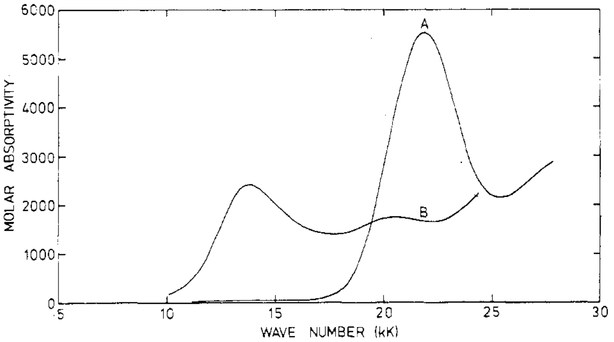

Figure 6. Calculated spectra of the models Se_4^{2+} (A) and Se_8^{2+} (B). Se_4^{2+} was calculated on basis of 10 measured spectra; Se_8^{2+} was calculated on basis of 14 measured spectra.

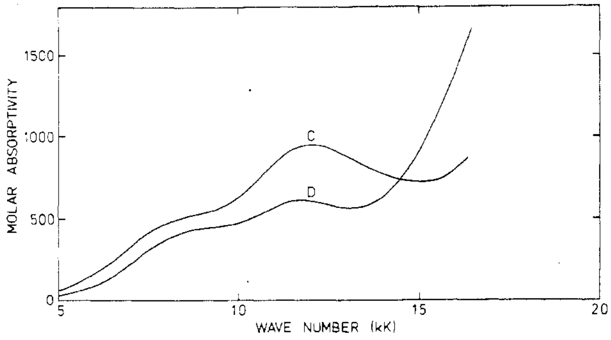

Figure 7. Calculated spectra of the models Se_{12}^{2+} (C) and Se_{16}^{2+} (D). Both Se_{12}^{2+} and Se_{16}^{2+} were calculated on basis of 9 measured spectra.

equilibria one obtains at the same time the spectra for all species in the equilibria. In Figures 6 and 7 are shown the calculated spectra of the models Se_4^{2+}, Se_8^{2+}, Se_{12}^{2+}, and Se_{16}^{2+}. The equilibrium constants for all of the model reactions described above are of course also calculated together with the variances, but since it is not possible to distinguish between many of the possible reactions, the equilibrium constants are not included in the present paper. However, by a newly developed potentiometric method[24] there seems to be hope to distinguish between different reactions. Under these circumstances it will be important to compare the equilibrium constants obtained by the spectrophotometric method with the constants obtained by the potentiometric method.

Acknowledgment. The authors wish to acknowledge the financial support of Statens teknisk-videnskabelige Forskningsrad. Further thanks are due to the Northern Europe University Computing Center (NEUCC) for computing time.

Registry No. Se, 7782-49-2; $SeCl_4$, 10026-03-6.

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Bis(dimethylamido)tin(II). Synthesis and Characterization[1]

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Bis(dimethylamido)tin(II) is prepared by amination of anhydrous $SnCl_2$ with $LiN(CH_3)_2$. The compound is a white crystalline solid which is a dimer in cyclohexane solution and a monomer in the vapor phase. The compound reacts with alcohols to give $Sn(OR)_2$, with *N*-methyldiethanolamine to give $\overleftarrow{Sn(OCH_2CH_2)_2N}CH_2$, and with pyridine to give $[(CH_3)_2N]_2Sn{\cdot}py$. Ir and mass spectra are reported. The oxidation state of the compound is confirmed by calomel precipitation and Mössbauer isomer shift. Variable-temperature ^1H NMR spectra indicate exchange of the dimethylamido groups between bridge and terminal positions of a dimer structure.

Introduction

Compared to the other main group 4 elements, the chemistry of tin(II) compounds has been a relatively neglected area of research. Preparative and analytical difficulties arising from the ease of oxidation of the element in its lower oxidation state has been cited as the principal cause of inactivity in this field.[2] Hence perusal of the literature reveals only few well-characterized covalent tin(II) compounds. Particularly elusive has been the tin(II)–nitrogen bond. This bond has been proposed for several compounds (viz., bis(methyl-*N*-phenylcarbamate)tin(II)[3] and 2,2'-biphenylenedicarbamatotin(II)[4]) in short communications without significant supporting data.

The present study describes the high-yield synthesis of bis(dimethylamido)tin(II) and the unequivocal identification and characterization of the Sn^{II}–N bond by chemical and spectroscopic properties.

Experimental Section

All operations were carried out either in a dry oxygen-free nitrogen

Table I. Molecular Weight Data for $Sn[N(CH_3)_2]_2$

g of **1**/kg of C_6H_{12}	ΔT, °C	Mol wt (exptl)^a	[Mol wt (exptl)]/[mol wt (calcd)]
59.526	2.42	545	2.64
32.059	1.72	413	2.00
19.214	0.97	438	2.12
4.530	0.27	371	1.80
		Av 441	Av 2.13

^{a} K_f(cyclohexane) = 22.16 determined from standard benzil solutions; m (ΔT_{av}) = 0.0068 (0.11), 0.0181 (0.39), 0.0383 (0.78).

environment or under vacuum using conventional high-vacuum procedures. All solvents were dried and distilled prior to use. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Consistent results were obtained only when freshly sublimed samples were submitted in vacuum ampoules. Infrared spectra as Nujol and fluorohydrocarbon oil mulls on KBr disks were recorded on a Perkin-Elmer 521 grating spectrometer. Proton resonance spectra were taken on a Varian A-60 spectrometer in pentane, benzene, and chlorobenzene relative to TMS as an internal reference. Solutions were prepared using freshly sublimed samples of compound and distilled, dry, degassed solvents. NMR tubes were sealed under vacuum. The mass spectrum was obtained on a Hitachi Perkin-Elmer RMU6 spectrometer by direct injection into the ionization chamber at 100° and 80 eV.

^{119m}Sn Mössbauer spectra were obtained with a Nuclear Science and Engineering Corp. Mössbauer effect spectrometer, Model NS-1, in a constant-acceleration mode with $Ba^{119m}SnO_3$ as a source. The data were collected with a NaI scintillation counter and accumulated with a Nuclear Data 2200 multichannel analyzer. Values of isomer shift and quadrupole splitting were obtained from computer analysis.[5] Reported values of isomer shift are relative to SnO_2.

Preparation of Bis(dimethylamido)tin(II), 1. Eighty milliliters (0.176 mol) of butyllithium (Alfa Inorganics, 2.2 *M* in hexane), 200 ml of pentane, and 50 ml of benzene were syringed into a 1-l. three-neck round-bottom flask fitted with two gas-inlet tubes. One of the tubes was connected to a dry nitrogen gas source and the other to a cylinder of dimethylamine (Matheson, dried in vapor over anhydrous NaOH). The flask was cooled to 0° and dimethylamine was bubbled through the stirred solution until a permanent white precipitate was formed. The amine gas inlet tube was replaced with a distillation head and the volume of liquid was reduced by distillation under a flow of nitrogen. Distillation must be stopped before dryness is attained. The flask was cooled to ambient temperature and the last traces of solvent and dimethylamine were removed under vacuum. The residual lithium dimethylamide was dissolved in 500 ml of benzene. The flask was equipped with a mercury-sealed mechanical stirrer. The distillation head was replaced with a solid addition tube containing 15 g (0.0791 mol) anhydrous $SnCl_2$. The angle of the flask was adjusted so that mechanical vibrations of stirring caused a slow addition of the solids to the lithium dimethylamide solution. After 7 hr, the stirring was stopped and solids were permitted to settle overnight. The clear supernatant liquid was decanted. The residue was washed with pentane and dried under vacuum to give 0.497 g (0.0117 mol) of LiCl confirmed by a qualitative test for chloride ion and determination of density: lit., 2.07 g/ml; found, 2.10 g/ml. The filtrate was evaporated to dryness under vacuum to give 15.0 g (92% yield based on starting $SnCl_2$) of crude pale yellow solids. The material may be purified by sublimation at 70° (10^{-4} Torr) to give 12.2 g (75%) of a white crystalline solid, mp 91–93°. Anal. Calcd for $C_4H_{12}N_2Sn$: C, 23.23; H, 5.81; N, 13.54; Sn, 57.38. Found: C, 23.50; H, 5.96; N, 13.36; Sn, 57.34. Ir (KBr mull, cm^{-1}): 440 (m), 505 (w), 722 (m), 770 (vw), 898 (s), 920 (vw), 945 (vs), 1038 (m), 1063 (w), 1122 (m), 1165 (m), 1213 (m), 1240 (m), 1300 (vw), 1440 (w), 1455 (w), 2260 (vw), 2780 (m), 2830 (m), 2860 (m), 2920 (m). The mass spectrum is summarized in Figure 1. The molecular weight of **1** in cyclohexane solution was determined by freezing point depression using established methods.[6] The data are reported in Table I. The ^{1}H NMR spectra at 60 MHz in chlorobenzene and benzene are summarized in Table II.

Reaction of 1 with HCl and $HgCl_2$. Freshly sublimed **1** (6.10 g, 0.0295 mol) was dissolved in 30 ml of benzene and added to a 500-ml, three-necked round-bottom flask fitted with a gas-inlet tube and a mechanical stirrer. The solution was cooled to 0° under dry N_2 and excess anhydrous HCl gas was bubbled through the solution with vigorous stirring. A white solid precipitated from solution. The solids were filtered, washed with benzene, and taken up in hot distilled water. An aqueous solution of 17 g of mercuric chloride was added slowly, with stirring. The white precipitate, Hg_2Cl_2, thus formed was filtered, washed several times with small portions of water, and dried under vacuum until constant weight was obtained (13.7 g; 98.4% based on starting **1**).

Table II. ^{1}H NMR Data for $Sn[N(CH_3)_2]_2$

Solvent	T, °C	τ, ppm	Solvent	T, °C	τ, ppm
Chlorobenzene	40	7.20	Benzene	75	7.22
	−20	7.43, 6.93		40	7.25
	−40	7.48, 6.85		−8	7.39, 6.88

Reaction of 1 with Ethanol. A sample of crude **1** was sublimed and transferred to a 100-ml round-bottom flask containing a magnetic stirring bar and a side arm which was sealed with a Teflon-lined serum cap. Benzene (~10 ml) was distilled into the flask to dissolve **1**. An excess of ethanol was added slowly to the solution of **1** with stirring until precipitation was complete. Solvents were removed by evaporation. The residue was a white powder. Identification of the solids as $Sn(OC_2H_5)_2$ was made by comparison of the ir and ^{1}H NMR spectra with the material prepared by the transesterification of $Sn(OCH_3)_2$ with ethanol.[7] Ir (Nujol mull, KBr, cm^{-1}): 1150 (w), 1093 (s), 1047 (vs), 886 (s), 720 (w), 575 (vs), 480 (w). ^{1}H NMR (60 MHz, *o*-$C_6H_4Cl_2$, 80°): τ 8.72, t, CH_3; τ 6.13, q, CH_2.

Reaction of 1 with *N*-Methyldiethanolamine. A sample of crude **1** (2.5 g) was sublimed and transferred to a 100-ml round-bottom flask. Benzene (10 ml) was distilled into the flask and excess *N*-methyldiethanolamine dissolved in benzene was added dropwise with stirring. After 10 min colorless crystals deposited from solution. The supernatant liquid was removed and the solids were washed with several small portions of cold benzene. The product was identified as $Sn(OC_2H_4)_2NCH_3$ (**2**) by comparison of the ^{1}H NMR spectra with the material prepared by transesterification of $Sn(OCH_3)_2$ with *N*-methyldiethanolamine;[8] mp 177–183 (188°). ^{1}H NMR (60 MHz, $CDCl_3$, 35°): τ 7.53, s, CH_3; τ 7.30, t, CH_2N; τ 6.00, t, CH_2O.

Reaction of 1 with Pyridine. Approximately 0.1 g of **1** (freshly sublimed) was dissolved in a small quantity of benzene. Pyridine was added dropwise until no further precipitation was observed. The product, **3**, is a white solid which decomposes when heated above 150°; it is insoluble in CH_2Cl_2 and CH_3CN. Anal. Calcd for $C_9H_{17}N_3Sn$: C, 37.81; H, 5.99; N, 14.69. Found: C, 36.62; H, 5.97; N, 14.44.

Results and Discussion

Bis(dimethylamido)tin(II), **1**, may be synthesized by amination of anhydrous tin(II) chloride with lithium dimethylamide in a mixed-hydrocarbon solvent (eq 1). The yield

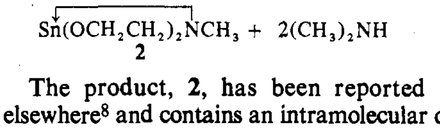
$$SnCl_2 + 2LiN(CH_3)_2 \rightarrow \underset{\mathbf{1}}{Sn[N(CH_3)_2]_2} + 2LiCl \qquad (1)$$

of product from the heterogeneous reaction is above 90% based on starting $SnCl_2$. Pure **1**, which may be obtained by sublimation at 70° (10^{-4} Torr), is a white crystalline solid (mp 91–93°) which is sensitive to trace quantities of oxygen and moisture and is soluble in aliphatic and aromatic hydrocarbon solvents. (A violent reaction occurs when **1** is added to chloroalkanes.)

1 is labile and, like the tin(IV) amines, readily undergoes esterification with alcohols to form tin alkoxides (eq 2). In

$$Sn[N(CH_3)_2]_2 + 2C_2H_5OH \rightarrow Sn(OC_2H_5)_2 + 2(CH_3)_2NH \qquad (2)$$

an unusual reaction, **1** undergoes an intramolecular esterification reaction with *N*-organodiethanolamines to give the same monomeric product which is obtained by transesterification of tin(II) alkoxides with amine diols (eq 3).



$$Sn[N(CH_3)_2]_2 + CH_3N(CH_2CH_2OH)_2 \rightarrow \underset{\mathbf{2}}{Sn(OCH_2CH_2)_2NCH_3} + 2(CH_3)_2NH \qquad (3)$$

The product, **2**, has been reported and characterized elsewhere[8] and contains an intramolecular dative bond between

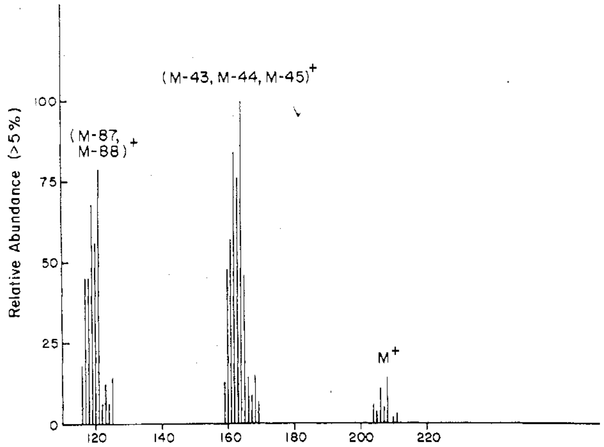


Figure 1. Mass spectrum of $Sn[N(CH_3)_2]_2$ at 80 eV.

nitrogen and tin. That only monomer is obtained from **1**, in spite of the relatively high concentrations of reactants in solution, suggests that the dative bond is important in the preliminary steps of esterification. Coordinate complexes with nitrogen bases are not unexpected in light of the fact that **1** and other tin(II) compounds form addition compounds with pyridine (eq 4).[9]

$$Sn[N(CH_3)_2]_2 + C_5H_5N \rightarrow Sn[N(CH_3)_2]_2 \cdot C_5H_5N \qquad (4)$$

The molecular weight of **1** in cyclohexane solution indicates that association occurs as a dimer. Dimer formation in solution has also been reported for tin(II) butoxide.[7] Although association persists in the vapor phase for the alkoxides,[7] the mass spectrum of **1** (Figure 1) contains no peaks above the monomolecular ion ($Sn[N(CH_3)_2]_2^+$, *m/e* 204–211) from 80 to 16 eV. In addition to that of the molecular ion, the spectrum of **1** consists of two clusters of peaks which correspond to the overlap of polyisotopic tin ions $HSnN(CH_3)_2^+$ (M − 43), $SnN(CH_3)_2^+$ (M − 44), and $SnN(CH_3)CH_2^+$ (M − 45) and to the overlap of SnH^+ (M − 87) and Sn^+ (M − 88). Thus fragmentation occurs predominantly through cleavage of the Sn–N bond. Rearrangements leading to SnH ions are well known for organotin compounds.[10]

Verification of the low oxidation state of **1** was obtained by chemical methods (quantitative recovery of Hg_2Cl_2 from the mercuric salt) and from Mössbauer spectral parameters ($\delta = 2.80 \pm 0.05$ mm/sec; $\Delta E_q = 3.17 \pm 0.05$ mm/sec). Isomer shift values agree with those reported for the alkoxides (~2.8 mm/sec);[7,11] however, the quadrupole splitting constant is unusually large comparing only with those constants found for $(R_2SnX)_2O$ and ionic and molecular complexes of organotin halides.[12]

No studies have been reported on the infrared absorption characteristics of the Sn^{II}–N bond. It is reasonable to assume that vibrations attributed to the Sn^{II}–N bond in **1** should appear at lower energy than comparable bonds in Sn(IV) compounds (e.g., $\nu_{as}(Sn^{IV}\text{–}N) = 535$ cm^{-1} in $Sn[N(CH_3)_2]_4$).[13] Similar observations are noted for Sn^{II}–O and Sn^{IV}–O vibrations which occur at 565–578 cm^{-1} and 605–650 cm^{-1}, respectively.[7,14-17] Thus, the band at 440 cm^{-1} in **1** has been assigned to Sn^{II}–N stretching. The medium intensity of this band is consistent with the substantial polarity expected for such a bond. It is noteworthy that the assignment is in agreement with the Cd–N stretching vibration in $Cd[N(Si(CH_3)_3)_2]_2$ ($\nu = 410$ cm^{-1}).[18] Other vibrational assignments for the principal absorptions in **1** are summarized in Table III.

The proton resonance spectrum of **1** in chlorobenzene (Table II, Figure 2) consists of a broad singlet at 40° (τ 7.20; $W_{1/2}$ = 5.5 Hz). The line sharpens with an increase in temperature ($W_{1/2}$ = 1.0 Hz at 80°) without a change in position. As the temperature is lowered, splitting is observed, and at −20° two broad lines become evident. At −40°, the spectrum contains two principal and at least three smaller lines.[19]

Table III. Vibrational Frequencies and Assignments for $Sn[N(CH_3)_2]_2$ and $Sn[N(CH_3)_2]_4$

Freq, cm^{-1}		
$Sn[N(CH_3)_2]_2$	$Sn[N(CH_3)_2]_4$[13]	Assignment
2920	2953	$\nu(CH_3)$
2860	2930	
2830	2871	
2780	2831	
	2775	
1455	1460	$\delta(CH_3)$
1440	1442	
	1430	
	1409	
1240	1252	$\rho(CH_3) + \nu_s(NC_2)$
1213	1177	
1165	1132	
1122		
1063	1069	$\nu_s(NC_2) + \rho(CH_3)$
1038	1036	
945	961	$\nu_s(NC_2)$
440	535	$\nu(SnN)$

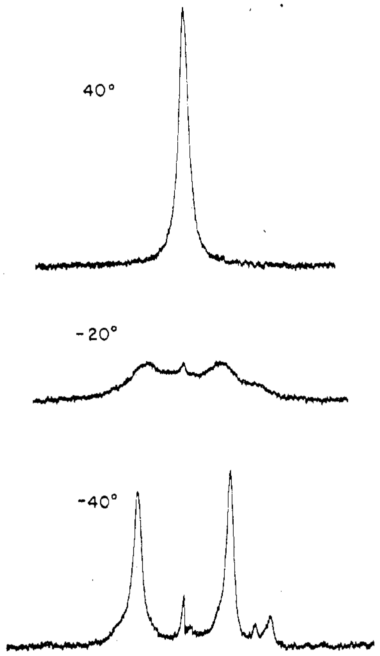
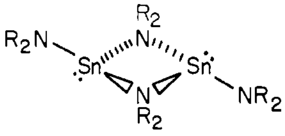


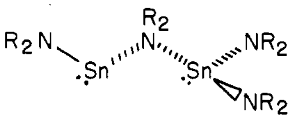
Figure 2. ^1H NMR spectrum of $Sn[N(CH_3)_2]_2$ at 60 MHz in *o*-dichlorobenzene at 40, −8, and −40°.

The thermal dependence of the spectrum is consistent with a dynamic process in which dimethylamido moieties exchange between nonequivalent sites on the molecule.[20] At low temperatures the exchange rate is slow and the observation of two principal lines of approximately equal area suggests two equal sets of magnetically nonequivalent methyl protons. Since **1** is a dimer in solution, structure I, consisting of a pair of bridging and a pair of terminal dimethylamido groups, is proposed. A double-bridge structure is not unique for tin(II) compounds and has been proposed recently for tin(II) methoxide.[7] The single-bridge structure, II, which is common for associated tin(II) compounds in the condensed phase,[7,21] is inconsistent with the area ratio data.

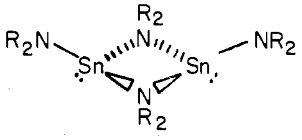
The additional lines observed at −40° are real and reproducible from sample to sample.[22] It is proposed that these lines either belong to methyl groups in molecules of higher asso-



I



II



III

ciation or, more likely, are a result of a slow exchange in the sterically less favorable cis isomer, III. The latter structure predicts three nonequivalent amido groups. Presumably steric effects favor the trans isomer. It should be noted that at elevated temperatures cis–trans isomerization, whether by an inter- or intramolecular mechanism, is expected to scramble all dimethylamido groups—hence the observation of only one singlet at 80°.

Registry No. **1**, 55853-40-2; C_2H_5OH, 64-17-5; $CH_3N(CH_2CH_2OH)_2$, 105-59-9; C_5H_5N, 110-86-1; **3**, 55853-44-6; **1** (dimeric), 55853-45-7.

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(22) ^{117}Sn and ^{119}Sn satellites are not observed.

Notes

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Kinetics of the Reaction of Ammonium Ion with Hydroborate Ion in Liquid Ammonia

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The acid-catalyzed hydrolysis of hydroborate has been thoroughly studied,[1] but little has been reported on the analogous ammonolysis in liquid ammonia. Armstrong[2] studied the reaction

$$(NH_4)_2SO_4 + 2NaBH_4 \rightarrow Na_2SO_4 + 2H_2 + 2BNH_6 \qquad (1)$$

in ammonia from 40 to 70°. The BNH_6 product was not completely identified. We have investigated the kinetics of this reaction from 25 to 45° using NH_4Br instead of $(NH_4)_2SO_4$. In addition to obtaining rate constants and a heat of activation, we have determined the effect of ionic strength from $\mu = 0.01$ *M* to $\mu = 1.92$ *M* and have identified the product as $BH_3 \cdot NH_3$.

Experimental Section

Reagent grade ammonium and sodium bromide (dried at 85°) and analytical reagent sodium hydroborate (Ventron) were used. Ammonia was distilled from a sodium solution.

The reactions were carried out in a magnetically stirred, glass-lined 128-ml Parr general-purpose bomb. This was connected by high-pressure fittings to one side of a mercury-containing U-tube manometer. The other side of the manometer was connected to a reference bomb containing pure liquid ammonia. The bombs were held in a thermostated water bath, and the entire apparatus was enclosed in an air bath thermostated at a temperature slightly above that of the water bath. The reaction rates were measured by reading the manometer with the aid of a cathetometer as a function of time.

The ammonia was first distilled into a separate bomb and weighed. The amounts of $NaBH_4$, NH_4Br, and NaBr required to make a solution of predetermined ionic strength were then weighed out into the reaction bomb, and the ammonia was finally distilled into the reaction bomb. Either the $NaBH_4$ or the NH_4Br was always in at least a ninefold excess. After each run, the evolved hydrogen was Toepler-pumped into a gas buret and measured.

The pressures measured with the manometer corresponded to the partial pressures of hydrogen gas in the reaction bomb side. Rate constants were determined from plots of log $[(P_\infty - P_t)/P_\infty]$ vs. time.

The BNH_6 product was isolated by removal of ammonia on a vacuum line and extraction of the residue with ethyl ether. Evaporation of the ether left a white, crystalline solid which melted at 110–113°. This melting temperature corresponds to $NH_3 \cdot BH_3$.[3] Anal. Calcd for BNH_6: B, 35.03; N, 45.48. Found: B, 35.24; N, 46.16.

Results and Conclusions

From log $[(P_\infty - P)/P_\infty]$ vs. time plots such as that shown in Figure 1, the reaction of NH_4^+ with BH_4^- was found to be first order in both NH_4^+ and BH_4^-. The second-order rate constants calculated from the slopes of such plots for various temperatures are given in Table I. A log *k* vs. $1/T$ plot of the data, shown in Figure 2, gave a least-squares heat of activation of 38.5 ± 0.6 kcal/mol. Our data may be compared with those of Gardiner and Collat,[4] who studied the aqueous reaction of NH_4^+ with BH_4^-. They obtained a rate constant of 2.4×10^{-4} M^{-1} sec^{-1} at $\mu = 1$ and 25° and a heat of activation of 23 ± 2 kcal/mol at $\mu = 0.5$. The higher rate constant and lower activation energy of the aqueous reaction may be due to the participation, in the aqueous reaction, of water molecules hydrogen bonded to the ammonium ion. A Grotthuss-type proton transfer such as the following may be