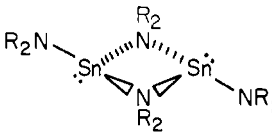

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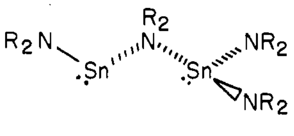
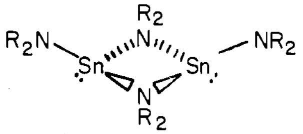


II



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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(19) Similarly, in benzene solution, more than two lines are observed prior to freezing (−8°).
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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 $2.4 \times 10^{-4}\ M^{-1}\ sec^{-1}$ 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

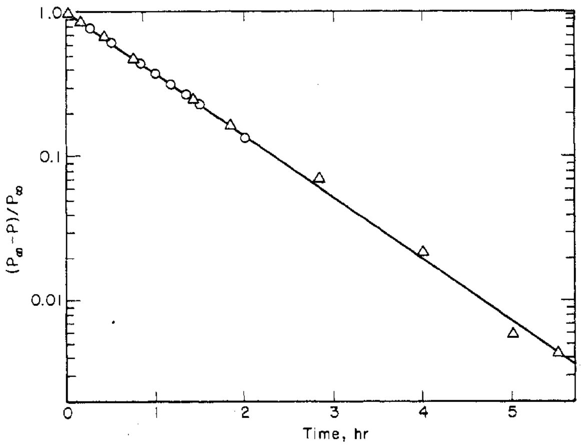


Figure 1. Plot of $\log[(P_\infty - P)/P_\infty]$ vs. time for reactions at 45° and $\mu = 0.9$: ○, from 0.08 *M* BH_4^- with 0.82 *M* NH_4^+; △, from 0.08 *M* NH_4^+ with 0.82 *M* BH_4^-.

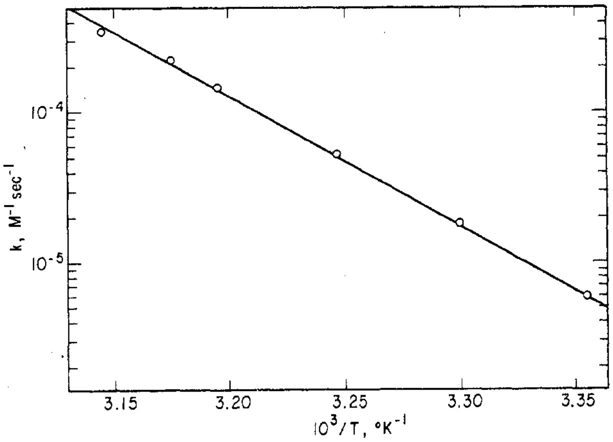


Figure 2. Temperature dependence of *k* at $\mu = 0.9$.

Table I. Rate Constants in Liquid Ammonia at $\mu = 0.9$

Temp, °C	*k*, M^{-1} sec^{-1}	Temp, °C	*k*, M^{-1} sec^{-1}
25	5.88×10^{-6}	40	1.43×10^{-4} [a]
30	1.79×10^{-5}	42	2.17×10^{-4}
35	5.04×10^{-5}	45	3.40×10^{-4} [b]

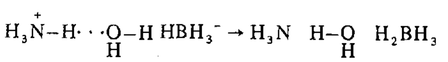
[a] Average of 1.49×10^{-4} and 1.37×10^{-4}, from separate experiments. [b] This value was obtained in two experiments.

Table II. Rate Constants in Liquid Ammonia at 30°

Ionic strength	$[BH_4^-]$, *M*	$[NH_4^+]$, *M*	*k*, M^{-1} sec^{-1}
0.0098	0.00888	0.00094	2.07×10^{-3}
0.049	0.0446	0.0045	6.23×10^{-4}
0.20	0.1954	0.0046	1.94×10^{-4}
0.90	0.818	0.0818	1.79×10^{-5}
1.92[a]	0.818	0.0818	4.95×10^{-6}

[a] NaBr was added to increase the ionic strength.

involved:



$$H_3\overset{+}{N}{-}H\cdots\underset{H}{O}{-}H\ HBH_3^- \rightarrow H_3N\ \ H{-}\underset{H}{O}\ \ H_2BH_3$$

Because hydrogen bonding is relatively unimportant in liquid ammonia, the analogous mechanism in liquid ammonia is unlikely.

The Bronsted-Bjerrum theory of ionic reaction leads to the expression

$$\log (k/k_0) = \frac{2\alpha Z_A Z_B \sqrt{\mu}}{1 + \beta a \sqrt{\mu}}$$

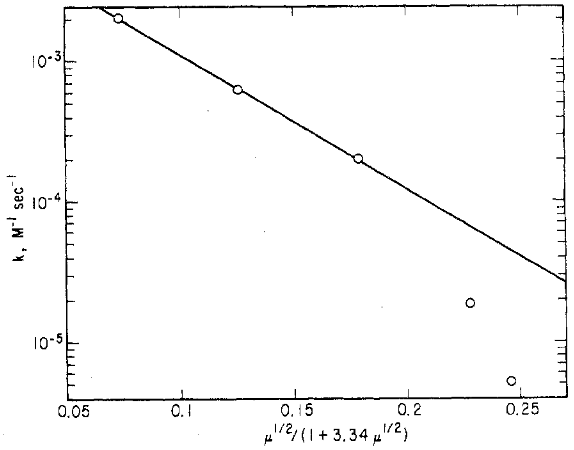


Figure 3. Ionic strength dependence of *k* at 30°. The line is drawn with the slope given by eq 2.

which was applied to rate constants measured at various ionic strengths at 30° (Table II). Using the dielectric constant[5] of 16.5 for ammonia at 30°, we calculated[6] $\alpha = 5.16$ and $\beta = 0.711$. A value for a of 4.7 Å was used in constructing the Bronsted-Bjerrum plot of the data, shown in Figure 3. The experimental points at relatively low ionic strengths have a slope close to that predicted by eq 2, whereas the points at higher ionic strengths are low, probably because of the pairing of reactant ions with inert ions. Dewald and Browall[7] correlated rate data for the reaction of the electron with the tri-*n*-butyl-*n*-propylammonium ion with the Bronsted-Bjerrum equation using a value for *a* of 6 Å.

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Registry No. BH_4^-, 16971-29-2; NH_4^+, 14798-03-9.

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Kinetics of the Oxidation of Antimony(III) by Vanadium(V)

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The kinetics of the oxidation of several organic[1] and inorganic[2-5] compounds by vanadium(V) have been studied. Kinetic studies of the oxidation of antimony(III) by inorganic oxidants[6-8] have also been reported. In continuation of our earlier work,[9-12] we have now studied the reaction between antimony(III) and vanadium(V) which has been incorporated in this report.