassium iodate in acid solution and back-titration with standard arsenite was used to assay the reducing power of the solution. Plots of $\log(\text{KIO}_3 \text{ used})$ vs. time gave straight lines over the range 2 to 85% reaction at a large excess of acid. The reaction thus gives the appearance of being first order in amine borane.

In reactions of polyfunctional compounds where the functional groups are removed in steps and the analytical method estimates the total remaining, the analytical results reflect directly the loss in starting material only if the second and following reaction steps have much larger specific rates than the first. On the other hand, an apparent straight line fit to a first order plot may be obtained within a given time interval if the rate constants of the several steps are in the proper ratio. In this case the slope would not measure unequivocally the rate of loss of starting material.

Calculated $\log[\text{B-H}]$ vs. time plots were examined for the system



The curves for a number of ratios k_1/k_2 were compared assuming $k_3 \gg k_2$.

It is felt that the excellent fit of the data to a first order plot over the range of half life, ionic strength, temperature and solvent composition studied make the assumption of a fortuitous ratio of rate constants untenable.

(1) S. H. Bauer, *THIS JOURNAL*, **78**, 5775 (1956), gives a summary of B_2H_6 reactions.

(2) M. F. Hawthorne, *ibid.*, **80**, 4296 (1958).

It is thus concluded that the reaction is first order in amine-borane and that the constants derived from the analytical plots correspond to the specific rates of the first step in the protolysis in the solutions in question.³ The observed first order rate constants are listed in Table I and II.

TABLE I
FIRST ORDER RATE CONSTANTS FOR THE PROTOLYSIS IN HCl

[H ⁺] mole/l.	Change with acid strength		
	$k' \times \log e \times 10^4$, aq. HCl	$k' \times \log e \times 10^4$, 20% dioxane	$k' \times \log e \times 10^4$, aq. HCl
0.0984	0.121		
.1503	.194	0.081	0.260
.1972	.265	.111	.361
.2484	.345	.144	.477
.2906	.420	.174	.569
.3960	.619	.260	.856
.4952	.840	.358	
.5862	1.047	.450	

TABLE II
FIRST ORDER RATE CONSTANTS FOR THE PROTOLYSIS IN H_2SO_4 SOLUTION AT 34.98°

[H ₂ SO ₄] mole/l.	$k' \times \log e \times 10^4$, sec. ⁻¹	[H ₂ SO ₄] mole/l.	$k' \times \log e \times 10^4$, sec. ⁻¹
0.0995	0.135	0.3040	0.481
.1405	.202	.4030	.661
.1810	.277	.4970	.886
.2425	.356	.5948	1.167
80% Dioxane by volume			
0.608	0.103	0.994	0.378
.807	.211	1.190	.675

Inspection of the data in Table I and II shows that the first order constants are not proportional to the acid concentration. They do fit an equation of the form

$$k' = k[\text{H}^+] \exp b[\text{H}^+] \quad (1)$$

The exponential concentration term in equation 1 could arise from the change in ionic strength with acid concentration⁴ and a corresponding change in the free energies of reactants and transition state.

Alternately, the data are reproduced, though not quite as well, by an equation of the form

$$k' = k[\text{H}^+](1 + b[\text{H}^+]) \quad (2)$$

Equation 2 could result from two competitive reactions, first order and second order in $[\text{H}^+]$, respectively. Equation 2 also results as a two term series expansion of equation 1.

Temperature Dependence.—The variation of rate with temperature follows the Arrhenius equation $\log k' = \log A' + \Delta E/2.303 RT$, where according to equation 1 $\log A' = \log A + \log[\text{H}^+] + 0.4343 b[\text{H}^+]$. The data in Table III for two acid concentrations in water and in 20% dioxane are

(3)(a) In a typical experiment a least squares treatment gave a standard deviation of 0.0017 on the log scale, corresponding to a 0.4% deviation in the titration data. No trend in the individual deviations was observed. (b) A reaction mixture quenched after 60% loss in reducing power and an amine borane solution of identical reducing strength per ml. were extracted with ether. After evaporation of the solvent both samples gave the same yield of amine borane (65%).

(4) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corporation, New York, N. Y., 1958, eq. 10-4-8.

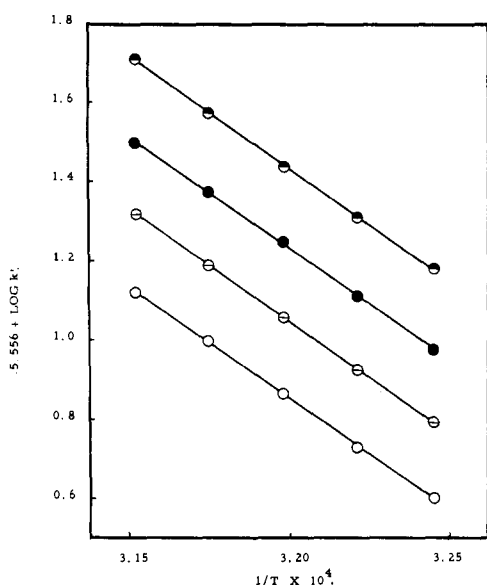


Fig. 1.—Variation of rate with temperature: ●, 0.1972 *M* HCl, H₂O; ○, 0.2906 *M* HCl in water; ○, 0.1972 *M* HCl in 20% dioxane by volume; ⊖, 0.2906 *M* HCl in 20% dioxane by volume.

plotted in Fig. 1. The results of a least squares treatment are given in Table IV. It is seen that the Arrhenius activation energies are the same in all four cases, 25.7 kcal./mole, within a rather small experimental error.

TABLE III

FIRST ORDER RATE CONSTANTS FOR THE PROTOLYSIS IN HCl. TEMPERATURE DEPENDENCE IN WATER AND 20% DIOXANE BY VOLUME

<i>T</i> , °C.	<i>k</i> ' × log <i>e</i> × 10 ⁴ , sec. ⁻¹			
	H ₂ O		20% Dioxane	
	[H ⁺] = 0.1972	[H ⁺] = 0.2906	[H ⁺] = 0.1972	[H ⁺] = 0.2906
34.98	0.265	0.420	0.111	0.174
37.27	.361	.477	.149	.234
39.54	.492	.777	.204	.319
41.83	.661	1.05	.278	.433
44.12	.883	1.42	.368	.581

TABLE IV

ACTIVATION ENERGIES FOR THE PROTOLYSIS OF TRIMETHYLAMINE BORANE IN HCl. VALUES OF Δ*E* AND LOG *A* BY FITTING THE EQUATION

$$\log k' = \log A + \log [H^+] +$$

$$0.4343(b[H^+] - \Delta E/RT) \text{ for } b = 0.80$$

Solvent	[H ⁺], mole/l.	Δ <i>E</i> , kcal./mole	log <i>A</i> ^a	Stand. dev. as % <i>k</i> '
H ₂ O	0.1972	25.647	14.704	0.4
H ₂ O	.2906	25.945	14.712	.4
20% Dioxane	.1972	25.619	14.323	.4
20% Dioxane	.2906	25.720	14.324	.5
Mean		25.73 ± 0.13		

^a Using the mean activation energy.

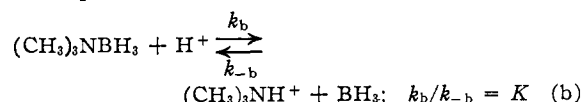
Anticipating that $db/d(1/T)$ is exceedingly small compared to ΔE , the experimental value corresponds to the Arrhenius energy for the second order rate constant, k .

The decreased rates in dioxane solutions are apparently caused by a decrease in the pre-exponential factor *A*. This suggests a larger positive en-

tropy of activation in water solution than in dioxane. A positive entropy change might be observed if the solvation sphere of the transition state were disoriented, or "loosened," relative to the ground state. The larger entropy change in water then would mean greater relative loosening of the solvation sphere on reaction than in dioxane.

Mechanism.—In the interpretation of the results a number of reaction steps seem reasonable. The dependence on amine-borane concentration requires as limiting cases of rate-determining steps either direct reaction with B-H in the amine borane or an equilibrium involving amine-borane followed by reaction of a B-H bond in the equilibrium product. Outside of H⁺, the other two acids in the system, trimethylammonium ion and water, could conceivably react. The steps considered are.

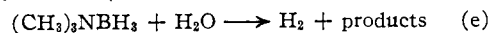
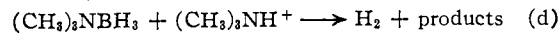
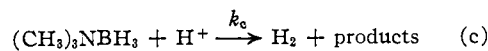
Displacement:



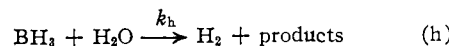
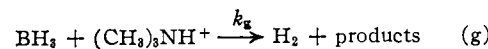
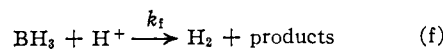
Dissociation:



Attack of protonic reagent on amine borane:



Reaction of borane intermediate with protonic reagent:



The reactions of amine borane with trimethylammonium ion or water (eq. d and e) are eliminated because of their extreme slowness (Table V.). The displacement equilibrium is a combination of the dissociation equilibrium b^1 and the extremely rapid proton-transfer equilibrium to trimethylamine. Thus if the equilibrium b^1 is established, the displacement equilibrium b should also be present and would be the predominant one at the low *pH* of the experiment.

TABLE V

EFFECT OF H₂O AND (CH₃)₃N·HCl ON TRIMETHYLAMINE BORANE AT 35°. EFFECT OF (CH₃)₃N·HCl AND NaCl ON THE PROTOLYSIS AT 35°

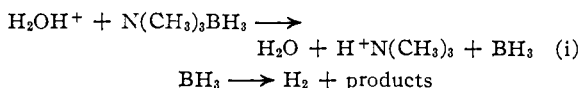
Conditions	<i>k</i> ' × log <i>e</i> × 10 ⁴ , sec. ⁻¹	Conditions [HCl]	[(CH ₃) ₃ N·HCl]	<i>k</i> ' × log <i>e</i> × 10 ⁴ , sec. ⁻¹
H ₂ O alone	>10 ⁻⁵	0.3960	0.0	0.619
0.67 <i>M</i> (CH ₃) ₃ N·HCl	>10 ⁻³	.3960	.17	.631
.64 NaCl		.3960	.34	.647
.3960 <i>M</i> HCl	1.17	.3960	.67	.694

First order kinetics in acid concentration would be observed from (c), direct attack of H⁺ on amine borane or from displacement equilibrium b followed by slow reaction of borane in step *g* or *h*. Second order kinetics in [H⁺] can result only if equilibrium

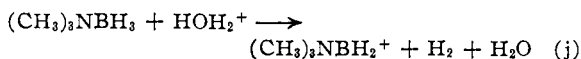
b is followed by slow reaction of BH_3 with a proton (step f). Since the equilibrium concentration of BH_3 depends inversely on the trimethylammonium ion concentration both (h) and (f) should be retarded during the progress of the reaction producing this ion according to (a), and addition of excess trimethylamine hydrochloride should decrease their rates. Actually, an increase in rate is observed when trimethylamine hydrochloride is added (Table V). Thus equation 2 cannot represent competitive second order kinetics in H^+ with the choices of steps given above.

We also would like to eliminate from consideration equilibrium b followed by slow reaction of $(\text{CH}_3)_2\text{NH}^+$ (step g) for the following reasons. Suppose that step g is analogous to reaction with hydronium ion (step f) and that the reactivity increases with the acid strength; then both steps should be competing and (f) should be faster. As long as equilibrium b is maintained, step f would produce second order kinetics in $[\text{H}^+]$, contrary to our results. If step f were so fast that equilibrium is not maintained, step c would then essentially symbolize the reaction.

The reaction is thus conceived to be the result of step c, the attack of a solvated proton on the amine borane molecule. Whether the reaction occurs as displacement of BH_3 by the proton and then a rapid reaction of BH_3



or whether there is a direct attack on the B-H bond



followed by rapid reaction of the resulting ion, is not obvious from our data. A situation similar to (j) has been proposed for the hydrolysis of pyridine diphenylborane but has not been compared to (i).² At any rate, the reaction system here is sufficiently different so that the proposed hydrolysis mechanism may not prevail.

Ionic Strength Dependence.—Equation 1 is now readily understood when the rate of reaction is expressed in terms of the activities of the reacting species and the transition state. Thus the concentration expression should be multiplied by the quantity

$$\gamma_{\text{H}^+} \gamma_{\text{NB}} / \gamma_{\text{t}^+} = Q$$

where the γ 's represent activity coefficients of H^+ , amine borane and transition state. Now⁵

$$\log \gamma_{\text{NB}} = k_{\text{NB}} \mu$$

and

$$\frac{1}{2} \log \frac{\gamma_{\text{H}^+}}{\gamma_{\text{t}^+}} = \log \frac{\gamma_{\text{HCl}}}{\gamma_{\text{tCl}}}$$

$\log \gamma_{\text{HCl}} / \gamma_{\text{tCl}}$ may be expressed in terms of the Debye-Hückel expression. A power series expansion of this expression about the midpoint of the ionic strength range rapidly converges and leads to the expression

$$\log \frac{\gamma_{\text{H}^+}}{\gamma_{\text{t}^+}} = AB \Delta a \mu$$

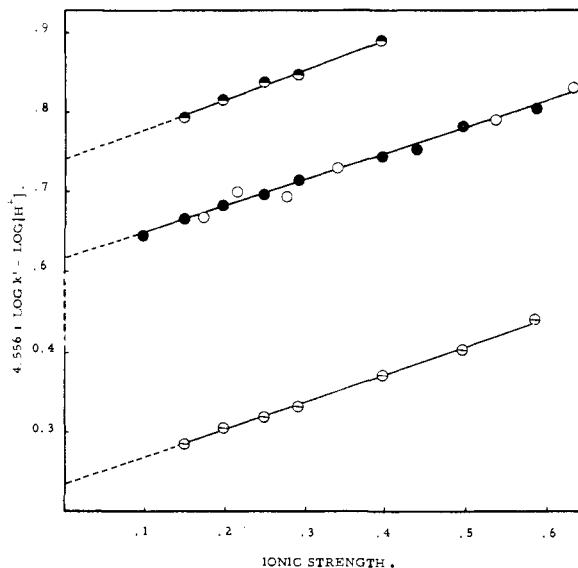


Fig. 2.—Ionic strength effect on rate: ●, aq. HCl, 34.98°; ○, aq. H_2SO_4 , 34.98°, assuming $Ka_1 = 2 \times 10^{-2}$; ◐, aq. HCl, 37.27°; ○, HCl in 20% dioxane by volume.

Introducing a solvation correction for higher ionic strengths,^{5,6} there results

$$\log \frac{\gamma_{\text{H}^+}}{\gamma_{\text{t}^+}} = 2[-AB(a_{\text{H}^+} - a_{\text{t}^+}) + 0.007(n_{\text{H}^+} - n_{\text{t}^+})]\mu$$

where A is the limiting Debye-Hückel slope, B is a composite constant resulting from the Debye-Hückel denominator and the series expansion, the a 's represent the "effective radius" of the ions, n is the "solvation number" of the ions and μ is the ionic strength. AB is inversely proportional to the reciprocal of dielectric constant and temperature, and $\mu = [\text{H}^+]$ if the acid is the only electrolyte present. Thus the activity correction is of the form $Q = \exp. b[\text{H}^+]$, in agreement with equation 1.

A comparison of literature data makes several choices reasonable

$$k_{\text{NB}} = 0.02,^7 a_{\text{H}^+} - a_{\text{t}^+} = 1 \text{ and } n_{\text{H}^+} - n_{\text{t}^+} = 7^8$$

This gives for a water solution a calculated value of $b = 0.59^\circ$ at 40° . HCl in 20% dioxane shows substantially the same deviation from ideality as aqueous HCl,⁹ implying little change in b in this solvent. Because of the dependence of AB on the dielectric constant, an increase in b is expected at high dioxane concentrations. Lastly, addition of strong electrolytes should increase the rate and the increase should be most pronounced for the most strongly hydrated ion.

The data in Tables I and II are plotted in Fig. 2 as $\log k' - \log[\text{H}^+]$ vs. μ , the ionic strength, and give a straight line fit. The results of the plots and the values of b calculated from the ratios of k' values in Table III are given in Table VI. It is seen that b has the expected order of magnitude. Since the activity correction has only a slight effect on the ratio $k'/[\text{H}^+]$, the precision of the experimental b

(5) Harned and Owen, ref. (4), p. 532.

(6) R. H. Stokes and R. A. Robinson, *THIS JOURNAL*, **70**, 1870 (1948).

(7) Ref. 4, table 12-10-1A.

(8) J. Kielland, *THIS JOURNAL*, **59**, 167b (1937).

(9) Ref. 4, Fig. 11-6-1.

TABLE VI

Values of b , For Equation 1, $k' = k[H^+] \exp b$

Solvent	$T, ^\circ\text{C.}$	b , mole $^{-1}$,	
		from Table I	from Table III
H ₂ O, HCl	34.98	0.76
H ₂ O, H ₂ SO ₄	34.98	.79 ^a
H ₂ O, HCl	37.27	.87
H ₂ O, HCl	0.82 ± 0.08
20% Dioxane, HCl	34.98	0.80
20% Dioxane, HCl	0.66 ± 0.05
80% Dioxane, H ₂ SO ₄	34.98	2.1 ^a

^a From Table II.

values is only about 10%, and the difference in the values should not be considered significant for the water and 20% dioxane solution. b is increased in 80% dioxane but less than predicted. The effect on the rate when NaCl or (CH₃)₃N·HCl is added is in accord with expectations, decreasing in the order H⁺, Na⁺, (CH₃)₃NH⁺ (Table V).

Acknowledgment.—Financial assistance in this work by the Research Corporation is gratefully acknowledged.

Experimental

Materials.—Several different lots of trimethylamine borane were kindly supplied by Callery Chemical Corporation. The samples were 98–100% pure based on iodate titration and were used without further purification. Only peroxide-free 1,4 dioxane was used after drying and distillation from calcium hydride. All other materials were reagent grade.

Kinetic Procedure.—All experiments were carried out at temperatures held constant to ±0.005°. Temperature intervals were measured with a Beckmann thermometer. In making an experiment, 50 ml. of an aqueous borane solution was pipetted into the reaction vessel and diluted either with 50 ml. of distilled water or with 50 ml. of 50.0% by volume aqueous dioxane. Then 25 ml. of standardized aqueous HCl were added and the mixture was thoroughly shaken. All solutions were thermostated and concentrations were calculated from the dilution ratios. The borane concentrations were about 0.01 *M*. At intervals 10-ml. aliquots were pipetted for analysis.

Analysis.—Samples were added to a measured amount of standard KIO₃ solution. In the acidic solution excess oxidant was converted to iodine which was titrated with sodium arsenite to the starch end-point after adding excess NaHCO₃.

[CONTRIBUTION FROM CHEMICAL DEPARTMENT, NAGOYA UNIVERSITY, CHIKUSA NAGOYA, JAPAN]

The Diamagnetic Anisotropy of a Borazole Ring

BY HARUYUKI WATANABE,¹ KAZUO ITO AND MASAJI KUBO

RECEIVED DECEMBER 21, 1959

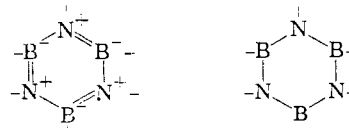
The diamagnetic susceptibilities of borazole and some of its derivatives were measured at room temperature. From these data and the diamagnetic susceptibility calculated from Pascal's constants along a direction parallel to the molecular plane, the diamagnetic anisotropy of a borazole ring was estimated at about -36×10^{-8} . Theoretical calculations based on molecular orbitals for the π -electron system of a borazole ring were carried out in order to evaluate the diamagnetic anisotropy as a function of molecular parameters. Comparison between the observed and calculated diamagnetic anisotropies led to the conclusion that the extent of contribution of the donor-acceptor double bond structure to the normal state of borazole is 24% and that the π -electron bond order of BN bonds in a borazole ring is 0.45.

Introduction

Borazole is isoelectronic with benzene. In fact, a number of physical properties of this compound and its derivatives bear fairly close resemblance to those of benzene and corresponding benzene derivatives.² For instance, the approximately planar hexagon form of a borazole ring in the molecules of borazole and some of its derivatives has been confirmed by electron diffraction^{3–5} as well as by X-ray analysis,⁶ the BN bond distance being intermediate between the B–N single bond distance and the B=N double bond distance.⁷ The ultraviolet absorptions of borazole and its derivatives are similar to those of benzene and the corresponding benzene derivatives, respectively.^{7–10} The infrared absorptions and Raman spectra of the former group of compounds can be interpreted on the basis of re-

sults on the latter group of compounds,^{11–13} the force constant of BN stretching vibrations being intermediate between those for a B–N single bond and a B=N double bond. The dipole moment data also suggest a nearly planar hexagon structure of a borazole ring.^{14,15}

These facts have led to the presumption that the electronic structure of a borazole molecule may well be represented by a resonance hybrid between the two electronic states.^{7,8}



This suggests that a borazole ring shows diamagnetic anisotropy due to π -electrons as does a benzene ring. However, the effective number of π -electrons contributing to the diamagnetic anisotropy of a borazole molecule is presumed to be

- (1) Shionogi Pharmaceutical Co. Ltd., Amagasaki.
- (2) E. Wiberg, *Naturwissenschaften*, **35**, 182, 212 (1948).
- (3) A. Stock and R. Wierl, *Z. anorg. allgem. Chem.*, **203**, 228 (1931).
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