Such a compound should retain ammonia more strongly than the "diammoniate" because the hydrogens of its ammonias are more acidic than those of the "diammoniate." For the same reason it should split out hydrogen more readily than the "diammoniate." The reaction of such a compound with sodium in ammonia would be represented as

$$[HB(NH_3)_3][BH_4]_2 + 2Na \longrightarrow H_2 + HB(NH_2)_2 + NH_3 + 2NaBH_4$$

The hydrogen produced is equal to 1.33 equivalents per mole of diborane. All of the foregoing properties have been reported for the "diammoniate II."[1,2] Furthermore its molecular weight in liquid ammonia is consistent with the above formula.[18] However, no direct physical evidence for the structure of the "diammoniate II" is yet available and its nature must still be regarded as subject to revision.

Acknowledgment.—This research was conducted under Contract AF33(616)-8 with the United States Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command.

[18] R. W. Parry, G. Kodama and D. R. Schultz, THIS JOURNAL, **80**, 24 (1958).

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Chemical Evidence for the Structure of the "Diammoniate of Diborane." V. A Tracer Study of the Reaction between Sodium and the "Diammoniate of Diborane"

BY S. G. SHORE, P. R. GIRARDOT AND R. W. PARRY

RECEIVED NOVEMBER 3, 1956

A tracer study of the reaction between sodium and the "diammoniate of diborane" in liquid ammonia, using deuterium as the labeling element, showed that in the low-temperature reactions with sodium only nitrogen–hydrogen bonds were broken; no boron–hydrogen bonds were ruptured. In the room-temperature ammonolysis reaction involving the residues of the sodium reaction, a boron–hydrogen and a nitrogen–hydrogen bond were broken. A rather high separation factor for the isotopes of hydrogen is suggested by the data.

In the preceding paper of this series[1] it was pointed out that the formation of the "diammoniate of diborane" is assured only by a very specific preparative method. Under slightly different conditions it appears to be possible to prepare what might be termed a solution of diborane in ammonia. Under relatively vigorous conditions a material of the same empirical formula as the diammoniate, $B_2H_6 \cdot 2NH_3$, but possessing different chemical properties appears to be formed. This material is named "diammoniate of diborane II."

In an exchange study of the "diammoniate" in ammonia, using deuterium as a tracer, Burg[2] demonstrated that H–D exchange between the solute and solvent occurs only between those hydrogens which were originally bound to nitrogen. His results indicate that the hydrogens which are bound to boron in the "diammoniate" are not sufficiently acidic to form an ammonium salt, since it is known[3] that rapid proton exchange takes place between an ammonium ion and ammonia, even at $-60°$. Burg's work refutes the early diammonium formulation, $(NH_4)_2B_2H_4$ of Stock.[4]

Insofar as exchange experiments can be accepted as a criterion for acidic character, Burg's evidence is convincing; however, his experimental conditions were mild. Of somewhat greater importance in evaluating the models proposed here is information concerning the source of the hydrogen which arises during various phases of reaction. A tracer study of the reaction between sodium and the various forms of the "diammoniate" has been conducted in order to determine whether H–B or H–N bonds are broken during hydrogen evolution.

A Tracer Study of the Reaction of the "Diammoniate of Diborane" with Sodium in Liquid Ammonia.—Since Burg[2] has demonstrated that hydrogen which is bound to boron does not exchange with hydrogen which is attached to nitrogen, the following species of the "diammoniate" may be regarded as being stable in liquid ammonia-h_3 or liquid ammonia-d_3: $B_2D_6 \cdot 2NH_3$, $B_2D_6 \cdot 2ND_3$ and $B_2H_6 \cdot 2ND_3$.[5]

When the classical "diammoniate of diborane" has been prepared under carefully prescribed conditions and when its ammonia solution has been always maintained at $-78°$ or below, it will react with sodium in liquid ammonia to produce one equivalent of hydrogen per mole of "diammoniate."[1] The species which are listed above were allowed to react with sodium in liquid ammonia; the results are summarized in Table I.

The complete absence of deuterium[6] in the gas evolved from the reaction between sodium and $B_2D_6 \cdot 2NH_3$ in ammonia-h_3 (run 2) confirms Burg's contention that the hydrogens which are bound to boron in the "diammoniate" have no acidic character. Even under the comparatively vigorous conditions of this reaction, no boron–hydrogen bonds were broken. However, the reaction between $B_2H_6 \cdot 2ND_3$ and sodium in ammonia-d_3 (run 3) produced gas which was only 77% deuterated. This result could not have arisen from contamina-

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[1] R. W. Parry and S. G. Shore, THIS JOURNAL, **80**, 15 (1958).

[2] A. B. Burg, *ibid.*, **69**, 747 (1947).

[3] C. J. Nyman, Si-Ghang Fung and H. W. Dodgen, *ibid.*, **72**, 1033 (1950).

[4] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[5] For the sake of simplicity, isotopically substituted "diammoniate" will be represented by its empirical formula.

[6] In discussing the tracer studies, the term hydrogen will refer to the elements of atomic number one. Protium and deuterium will refer to its isotopes of mass one and two, respectively.

TABLE I

A TRACER STUDY OF THE REACTION OF THE "DIAMMONIATE OF DIBORANE" WITH SODIUM IN LIQUID AMMONIA

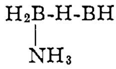
Run[a]	Solvent	Solute	Diborane, mmoles	Reaction time, (cumulative), hr.	Hydrogen equiv. evolved (cumulative) / diammoniate, mmoles	Isotopic analysis, total % D
1	NH_3	$B_2H_6 \cdot 2NH_3$	1.69	1	0.73	0.0
				2	.89	.0
				3	.99	.0
2	NH_3	$B_2D_6 \cdot 2NH_3$	1.87	1	.70	.0
				2	.77	.0
				6	1.00	.0
3	ND_3	$B_2H_6 \cdot 2ND_3$	1.92	2	0.77	74.3
				4	0.91	77.1
				8	1.00	
				14	1.02	
4	ND_3	$B_2H_6 \cdot 2ND_3$	1.95	1	0.51	72.5
				2	.56	73.4
				4	.62	75.7
				20	.86	80.3
				44	.98	81
5	ND_3	$B_2D_6 \cdot 2ND_3$	2.07	2	0.51	69.6
				5	.57	72.3
				27	.79	74.9
				33	.83	75.1
				56	.92	75.7
6	ND_3[b]	$B_2D_6 \cdot 2ND_3$	1.91	1	0.62	
				2	.71	
				4	.75	
				16	.88	
				36	1.00	

[a] In all cases sodium and diborane were used in a 10–15 mole ratio in about 5 ml. of solution at −78°. The concentration of the "diammoniate" was about 0.01 *M*. The diborane-d_6 was about 98% deuterated and the ammonia-d_3 was about 96% deuterated. [b] In an attempt to decrease the reaction time, solid $B_2D_6 \cdot 2ND_3$ was aged for 22 hr. at −78°.

tion of the system because of the elaborate experimental procedures which were employed.[7] Therefore, the possibility of B–H bond rupture in this particular reaction was considered. If the protium which was given off did come about through the rupture of B–H bonds, then one would expect $B_2D_6 \cdot 2ND_3$ to give off gas which is much richer in deuterium. However, the gas which was produced in the reaction between $B_2D_6 \cdot 2ND_3$ and sodium in ammonia-d_3 was about 78% deuterated (average of runs 4 and 5). Since the diborane-d_6 which was used in this latter case was about 96% deuterated and since the hydrogen which is bound to boron does not exchange with hydrogen which is bound to nitrogen,[2] there was insufficient protium in the form of B–H bonds to account for the composition of the gas. Therefore, the most reasonable interpretation of these observations is that the "diammoniate of diborane" reacts with sodium through the rupture of nitrogen–hydrogen bonds only. Since the ammonia-d_3 was about 96% deuterated, it contained N–H as well as N–D bonds. The fact that the evolved gas from $B_2H_6 \cdot 2ND_3$ and $B_2D_6 \cdot 2ND_3$ was greatly enriched in protium is attributed to an isotope effect in which the N–H bond was preferentially ruptured.

In view of the foregoing discussion one might expect "diammoniate" which contains ammonia-d_3 to react more slowly with sodium than "diammoniate" which contains ammonia-h_3. The results are roughly consistent with this expectation. In fact, the reactions of $B_2D_6 \cdot 2ND_3$ with sodium were much slower than any of the other reactions, even when a deliberate attempt was made to increase the rate of hydrogen evolution (footnote *b*, Table I). The reason for the much slower rate in this case is not immediately obvious since differences are greater than might be expected, but the observations appear to be real.

A Tracer Study of the Reaction of Sodium with Solutions of Diborane in Ammonia.—It has been suggested that the so-called solution of diborane in ammonia may be



$$\underset{\displaystyle NH_3}{H_2B\text{-}\underset{|}{H}\text{-}BH_3}$$

This solution produces hydrogen upon reaction with sodium but much more slowly than the "diammoniate." Tracer studies of the reaction with sodium were carried out and the results are presented in Table II.

It was found that the reaction between sodium and a solution of diborane-d_6 in ammonia-h_3 produced essentially pure protium (run 3), but the reaction between sodium and diborane-h_6 in ammonia-d_3 produced hydrogen gas which was about 74% deuterated (average of runs 4, 5 and 6). These observations, with respect to the isotopic composition of the gas evolved, are in complete accord with the tracer studies of comparably deuterated "diammoniate of diborane" and indicate that the rupture of nitrogen–hydrogen bonds is the only source of hydrogen in the reaction.

A Tracer Study of the Reaction of "Diammoniate of Diborane II" with Sodium in Liquid Ammonia.—Based upon its chemical properties and molecular weight in liquid ammonia the "diammoniate II" has been assigned the formula $[HB(NH_3)_3][BH_4]_2$. It reacts with sodium in liquid ammonia to produce around 1.3 equivalents of hydrogen per mole of diborane used in its preparation. This model suggests that only nitrogen–hydrogen bonds should be broken in the reaction with sodium, and the hydrogen which is given off in excess of one equivalent per mole of diborane should not come from the interaction of protonic and hydridic hydrogen, but rather from the direct sodium–cation interaction.

The results of this investigation plus the more recent observations of Jolly[8] are summarized in

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[7] In order to be certain that any protium enrichment in the evolved gas did not arise from the contamination of the system, control experiments were carried out concurrently with the regular tracer studies under identical conditions of handling and analysis. The control experiments consisted of a tracer study of the reaction of sodium with ammonia-d_3 in the presence of a catalyst.

$$Na + ND_3 \xrightarrow[-45°]{Fe_2O_3\text{–}PtO_2} {}^1/_2D_2 + NaND_2$$

There was little, if any, isotopic fractionation. The vapor pressure of the ammonia-d_3 indicated that it was about 97% deuterated, and the samples of gas which were obtained from two separate control experiments were 95.9 and 95.1% deuterated.

[8] W. L. Jolly, Univ. of Calif. Radiation Laboratory, Livermore Site, Livermore, Calif., Contract No. W-7405-eng-48, UCRL-4504 (1955).

TABLE II

A TRACER STUDY OF THE REACTION OF SODIUM WITH SOLUTIONS OF DIBORANE IN AMMONIA

Run	Solvent[a]	Solute	Diborane, mmoles	Sodium/diborane	Reaction time hr.	Reaction temp., °C.	Hydrogen equiv. evolved diborane, mmoles	Isotopic analytical, total % D
1	NH_3	B_2H_6	0.51	1.0	1.8	−81	0.57	0.0
2	NH_3	B_2H_6	2.3	1.02	2.7	−80 to −50	.64	.0
3	NH_3	B_2D_6[b]	1.55	1.00	0.83	−81	.59	.25
4	ND_3[b]	B_2H_6	0.97	1.01	1.7	−79	.50	70.0
5	ND_3	B_2H_6	1.57	0.92	0.67	−79	.59	76.3
6	ND_3	B_2H_6	1.96	10–15	4	−78	.55	74.6
					4.5 weeks[c]	−78	1.04[d]	75.3[d]

[a] About 5 ml. of solution was used in all the reactions. [b] The ammonia-d_3 was about 96% deuterated and the diborane-d_6 was about 98% deuterated. [c] An interval somewhere between 1 and 4.5 weeks may be adequate; 4.5 weeks was simply a matter of experimental convenience. [d] These values represent the total amount of gas given off and the deuterium content of that gas.

TABLE III

A TRACER STUDY OF THE REACTION OF "DIAMMONIATE OF DIBORANE" WITH SODIUM IN LIQUID AMMONIA

Source	NH_3, ml.	B_2D_6, mmoles	$\frac{Na}{B_2D_6}$	Reaction time, (cumulative), hr.	Reaction temp., °C.	Hydrogen equiv. evolved (cumulative) diborane, mmoles	Isotopic analysis, total % D
This investigation[a]	5	2.06	10–15	0.75	−78	0.65	0.0
				3	−78	0.94	.0
				21	−78	1.13	.0
Jolly[b]	15	1.42	4.3	0.33	−64	1.28	0.0

[a] In this investigation diborane was added to ammonia in the usual fashion for preparing the "diammoniate," but the excess ammonia was removed at −45° and the solid was stored at −45° for 5 hr. [b] Jolly prepared "diammoniate II" through the rapid addition of diborane to ammonia above −78°.

Table III. In agreement with the model which is proposed for the "diammoniate II" the results show that all the hydrogen which is given off in the reaction with sodium, even that which is in excess of one equivalent per mole of diborane, arises from the rupture of nitrogen–hydrogen bonds.

Ammonolysis Reactions.—Schaeffer, Adams and Koenig[9] report that the non-volatile products from the reaction of the "diammoniate of diborane" with sodium in liquid ammonia are sodium borohydride and $(H_2NBH_2)n$. They observed that this residue reacts with ammonia at temperatures above −78°; hydrogen gas is produced. This reaction was noted also in this Laboratory. After the reaction with sodium had taken place, all the solvent ammonia was sublimed away at −78° and the reactor was warmed to room temperature. Only small quantities of hydrogen were split out from the solid residue; however, when gaseous ammonia was introduced above this solid, hydrogen evolution at room temperature was rapid. The maximum amount of hydrogen which was obtained from the reaction with ammonia was 3.10 equivalents per mole of diborane, or a total of 4.10 equivalents including the quantity of gas which was given off in the reaction with sodium.

A tracer study of the reaction between ammonia and the residue from the "diammoniate"–sodium reaction demonstrated, unequivocally, that hydrogen is produced through the interaction of acidic hydrogen which is bound to nitrogen and a hydridic hydrogen which is bound to boron. The results are summarized in Table IV. It should be noted in run 1 that D from N–D bonds reacted with H from B–H bonds to form HD which was identified through the use of a mass spectrometer. Furthermore, it is of interest to point out that the residue from the "diammoniate II"–sodium reaction undergoes ammonolysis also. The hydrogen which was given off in run 3 was 50% deuterated,[10] presumably HD.

TABLE IV

AMMONOLYSIS REACTIONS

Run	Residue from	Ammonia	Isotopic compn. o gas produced, total % D	% HD
1	$B_2H_6 \cdot 2ND_3$	ND_3	49.4	88.2
2	$B_2D_6 \cdot 2ND_3$	ND_3	97	
3	$B_2D_6 \cdot 2NH_3$ (II)	NH_3	47	

Discussion

The results of this investigation are in accord with the models which have been proposed for the "diammoniate of diborane" and "diammoniate of diborane II." The reactions with sodium in liquid ammonia take place through the rupture of nitrogen–hydrogen bonds only and may be represented as

$$[H_2B(NH_3)_2]BH_4 + Na \longrightarrow {}^1/_2H_2 + NaBH_4 + H_2NBH_2 + NH_3$$

$$[HB(NH_3)_3][BH_4]_2 + Na \longrightarrow H_2 + 2NaBH_4 + (H_2N)_2BH + NH_3$$

The production of hydrogen in the reaction of sodium with a solution of diborane in ammonia comes from the rupture of nitrogen–hydrogen bonds.

The isotope effect which occurred when ammonia-d_3 was the coördinated ligand (*e.g.*, $B_2D_6 \cdot 2ND_3$) arose from the fact that since the ammonia-d_3 was not completely deuterated, it contained N–H bonds which were ruptured preferentially over the

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(9) G. W. Schaeffer, M. D. Adams and F. J. Koenig, THIS JOURNAL, **78**, 725 (1956).

(10) This sample was analyzed by a thermal conductivity technique which gives the total % D.

N–D bonds. Since all the nitrogen hydrogen bonds in the system, including solvent ammonia-d_3, were not ruptured in the reaction with sodium, the evolved gas was enriched in protium. The calculation of an instantaneous separation factor[11] α_0 seemed to be attractive, but the complexity of the system and the large errors which are introduced by the comparatively small errors in hydrogen analysis have made its value uncertain. The best estimate is 17 ± 4.[12]

The presence of the isotope effect implies that the rate-determining step in the process is the rupture of the nitrogen–hydrogen bond. In contrast to the regular tracer studies, the control reaction[7] in which sodium reacted with ammonia in the presence of a catalyst showed little evidence of an isotope effect, which implies that the slow step of the reaction is not the rupture of the nitrogen–hydrogen bond.

Schaeffer, Adams and Koenig[9] report that ammonia attacks polymeric aminoborine in the ammonolysis reaction of the non-volatile residue from the sodium–"diammoniate" reaction. They represent the reaction, empirically, as

$$H_2NBH_2 + xNH_3 \longrightarrow BH_{2-x}(NH_2)_{1+x} + xH_2$$

This is in accord with the tracer study.

Experimental[13]

1. Ammonia—commercial tank NH_3 was dried and stored over sodium metal in the vacuum system.

Mg_3N_2 was prepared by passing pure, dried nitrogen gas for 12 hr. over 20 g. of highest purity Dow magnesium metal which was heated to 650° in a stainless steel tubular furnace. The Mg_3N_2 was then transferred as rapidly as possible to a 125-ml. round-bottom flask which was connected to the vacuum system. ND_3 was prepared through the action of D_2O (*ca.* 99% deuterated) upon Mg_3N_2 at room temperature. The ND_3 was purified by sublimation at −78° and by drying it over distilled sodium metal. Its vapor pressure indicated that it was about 97% deuterated.

Obsd. vapor pressure (cor.): 110.2 mm. at −63.5°; 354.2 mm. at −45.2°. Reported[14] vapor pressure (cor.) for ND_3, 98% deuterated: 109.7 mm. at −63.5°; 353.8 mm. at −45.2°.

The hydrogen which was obtained from the control reactions

$$Na + ND_3 \xrightarrow{Fe_2O_3\text{–}PtO_2} {}^1/_2D_2 + NaND_2$$

was between 96 and 95% deuterated. The latter value probably represents a lower limit on the purity of the ND_3.

2. Diborane—B_2H_6 was prepared from BF_3 etherate and $LiAlH_4$.

B_2D_6 was prepared from $LiAlD_4$ and BF_3 etherate. The $LiAlD_4$ was prepared *in situ* from LiD and $AlCl_3$ in ether. A small quantity of $LiAlD_4$ served to initiate the $LiAlD_4$ synthesis. Both the LiD and $LiAlD_4$ were obtained from Metal Hydrides, Inc., Beverly, Mass. The yield of B_2D_6 was about 80% of theory. Its vapor pressure was in excellent agreement with the only reported value for B_2D_6.[15]

Obsd. vapor pressure (cor.): 238.3 mm. at −111.9°. Reported vapor pressure (cor.) for B_2D_6, 98% deuterated: 238.3 mm. at −111.9°.

Further evidence for the purity of the B_2D_6 was given through its quantitative hydrolysis.

$$B_2D_6 + 6H_2O \longrightarrow 6HD + 2H_3BO_3$$

The gas obtained was 48.5% D.

3. Sodium—all the sodium which was used in the tracer studies was distilled *in vacuo* at about 480°. The distilled metal, still *in vacuo*, was then warmed and allowed to run into small glass balls (1.5–2 cm.³) which were then sealed off.

4. Catalytic mixed oxides for the control reaction between sodium and ammonia-d_3—reagent grade $Fe(NO_3)_3 \cdot 9H_2O$ was decomposed, thermally, at 300°. The resultant Fe_2O_3 was heated at 700° for two days in order to remove traces of water. The mass was then pulverized. About 10% by weight of PtO_2 was thoroughly mixed with the Fe_2O_3 and the mixture was heated for another day at 700°. About 0.2 g. of the hot catalyst was transferred to a bulb crusher-reactor on the vacuum system. The catalyst was heated *in vacuo* at 300–400° (at least 24 hr.) until it was used.

Procedures.[13]—A high vacuum system was used throughout. All the stopcocks and joints which had to be rotated were greased with Apiezon N; all the stationary joints were sealed with Apiezon W. The system was provided with space for two bulb-crusher reactors[13] so that a tracer study and a control experiment could be carried out simultaneously.

The procedures which were used in the tracer studies were essentially the same as those which have been used previously[1] except that great care was taken to prevent contamination of ammonia-d_3 by H–D interchange which can arise from the presence of impurities containing active protons. In order to minimize errors due to this source, the system was conditioned as described below.

The vacuum system, with the bulb crushers in place, was out-gassed for one day under high vacuum; then a small amount of D_2O, in the vapor phase, was admitted to the system and allowed to equilibrate, for one day, with the active hydrogen of the residual impurities. Following equilibration the system was again out-gassed under high vacuum for a minimum of three days. This procedure guaranteed that any traces of impurities would be rich in deuterium and thus would not seriously contaminate the highly deuterated ammonia. Once the system was conditioned it was never opened until a given run was completed.

In a typical tracer run a control experiment was set up in one bulb-crusher reactor. This amounted to maintaining a sodium–ammonia-d_3 solution in the presence of the mixed-oxides catalyst at −45°. The regular tracer experiment was set up in the second reactor. After the control had produced a significant quantity of hydrogen, it was quenched by immersing the reactor in liquid nitrogen. The hydrogen was freed of traces of ammonia-d_3 by passing it through a U-trap which was packed with glass helices and immersed in liquid nitrogen. Then the gas was passed into a sample bulb and into a previously calibrated thermal conductivity cell for H–D analysis. After the gas was analyzed, the stopcock on the sample bulb was closed and the system was evacuated. The sample bulb was sealed off at the constriction. The gas in the sample bulb was submitted to mass-spectrometer analysis in order to cross-check the thermal conductivity method.

The same procedure was followed in the regular tracer experiment. At various intervals the reaction was quenched, the hydrogen was freed of traces of ammonia and the gas was passed into a sample bulb and the thermal conductivity cell for H–D analysis. Since the volume of the system was known, the amount of hydrogen gas which was produced in the reaction could be determined from *PVT* measurements.

Analytical.—The magnitude of the isotope effect observed made it possible to use a relatively simple thermal conductivity technique for analyzing the H–D gas mixtures. The particular procedure which was used was patterned after that of Peri and Daniels[16] with a few modifications.[13] Several of the analyses were cross-checked by mass spectrometer analyses; the agreement was very good. The precision of individual measurements, for the most part, was within 1% D. Considering the good agreement between analyses which were obtained by both mass analysis and thermal conductivity techniques and considering the general con-

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[11] $\alpha_0 = \dfrac{\text{H/D (hydrogen evolved)}}{\text{H/D (ammonia-}d_3\text{ ligand)}}$ at zero extent of reaction.

[12] Details concerning its estimation and the complexity of the system are summarized in the doctoral dissertation of S. G. Shore, Univ. of Mich., Ann Arbor, Michigan, 1956.

[13] Details of experimental procedure and techniques may be found in the doctoral dissertation of S. G. Shore, Univ. of Mich., Ann Arbor, Mich., 1956.

[14] I. Kirschenbaum and H. C. Urey, *J. Chem. Phys.*, **10**, 706 (1942).

[15] A. B. Burg, THIS JOURNAL, **74**, 1340 (1952).

[16] J. B. Peri and F. Daniels, *ibid.*, **72**, 424 (1950).

sistency of the results, it is believed that the accuracy of the thermal conductivity technique was well within 3% D in the range 50–100% D.

Acknowledgment.—This research was conducted under Contract AF33(616)-8 with the United States Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command.

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Molecular Weight Measurements in Liquid Ammonia. The Molecular Weights of the Methylamine–Boranes, the "Diammoniate of Diborane," Ammonia–Boron Trifluoride and other Substances

BY R. W. PARRY, G. KODAMA AND D. R. SCHULTZ

RECEIVED NOVEMBER 3, 1956

Molecular-weight measurements in liquid ammonia by vapor-pressure depression show that H_3NBF_3, MeH_2NBH_3, Me_2HNBH_3 and Me_3NBH_3 are all monomeric in liquid ammonia under conditions comparable to those used for studying the "diammoniate of diborane" prepared at −78.5°, but a higher value above 80 is indicated for the diammoniate prepared at −45°. The conversion of H_3NBF_3 to NH_4BF_4 in water solution is noted.

The original problem associated with the formulation of the ammonia–diborane addition compound arose from the early observation of Stock and Pohland[1] showing that the product corresponded to the formula $B_2H_6 \cdot 2NH_3$ in liquid ammonia. Rathjens and Pitzer[2] reported that freezing-point depression measurements confirmed the conclusions of Stock and Pohland[1]; however, recent work[3] has shown that the technique which Rathjens and Pitzer used does not produce the so-called classical "diammoniate" in liquid ammonia.

Although the "diammoniate of diborane" has long been considered to be unique among the boron hydride addition compounds, no molecular-weight measurements on H_2MeNBH_3, HMe_2NBH_3, Me_3NBH_3 or H_3NBF_3 have been carried out under conditions comparable to those used in the study of the diammoniate, hence the generality of the "diammoniate" structure under low-temperature conditions remains undetermined.

A study of molecular weights in liquid ammonia was undertaken: 1, to check the validity of Stock's observations as to the molecular weight of an authentic sample of the "diammoniate"; 2, to check the molecular weights of other better-known ionic solids in liquid ammonia in order to provide a frame of reference for interpretation; and 3, to check the molecular weights in liquid ammonia of methylamine–borane, dimethylamine–borane, trimethylamine–borane and ammonia–boron trifluoride.

These compounds had not been measured under conditions comparable to those used in studying the "diammoniate," hence a real question existed as to their nature in relation to the "diammoniate."

Experimental

A. Materials.—Commercial amines (Eastman Kodak Co.) were distilled through a low-temperature fractionating column at 400 mm. pressure and dried over sodium metal before use.

Commercial $NaBH_4$ (Metal Hydrides) was placed on the sintered glass frit of a vacuum-line extraction apparatus and extracted directly into the molecular-weight apparatus with liquid ammonia.

NH_4Br, reagent grade, was dried at 80° for 3 hr. then stored over $Mg(ClO_4)_2$ before use.

Ammonia–boron trifluoride was prepared by the interaction of dry NH_3 and commercial tank BF_3 which had been passed through a B_2O_3–H_2SO_4 mixture. A one-liter, three-necked flask cooled in ice-water served as the reaction vessel. The solid product was placed on a sintered glass frit and leached into the molecular-weight vessel with liquid ammonia. Ammonia analysis of the product gave 20.01% as compared to 20.05% theoretical for H_3NBF_3. An X-ray powder pattern of the solid checked the pattern reported by Keenan and McDowell,[4] by Koenig[5] and by Jenkins,[6] but not the pattern reported by Laubengayer and Condike.[7] It was also found that H_3NBF_3 was converted to NH_4BF_4 under conditions of this experiment by slow crystallization from water at room temperature. Isolation of crystalline NH_4BF_4 from the solution and precipitation of $As(C_6H_5)_4BF_4$ from the water solution indicated the change.

An X-ray powder pattern of H_3NBF_3 taken before and after the molecular-weight measurement in liquid ammonia showed that the sample had not changed on standing in liquid ammonia at −40°. No lines for NH_4BF_4 were found in the product. The observation confirms a similar report by Jenkins.[6]

The "diammoniate of diborane" was prepared in accordance with standard procedures described elsewhere.[3] The trimethylamine–borane was prepared by Dr. T. C. Bissot from diborane and trimethylamine, using standard procedures. Its observed melting point of 93° (lit., 94°) and the analytical hydridic H/B ratio of 3.03/1.00 establish its identity.

Dimethylamine–borane was prepared by condensing diborane and excess dimethylamine in a reactor at −160°. The system was allowed to warm up very slowly. At 0° excess amine was removed. The ratio of amine used in reaction to diborane consumed was 1.95/1.

Monomethylamine–borane was prepared from pure methylamine and diborane according to standard procedures. Although no analyses were run to confirm the identity of this material, it was noticed that when a small sample was warmed from ice temperature to room temperature, it melted just above ice temperature evolving a gas. The reported melting point of the compound is 5–10°.[8]

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