[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

Disproportionation Reactions of the Dimethylaminoboron Hydrides

BY ANTON B. BURG AND CARL L. RANDOLPH, JR.[1]

The vapor-phase monomer–dimer equilibrium of $(CH_3)_2NBH_2$ is accompanied by the reversible disproportionation $3(CH_3)_2NBH_2 \rightleftarrows [(CH_3)_2N]_2BH + (CH_3)_2NB_2H_5$. Data on the extent of this reaction are used to correct the monomer–dimer equilibrium data to give the new free-energy equation $\Delta F_T{}^0 = 20.74 - 0.0509\ T$ (kcal./mole dimer). More extensive disproportionation of $(CH_3)_2NBH_2$ occurs if either $(CH_3)_3N$ or NaH is used to remove BH_3 groups. On heating $(CH_3)_2NBH_2$ with $(CH_3)_3N$, some $[(CH_3)_2N]_3B$ is obtained, and the new and unexpectedly volatile but unstable compound $(CH_3)_2NBH_2{\cdot}N(CH_3)_3$ is observed. The compounds $[(CH_3)_2N]_2BH$ and $[(CH_3)_2N]_3B$ are obtainable in pure form by aminolytic methods; new m.p. and volatility data are presented. Both react with diborane to form $(CH_3)_2NBH_2$, $(CH_3)_2NB_2H_5$, a copolymer of $(CH_3)_2NBH_2$ with $[(CH_3)_2N]_2BH$, and complex intermediates. Aluminum borohydride reacts with $(CH_3)_2NBH_2$ to form $(CH_3)_2NB_2H_5$ and apparently aminoborohydrides of aluminum. These are violently attacked by air or moisture, and react with diborane to form $(CH_3)_2NB_2H_5$ and aluminum borohydride.

The ability of the B–H bond to exchange for the $(CH_3)_2N$–B linkage in a dimethylaminoboron hydride has been indicated in the reaction between boron trifluoride and N,N-dimethylaminoborine.[2] Further examples of the same principle now are offered by the new reactions

$$3(CH_3)_2NBH_2 \rightleftarrows [(C_3H)_2N]_2BH + (CH_3)_2NB_2H_5 \qquad (1)$$

$$2(CH_3)_2NBH_2 + (CH_3)_3N \rightleftarrows [(CH_3)_2N]_2BH + (CH_3)_3NBH_3 \qquad (2)$$

$$3[(CH_3)_2N]_2BH + (CH_3)_3N \rightleftarrows 2[(CH_3)_2N]_3B + (CH_3)_3NBH_3 \qquad (3)$$

$$2(CH_3)_2NBH_2 + NaH \longrightarrow NaBH_4 + [(CH_3)_2N]_2BH \qquad (4)$$

$$2[(CH_3)_2N]_2BH + 3B_2H_6 \longrightarrow 4(CH_3)_2NB_2H_5 \qquad (5)$$

$$2[(CH_3)_2N]_2BH + B_2H_6 \longrightarrow 4(CH_3)_2NBH_2 \qquad (6)$$

$$2[(CH_3)_2N]_3B + 5B_2H_6 \longrightarrow 6(CH_3)_2NB_2H_5 \qquad (7)$$

$$2[(CH_3)_2N]_3B + 2B_2H_6 \longrightarrow 6(CH_3)_2NBH_2 \qquad (8)$$

These reactions were demonstrated by quantitative experiments in which the products were isolated by fractional condensation in the high-vacuum apparatus. An incidental by-product was the unstable and curiously volatile new compound $(CH_3)_2NBH_2.N(CH_3)_3$. It was also noted, in exploratory experiments, that $(CH_3)_2NBH_2$ reacts with aluminum borohydride to form aminoborohydrides, a fuller study of which is now in course.

Reaction (1) is very slow and incomplete at ordinary temperatures, but above 80° it proved to be sufficiently rapid and extensive to cause serious errors in any study of the vapor-phase association of $(CH_3)_2NBH_2$, such as that reported by Wiberg, Bolz and Buchheit.[3] It was feasible, however, to obtain good pressure data (0.01 mm. precision) describing the slightly disturbed equilibria at various temperatures, and to use such data in rougher determinations of the equilibrium constant of reaction (1); the results then were used for correction of the original data for the effects of reaction (1). The corrected data agreed very well with the assumption that $(CH_3)_2NBH_2$ associates only to the dimer form in the vapor phase—as suggested but not clearly proved by the earlier workers.[3]

Reaction (2) offers a means of carrying reaction (1) nearly to completion, at the expense of the $(CH_3)_2NB_2H_5$ which, if formed, would react with trimethylamine to give $(CH_3)_3NBH_3$ and $(CH_3)_2NBH_2$.[2] The opposite way of carrying reaction (1) forward—by a BF_3 reaction to remove $[(CH_3)_2N]_2BH$—was indicated before.[2]

Reaction (3) was observed as a further stage of reaction (2), giving a very small yield of $[(CH_3)_2N]_3B$ after extended heating at 140°. Reaction (4) is related to (2), in the sense that hydride ion serves as the base, holding a BH_3 group just as trimethylamine does. It occurs fairly readily at 110°, but the corresponding reaction with lithium hydride does not occur under similar conditions.

Reactions (5) and (6) are ostensibly two stages of the same process, but it is notable that some $(CH_3)_2NB_2H_5$ is formed at −58°, along with materials which seem to be borine complexes and which precede the formation of any observable $(CH_3)_2NBH_2$. Another intermediate stage is the formation of a 10:1 copolymer of $(CH_3)_2NBH_2$ with $[(CH_3)_2N]_2BH$. This is a non-volatile solid, apparently similar to the copolymer recognized by Wiberg and Bolz.[4] Like the rest of the mixture, it is converted entirely to $(CH_3)_2NB_2H_5$ by heating with diborane at 85° or higher.

Reactions (7) and (8) are very like (5) and (6), having similar intermediate steps and reaction conditions. The potential reversibility of all four of these reactions is demonstrated by reactions (2) and (3).

Experimental Part

I. The Vapor Phase Association of N,N-Dimethylaminoborine, and Reaction (1)

Pressure Measurements on Unsaturated Vapor.—N,N-Dimethylaminoborine was purified by recrystallization from pentane (under dry nitrogen) and subsequent resublimation in the high-vacuum apparatus. The various samples were weighed to 0.05 mg. precision and completely sublimed into an immersible tensimeter, similar to that described before,[5] except that the vacuum arm contained a trap for mercury vapor,[6] and the spherical bulb was replaced by a vertical cylinder. This shape permitted the use of horizontal-sheet light (from a fluorescent lamp shining through a stack of black horizontal plates) to give an accurate silhouette of the mercury levels. The bath temperature (range 40–140°) was controlled to 0.1° and measured by Bureau of Standards thermometers. The pressures were observed by means of a micrometer-scale cathetometer to 0.01 mm. The volume of the tensimeter chamber was determined by comparison

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(1) The precision measurements of the vapor-phase equilibrium pressures of N,N-dimethylaminoborine, and experiments on its reactions with sodium hydride and with aluminum borohydride, are reported (in more detail) in Dr. Randolph's Ph.D. dissertation (University of Southern California Libraries, June, 1949), the major contents of which were summarized in an earlier paper, reference (2).

(2) Burg and Randolph, THIS JOURNAL, **71**, 3451 (1949).

(3) Wiberg, Bolz and Buchheit, *Z. anorg. Chem.*, **256**, 285 (1948).

(4) Wiberg and Bolz, *ibid.*, **257**, 131 (1948).

(5) Burg and Schlesinger, THIS JOURNAL, **59**, 785 (1937).

(6) Brown, Taylor and Gerstein, *ibid.*, **66**, 432 (1944).

TABLE I

DETERMINATIONS OF THE EQUILIBRIUM CONSTANT k, FOR REACTION (1)

Weight (mg.) of $(CH_3)_2NBH_2$	397.2	431.9	435.0	224.4	229.1	347.6	480.0	416.9	325.0
t, °C.	107.0	106.6	106.5	106.6	106.6	129	128	129	128
Time, hr.	181	14	11	22	12	12	61	3	1
Bulb vol., cc.	240.0	237.0	237.0	240.0	233.8	240.0	237.0	233.9	233.8
Vol. $(CH_3)_2NB_2H_5$, cc. gas at S.C.	5.60	6.25	5.75	3.35	3.75	8.05	9.80	9.71	8.60
p_0, atm.	0.4043	0.4438	0.4519	0.2329	0.2349	0.3705	0.4947	0.4253	0.3211
d, atm.	0.03248	0.03667	0.0337	0.01992	0.02230	0.0494	0.0607	0.0612	0.0540
P, atm.	0.10905	0.1179	0.1178	0.1179	0.1179	0.07128	0.07057	0.07128	0.07057
P_0, atm.	0.07303	0.0800	0.0800	0.0800	0.0800	0.03958	0.03947	0.03958	0.03947
p, atm.	0.5070	0.5505	0.5593	0.3062	0.3086	0.558	0.709	0.633	0.488
D, atm.	0.0059	0.0068	0.0062	0.0065	0.0071	0.0032	0.0031	0.0034	0.0039
K, atm.	0.141	0.135	0.134	0.135	0.135	0.770	0.660	0.796	0.763
k, atm.$^{-1}$	0.120	0.138	0.115	0.126	0.155	0.046	0.047	0.052	0.078

with a water-calibrated bulb of similar size, using pure carbon dioxide as the reference gas.

The preliminary values of the equilibrium constant, for the dimer dissociating to monomer, were computed from the definition $K = 4(p - p_0)^2/(2p_0 - p)$, where p is the total pressure (atmospheres), and p_0 is the pressure to be expected if the vapor were all $[(CH_3)_2NBH_2]_2$. Plotting log K against $1/T$ gave a well-defined line, having such a pronounced downward concavity as to demand an interpretation other than a pure dimer–monomer equilibrium. The presence of a trimer was discounted by the purely dimeric value of the molecular weight in freezing benzene; hence new impurities were sought in the heated samples. Thus the decomposition reaction (1) was discovered, and found to account for as much as 15% of the sample.

The Decomposition Reaction.—Reaction (1) is illustrated by an experiment in which 397.2 g. of pure $(CH_3)_2NBH_2$, after a week in a sealed 240.0-cc. bulb at 105.8°, was resolved into 5.60 cc. (gas at S.C.) of $(CH_3)_2NB_2H_5$, 5.70 cc. of $[(CH_3)_2N]_2BH$, 347.6 mg. of $(CH_3)_2NBH_2$, and a trace of non-volatile solid. This solid appears to be similar to the polymer which was observed as an important intermediate in reactions (5)–(8); hence it would account for the slightly low recovery of $(CH_3)_2NBH_2$. It is clear, however, that the main reaction, occurring to the extent of 12%, was $3(CH_3)_2NBH_2 \rightarrow [(CH_3)_2N]_2BH + (CH_3)_2NB_2H_5$. The reverse reaction was tested by heating together 3.76 cc. each of $(CH_3)_2NB_2H_5$ and $[(CH_3)_2N]_2BH$ for 12 hours at 108°; the result was a 90% yield of $(CH_3)_2NBH_2$.

The decomposition reaction was observed also in a sample of $(CH_3)_2NBH_2$ which had remained for 5 months at room temperature. This sample had been a fractionating-column residue, containing a less-volatile impurity but none of the (more volatile) products of reaction (1). A highly purified sample, in contact only with Pyrex glass and Apiezon grease L for 6 months at room temperature, showed no decomposition; hence it appears that the decomposition at room temperature may require a catalytic impurity.

The Decomposition Equilibrium.—In order to obtain further data for evaluation of the equilibrium constants of reaction (1) at various temperatures, weighed samples of $(CH_3)_2NBH_2$ were heated in bulbs of known volume, in a bath near 106.7° or 128.5° for varying lengths of time; then the bulbs were cooled suddenly to −196° and the contents separated by a meticulous process of resublimation and fractional condensation *in vacuo*. The $[(CH_3)_2N]_2BH$ never could be obtained quite pure, and the recovery of $(CH_3)_2NBH_2$ never was quite satisfactory; hence the yield of $(CH_3)_2NB_2H_5$ (easily isolated and purified) was taken as the measure of the formation of the bis-compound, and the depletion of $(CH_3)_2NBH_2$.

In the experiments at 106.5°, it was found that a 3-hour heating period was insufficient for complete equilibrium, but far shorter periods were adequate at 128°.

The equilibrium constant for reaction (1) was defined as $k = BD/M^3$, where B, D and M are the partial pressures (in atm.) of $[(CH_3)_2N]_2BH$, $(CH_3)_2NB_2H_5$ and the monomeric $(CH_3)_2NBH_2$, respectively. The values of k and K thus were mutually dependent, but could be evaluated by making the assumption (later justified by the results) that the vapor of $(CH_3)_2NBH_2$ exists only as monomer and dimer, and deriving from the definitions of k and K a general set of simultaneous equations, of the form

$$8(p - p_0)^3k = d^2 \qquad \text{(a)}$$

$$4(p - p_0)^2 = K(2p - p_0) \qquad \text{(b)}$$

$$[2(P - P_0) - D]^3k = D^2 \qquad \text{(c)}$$

$$[2(P - P_0) - D]^2 = K(2P_0 - P - D) \qquad \text{(d)}$$

Equations (a) and (b) refer to the experiments in which the equilibrated bulb-contents were analyzed: p is the unknown total pressure; p_0 is the pressure calculated for pure dimer; and d is the partial pressure of either $[(CH_3)_2N]_2BH$ or $(CH_3)_2NB_2H_5$. Equations (c) and (d) represent the precision pressure experiments: P and P_0 are as previously defined and D is the unknown partial pressure of either product of the decomposition reaction (1).

The values of p_0 and d from the nine most trusted decomposition experiments, taken with the values of P and P_0 from tensimeter experiments at the same temperatures, determined nine sets of these simultaneous equations, from which consistent values of the four variables p, k, D and K were obtained by successive approximations.[7] The data and results are presented in Table I.

Calculations of K.—The average k values from Table I, namely, 0.131 at 106.7° and 0.056 at 128.5°, determined the equation $\log_{10} k = (2558/T) - 7.620$. With this as a rough basis for estimating k at any temperature corresponding to useful data,

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[7] The method was as follows: (1) insert a reasonable value of K into equation (b) and, p_0 being known, solve for p: (2) evaluate k from equation (a); (3) solve equation (c) for D, knowing k, P and P_0; (4) solve equation (d) for K and compare with the postulated value. The true value of K always fell between the postulated and calculated values; for the present series of data, nearest to the latter. The process was repeated with better and better values of K until the postulated and calculated values were the same; then the corresponding values of p, k and D were taken as correct. The method succeeded because, with the available data, each equation had only one real and positive root.

TABLE II

FINAL DETERMINATIONS OF K FOR DISSOCIATION OF $[(CH_3)_2NBH_2]_2$

Sample number	t, °C.	P, atm.	P_0, atm.	k, calcd.	D, atm.	K, atm.	K, calcd.
9	41.5	0.02419	0.02240	3.23	0.00033	0.00052	0.00052
1	52.6	.05082	.04670	....	.....	.00159	.00162
9	53.4	.02649	.02325	1.63	0.00058	.00179	.00176
8	54.0	.03440	.03053	1.58	.00074	.00189	.00186
9	58.8	.02772	.02363	1.22	.00071	.00296	.00296
8	63.8	.03756	.03143	0.935	.00114	.00488	.00471
2	63.9	.07283	.06745	....	.....	.00461	.00476
9	65.2	.02935	.02409	0.871	0.00088	.00518	.00536
5	66.5	.04558	.03866	....	.....	.00604	.00603
9	71.1	.03113	.02451	0.646	0.00108	.00879	.00909
8	71.4	.04032	.03215	.637	.00145	.00985	.00934
2	75.7	.08049	.06701	....	.....	.0136	.0136
9	77.9	.03343	.02500	0.462	0.00132	.0159	.0164
5	78.8	.05136	.04003	....	.....	.0179	.0177
8	79.9	.04389	.03293	0.422	0.00185	.0200	.0194
8	88.6	.04787	.03374	.282	.0022	.0391	.0394
1	97.5	.07720	.05312	.191	.0040	.0781	.0788
1	112.2	.08991	.05522	.104	.0052	.269	.231
2	117.1	.11976	.07497	.0860	.0070	.294	.324
4	117.5	.06571	.03846	.0847	.0034	.333	.333
5	118.1	.07534	.04451	.0828	.0040	.343	.347
4	127.9	.07056	.03947	.0573	.0034	.695	.666
6	140.3	.07746	.04153	.0368	.0034	1.478	1.453
..	106.7	Averages from Table I		.131	.....	0.136	0.156
..	128.5	Averages from Table I		.056	.....	.747	.692

it became feasible to compute correct K values from properly selected pressure data. Each datum was selected in terms of its history: thus all measurements above 117° (2 to 3-hour equilibration), or pressures measured after some hours at 60° or higher, following measurements at higher temperatures, were considered valid for correction by means of the k values. On the other hand, some pressure data on pure samples, heated quickly to temperatures not over 80° and measured at once, were regarded as valid without correction; in fact, the K values directly calculated from these were in good agreement with those derived from corrected data.

Table II summarizes the accepted pressure data and the final results. The data which did not require correction may be recognized by the absence of k and D values. The results determine the equation $\log_{10} K_{(\text{atm.})} = 11.126 - (4533/T)$, from which the final column of Table II was calculated. This implies that $\Delta F^0{}_T = 20.74 - 0.0509T$ kcal., or $\Delta F^0{}_{298.16} = 5.56$ kcal. for the dissociation of one mole of dimer. The reasonable agreement between the log K equation and the data, in each range of temperature, speaks well for the assumption that the monomer–dimer equilibrium of $(CH_3)_2NBH_2$ is not seriously disturbed except by reaction (1).

II. Reactions (2), (3) and (4); the Complex $(CH_3)_2NBH_2 \cdot N(CH_3)_3$

Base-Driven Decompositions of the Aminoborines.—Reaction (2) was first realized by an experiment in which 1.683 g. of $(CH_3)_2NBH_2$ (662 cc. monomer gas at S.C.) and 317 cc. (0.480 volume) of $(CH_3)_3N$ were heated 19 hours in a bomb-tube at 140°. After slow cooling, the tube-contents were separated as well as possible and, assuming that the resulting $[(CH_3)_2N]_2BH$ contained an unremovable 5 mole per cent. of $(CH_3)_2NBH_2$ (*cf.* section III), it appeared that 484 cc. of $(CH_3)_2NBH_2$ and 242 cc. of $(CH_3)_3N$ had reacted to form 240 cc. of $[(CH_3)_2N]_2BH$ and 239 cc. of $(CH_3)_3NBH_3$, in good agreement with equation (2).

Reaction (3) was observed by reheating the sample of $[(CH_3)_2N]_2BH$ from the preceding experiment, first with 75 cc. of $(CH_3)_3N$ for 35 hours at 140°, and then with 245 cc. of $(CH_3)_3N$ for 9 days at 140°, yielding 18 cc. of $(CH_3)_3NBH_3$, a purified sample of $[(CH_3)_2N]_2BH$ (as judged by its vapor tensions; *cf.* section III), and 1.6 cc. (gas at S.C.) of a liquid having vapor tensions of 1 mm. at 0°, 3.4 mm. at 21.5°, and 10.2 mm. at 39.3°—values accurately corresponding to $[(CH_3)_2N]_3B$, as presented in section IV.

Reaction (4) was demonstrated by an experiment in which a portion of sodium hydride estimated as 9 mmoles (du Pont sample, finally ground under dry nitrogen) and 25.747 mmoles of pure $(CH_3)_2NBH_2$ were heated together in a 10 ml. bomb-tube, for 72 hours at 110°, with occasional shaking. The volatile contents then were determined to be 8.939 mmoles of nearly pure $[(CH_3)_2N]_2BH$ and 6.807 mmoles of $(CH_3)_2NBH_2$. This meant that 18.9 mmoles of $(CH_3)_2NBH_2$ and 9 mmoles of NaH had reacted to form 8.9 mmoles of $[(CH_3)_2N]_2BH$, and the reaction balance required that the white solid residue be almost 9 mmoles of nearly pure $NaBH_4$. Similar experiments with lithium hydride showed no reaction at all.

Discovery of $(CH_3)_2NBH_2 \cdot N(CH_3)_3$.—Attempts to determine the vapor-phase equilibrium constant of reaction (2), at 122, 156 and 200°, by heating known samples of the reactants together in sealed containers and isolating the products and unused reactants, gave results seriously out of agreement with the van't Hoff equation. The difficulty was understood when it was found that portions of the otherwise unused trimethylamine and $(CH_3)_2NBH_2$ were contained in a new substance which separated from the $[(CH_3)_2N]_2BH$ by passing a trap at −60°, and from the trimethylamine by condensing in a trap at −78°. The new product proved to be stable enough for repetition of this process of purification without appreciable loss, but at higher temperatures it decomposed so rapidly that no melting point nor vapor tensions could be measured. One sample, upon complete resolution, yielded 5.3 cc. (gas at S.C.) of trimethylamine and 14.6 mg. (5.7 cc. monomer gas) of $(CH_3)_2NBH_2$, nearly free of $[(CH_3)_2N]_2BH$. The substance thus was composed according to the formula $(CH_3)_2NBH_2 \cdot N(CH_3)_3$, which doubtless also represents its molecular weight.

Such an addition complex might have been expected to have such high internal dipole effects as to be only very slightly volatile at room temperature. Actually, it seems to be a little more volatile than the structurally most comparable hydrocarbon, 2,2,4-trimethylpentane. It would be difficult to account for such volatility on the basis of reversible dissociation during the process of fractional condensation *in vacuo*, for it condenses at −78° without loss of trimethylamine, and passes −60° without condensing out any $(CH_3)_2NBH_2$—a substance which in a pure state would be trapped completely at −30°. Perhaps the N–B dative bond in monomeric $(CH_3)_2N \rightleftarrows BH_2$ is weakened and electrically balanced by a weak dative bond from trimethylamine to the BH_2 group—a possible although not very probable coincidence.

III. Studies of Bis-dimethylamino-borine; Reactions (5) and (6)

Preparation of Pure $[(CH_3)_2N]_2BH$.—If one heats $(CH_3)_2NBH_2$ with just the calculated proportion of dimethylamine,[4] the conversion to $[(CH_3)_2N]_2BH$ never is quite complete. The remaining $(CH_3)_2NBH_2$ cannot be eliminated by distillation methods, for, even though in solid form it is not volatile at −40°, it readily distils with $[(CH_3)_2N]_2BH$ at that temperature. It would appear that the dissolved dimer of $(CH_3)_2NBH_2$ rapidly generates an equilibrium-trace of monomer, which should be more volatile than $[(CH_3)_2N]_2BH$; however, no amount of redistillation will remove all of the dimer through conversion to monomer.

To obtain pure $[(CH_3)_2N]_2BH$, therefore, one uses a 10% excess of dimethylamine; then it is sufficient to heat 12 hours at 150°, and finally to distil the product through a reflux tube at −42° (boiling propane). Under such heating conditions there is very little third-stage aminolysis; however, a mixture formed from 126.4 cc. of diborane and 689 cc. of dimethylamine, after 11 days in an 80-ml. bomb-tube at 205°, yielded 0.40 g. of $[(CH_3)_2N]_3B$.[8] In this case, 5.3 cc. of ethane also was found, and there seemed to be ineradicable impurities in the $[(CH_3)_2N]_2BH$.

Physical Properties.—The freezing point of purified $[(CH_3)_2N]_2BH$ was determined by a cooling curve having a level region at −57.5° (established after supercooling to −61°). The somewhat less satisfactory warming curve indicated major melting at −56.8°. Hence the true melting point probably falls slightly below −57°. The purity of the substance was indicated in a quantitative experiment (equivalent to analysis) in which a weighed sample was converted to $(CH_3)_2NB_2H_5$ by reaction (4) as described in a later section.

The vapor tensions of purified $[(CH_3)_2N]_2BH$, presented in Table III, led to the equation $\log_{10} p_{\text{mm}} = -(2362/T) + 1.75 \log_{10} T - 0.00639T + 7.0240$, from which the calculated values were obtained. This implies a normal boiling point of 378.85°K., or 105.7°C. The Trouton constant is estimated as 20.7 cal./deg. mole.

TABLE III

VAPOR TENSIONS OF PURE $[(CH_3)_2N]_2BH$

Temp., °C.	0.0	7.9	13.4	23.2	30.4	30.5	37.5
$p_{\text{mm.}}$ (obsd.)	7.90	12.87	17.88	30.8	44.3	44.6	62.9
$p_{\text{min.}}$ (calcd.)	7.86	12.87	17.80	30.6	44.4	44.5	62.7

Temp., °C.	49.8	56.2	63.7	72.0	79.8	89.5	99.2
$p_{\text{mm.}}$ (obsd.)	108.8	142.0	191.7	261.3	344.2	469.2	631.9
$p_{\text{mm.}}$ (calcd.)	109.1	142.5	191.7	260.9	342.8	470.7	631.7

Addition of small proportions of $(CH_3)_2NBH_2$ to pure $[(CH_3)_2N]_2BH$ increases the vapor tensions in the lower temperature range in such a way that the increase passes through a maximum as the concentration is raised. Thus at 4.3 mole per cent. (based upon monomer), the vapor tensions are 9.17 mm. at 0° and 31.60 mm. at 23.2°, whereas at 10% the results are 8.69 at 0° and 31.12 at 23.2°. Such effects are easily understood by the assumption that the monomer $(CH_3)_2NBH_2$, in equilibrium with considerably more of the dimer, acts as a more volatile additive. The same idea would explain the presence of $(CH_3)_2NBH_2$ in all fractions when impure $[(CH_3)_2N]_2BH$ is distilled.

Bis-dimethylamino-borine and Diborane.—Preliminary experiments showed that the reactions $2[(CH_3)_2N]_2BH + 3B_2H_6 \rightarrow 4(CH_3)_2NB_2H_5$ and $2[(CH_3)_2N]_2BH + B_2H_6 \rightarrow 4(CH_3)_2NBH_2$ occur quantitatively at temperatures near 100°; with an intermediate proportion of diborane, one obtains the two products in just such proportions as to account for all atoms supplied by the reactants. It was also observed that a reaction begins below room temperature, with occurrence of metastable intermediates.

In an attempt to elucidate these intermediates, 174.1 mg. (39.02 cc. gas at S.C.) of $[(CH_3)_2N]_2BH$ and 54.9 cc. of B_2H_6 were allowed to react at −58°. The pressure (diborane) fell to a constant value during 20 minutes, after which vacuum distillation at −57° yielded 30.7 cc. of B_2H_6 and 1.9 cc. of $(CH_3)_2NB_2H_5$. The residue thus was equivalent to 22.8 cc. of B_2H_6 with 38.1 cc. of $[(CH_3)_2N]_2BH$, or in terms of the most obvious addition compounds, 7.5 cc. of $[(CH_3)_2NBH_3]_2BH$ and 30.6 cc. of $(CH_3)_2NBH_3BHN(CH_3)_2$. This residue was warmed to room temperature, with the vapors passing into a series of traps at −78.5 and −196°, thus yielding a further 3.05 cc. of $(CH_3)_2NB_2H_5$. The condensate at −78.5° upon warming to room temperature, appeared as a mixture of liquid and solid; after standing 18 hours it yielded a further 3.83 cc. of $(CH_3)_2NB_2H_5$ and a less volatile solid (but apparently no $(CH_3)_2NBH_2$); finally this solid was heated with 5.1 cc. of B_2H_6, converting it to 13.4 cc. of $(CH_3)_2NB_2H_5$ and 7.4 cc. of $(CH_3)_2NBH_2$ (monomer gas at S.C.). The whole condensate thus was equivalent to 7.0 cc. of $(CH_3)_2NB_2H_5$ and 17.6 cc. of $(CH_3)_2NBH_2$, partly combined in some other form.

The fractional condensation had left a residue, not volatile at room temperature, but capable of forming vapor during some hours of standing at room temperature. This was heated with diborane, 25.0 cc. of which was absorbed to yield 48.0 cc. of $(CH_3)_2NB_2H_5$ and 0.5 cc. of $(CH_3)_2NBH_2$. Hence the residue was equivalent to 4.05 cc. of $[(CH_3)_2N]_2BH$ with 40.5 cc. of $(CH_3)_2NBH_2$. The latter evidently formed an unstable polymer chain, by the aid of the former as a complexing agent.

The over-all result was that 70.2 cc. of $(CH_3)_2NB_2H_5$ and 7.9 cc. of $(CH_3)_2NBH_2$ were formed by the reaction between 39.02 cc. of $[(CH_3)_2N]_2BH$ and 54.9 cc. of B_2H_6. The recovery of the $(CH_3)_2N$ groups was 0.1% high, of B-atoms 0.3% low, and of H-atoms, 0.4% low. These errors are in the right direction and of the right magnitude to be attributed to gas-law deviations in measurement, and accordingly the experiment demonstrated that the melting-point sample of $[(CH_3)_2N]_2BH$ was practically free of the impurity $(CH_3)_2NBH_2$.

IV. Studies on Tris-dimethylamino-borine; Reactions (7) and (8)

Preparation.—An adequate sample of $[(CH_3)_2N]_3B$ was obtained from the previously mentioned reaction between 126.4 cc. of diborane and 689 cc. of dimethylamine during 11 days at 205°. It was purified by means of a wire-spiral reflux tube operating *in vacuo* at 0°; thus a slightly more volatile impurity was removed, leaving one-third of the batch as a pure tail-fraction. The purity was established by reaction (7) as described below.

Physical Properties.—The melting range of the purest fraction was visually determined as −16.5 to −16.1°, in contrast to the −40° reading reported by Wiberg and Schuster.[8]

The vapor tensions also were somewhat at variance with the earlier results, and accordingly are presented in Table IV. These values determine the equation $\log_{10} p_{\text{mm.}} = -(2816.8/T) + 1.75 \log T - 0.006631T + 7.729$, implying that the normal boiling point is 152 ± 2° and the Trouton constant 20.6 cal./deg. mole.

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(8) Previously prepared from boron trichloride by Wiberg and Schuster, *Z. anorg. allgem. Chem.*, **213**, 77 (1933).

TABLE IV

VAPOR TENSIONS OF LIQUID $[(CH_3)_2N]_3B$

Temp., °C.	21.5	30.1	35.0	39.6	42.9	49.5	58.0
$p_{mm.}$ (obsd.)	3.44	5.82	8.05	10.35	12.44	17.85	27.33
$p_{mm.}$ (calcd.)	3.44	5.93	7.95	10.36	12.46	17.77	27.31
Temp., °C.	58.25	66.3	70.25	77.85	85.3	99.5	
$p_{mm.}$ (obsd.)	27.86	40.51	48.48	67.78	91.85	158.7	
$p_{mm.}$ (calcd.)	27.71	40.65	48.65	67.76	92.11	158.6	

Tris-dimethylamino-borine and Diborane.—Like $[(CH_3)_2N]_2BH$, the compound $[(CH_3)_2N]_3B$ reacted in a stage-wise manner with diborane, quantitatively yielding $(CH_3)_2NB_2H_5$ and $(CH_3)_2NBH_2$. The start of the reaction required a higher temperature—presumably on account of the higher melting point of $[(CH_3)_2N]_3B$—hence it was even less feasible to recognize distinct intermediate compounds. For example, a 67.4-mg. sample (calcd. as 10.56 cc. standard gas) absorbed no more than 17.4 cc. of diborane during 10 minutes at 0–20°, yielding 8.3 cc. of $(CH_3)_2NB_2H_5$ and the previously observed difficultly volatile liquids and solids. These residues were heated with diborane at 85–95°, bringing the total $(CH_3)_2NB_2H_5$ to 30.4 cc. The total absorbed diborane was 25.7 cc., and the yield of $(CH_3)_2NBH_2$ was 1.2 cc. (monomer gas at S.C.); hence the recovery of $(CH_3)_2N$ groups was 99.7%; of B and H atoms, 100.1%. This quantitative realization of the equations $2[(CH_3)_2N]_3B + 5B_2H_6 \rightarrow 6(CH_3)_2NB_2H_5$ and $[(CH_3)_2N]_3B + B_2H_6 \rightarrow 3(CH_3)_2NBH_2$ is clear evidence of the purity of the sample of tris-dimethylamino-borine.

V. The Existence of Aluminum Aminoborohydrides

The recognition of BHB bridge-bonding in the aminodiboranes[2] and the recent evidence for the AlHB bridging in aluminum borohydride[9,10] led to the question whether such a bond system as $\mathrm{Al}\begin{smallmatrix}\diagup\mathrm{N}\diagdown\\ \diagdown\mathrm{H}\diagup\end{smallmatrix}\mathrm{B}$ also might be stable. In the first experiment on this subject, one gas-volume of $(CH_3)_2NB_2H_5$ and two gas-volumes of aluminum borohydride were heated together for 45 minutes at 100°, yielding a scarcely volatile oily liquid and 0.15 gas volume of diborane. The displacement of the latter suggested that a more direct approach would employ $(CH_3)_2NBH_2$ instead of $(CH_3)_2NB_2H_5$; hence in another experiment 42.5 cc. of $(CH_3)_2NBH_2$ (monomer gas at S.C.) and 45.3 cc. of $Al(BH_4)_3$ were heated 45 minutes at 92°, to give 1.4 cc. of diborane, a trace of highly reactive solid, the oily liquid again, and a mixture which was resolved into 15.5 cc. of $(CH_3)_2NB_2H_5$ and 28.6 cc. of $Al(BH_4)_3$, the latter being isolated in the form of a complex with methyl ether. The reaction balance thus indicated that 1.1 BH_4 groups, per mole of aluminum borohydride, were replaced by $(CH_3)_2NBH_3$ groups, and that the product contained a half-mole proportion of complex-bonded $(CH_3)_2NBH_2$. Attempts to isolate the main product led to a fraction (43% of the Al) in which hydrolytic analysis showed the atomic H:Al ratio to be 10.9 and the N:Al ratio 2.18. This result would suggest mainly $[(CH_3)_2NBH_3]_2AlBH_4$, with a little additional $(CH_3)_2NBH_2$. Larger samples of the oily product were obtained by a process in which $Al(BH_4)_3$ vapor streamed across a sample of $(CH_3)_2NBH_2$ in a U tube, and passed through a Pyrex tube at 120°. Again, however, it was not feasible to isolate single pure components.

The oily liquid products proved to be spontaneously inflammable in air and violently reactive with water. They can be distilled at a practical rate *in vacuo* at 50–60°, without decomposition. With diborane at 90–100°, they react extensively to form $(CH_3)_2NB_2H_5$ and aluminum borohydride—essentially reversing the preparation. They dissolve, apparently without reaction, in dry benzene, carbon tetrachloride or diethyl ether. They react with trimethylamine, but the question whether an amine complex on Al is formed, or a BH_3 group delivered to form $(CH_3)_3NBH_3$, or both effects in succession, has not been fully investigated.

Acknowledgment.—The generous support of this work by the Office of Naval Research is gratefully acknowledged.

LOS ANGELES 7, CALIF. RECEIVED AUGUST 7, 1950

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[9] Price, Longuet-Higgins, Rice and Young, *J. Chem. Phys.*, **17**, 217 (1949).

[10] Bauer, THIS JOURNAL, **72**, 622 (1950).

[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

Cuprammonium-glycoside Complexes. VI. The D-Mannosan Complex[2]

BY RICHARD E. REEVES

Complex formation between cuprammonium and D-mannosan produces a visible color change and increased absorption of light in the near ultraviolet, a shift in optical rotation, and a decrease in the conductance of a dilute cuprammonium solution. Measurements at equilibrium conditions by four techniques indicate a single stoichiometric reaction involving one mole of D-mannosan and one mole of cuprammonium. The reaction constant for formation of the cuprammomium-D-mannosan complex is approximately 2.5×10^3 at 25° with the cuprammonium employed in the present work.

The exact nature of cuprammonium-glycol complexes has remained uncertain despite their practical importance in systems involving cuprammonium solutions of cellulose. As an approach to this problem the complex formed by cuprammonium and a glycol grouping in D-mannosan$<1,5>\beta<1,6>$ was selected for further study because mannosan was the most active complex-forming substance encountered in a survey of several score of sugar derivatives.

Since cuprammonium-glycol complexes are stable only under very restricted conditions, it is ordinarily difficult to differentiate the properties of the complex from those of free cuprammonium and uncombined glycol. In the present studies, taking advantage of the great affinity of D-mannosan for cuprammonium, reaction was driven essentially to completion by employing excesses of glycol.[3] By this means the properties of the cuprammonium-mannosan complex were determined and distinguished from the properties of uncombined cuprammonium and mannosan.

Reaction between glycols and cuprammonium proceeds to equilibrium very rapidly. No data on the kinetics of the reaction have been obtained for equilibrium has been reached even when measurements were made within a minute from the time of mixing the components. The amount of complex at equilibrium is dependent, first, upon the

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] The data and calculations of reaction constants for this manuscript are contained in four tables available from the American Documentation Institute, 1719 N St., N. W., Washington 6, D. C., by requesting serial number 3000.

[3] The glycol grouping involved in reaction with cuprammonium is the pair of hydroxyl groups on carbon atoms 2 and 3 in the D-mannosan.