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Dimethylaminomethylborine

BY ANTON B. BURG AND JAMES L. BOONE

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The new compound $(CH_3)_2NBHCH_3$ (m.p. −136.2°; b.p. est. 43°)—made from $(CH_3BH_2)_2$ and $(CH_3)_2NH$—is almost wholly monomeric as a vapor, but in the liquid state it soon develops a high proportion of the dimer; in pure form at room temperature, this is an unstable white solid. The disproportionation of $(CH_3)_2NBHCH_3$ yields $[(CH_3)_2NBH_2]_2$ and $(CH_3)_2NB(CH_3)_2$, and the reverse reaction can be used for synthesis.

Dimethylaminoborine, $(CH_3)_2NBH_2$, has been shown to exist chiefly as a dimer[1] whose dissociation to monomer is described by the equation $\Delta F_T{}^\circ = 20.74 - 0.0509T$ kcal.[2] On the other hand, its dimethyl derivative $(CH_3)_2NB(CH_3)_2$[3,4] is known only as a monomer. We now have prepared the intermediate compound $(CH_3)_2NBHCH_3$, by the reaction of dimethylamine with 1,2-dimethyldiborane, and find that it exists mostly as the dimer in the liquid state, but almost wholly as the monomer in the vapor phase. The conversion of one form to the other is slow enough to permit the isolation of each form in pure condition. The slow conversion contrasts with the behavior of $(CH_3)_2NBH_2$, which reaches its monomer–dimer equilibrium almost instantly; another difference is that $(CH_3)_2NBHCH_3$ has no appreciable tendency to shift $(CH_3)_2N$ groups from one molecule to another at 100°. However, it does rather easily exchange CH_3 for H on boron, reversibly forming $(CH_3)_2NB(CH_3)_2$ and dimeric $(CH_3)_2NBH_2$.

This new member of the class of methyl-substitution derivatives of the H_2NBH_2 unit serves to confirm further the general observation that progressive substitution of CH_3 for H decreases the strength and degree of $(\text{-B-N-})_n$ polymerization.

Experimental

Preparation of 1,2-Dimethyldiborane.—The compound $(CH_3BH_2)_2$ was prepared from $CH_3B_2H_5$ by a procedure which differed from the original[5] in that the BH_3 group was removed by tetrahydrofuran[6] rather than by dimethyl ether. Very little of the desired $(CH_3BH_2)_2$ could be obtained by distillation from a container at −78°—evidently on account of complexing with the C_4H_8O—but it was not difficult to distil it off *in vacuo* by warming to slightly higher temperatures, at which the complex $C_4H_8O\cdot BH_3$[7] remained stable. The pure $(CH_3BH_2)_2$ was isolated by high-vacuum fractional condensation, appearing in the trap at −125°.

The Formation of Dimethylaminomethylborine.—The non-volatile complex empirically designated as $CH_3BH_2\cdot HN(CH_3)_2$ was formed in the presence of an excess either of $(CH_3BH_2)_2$ or of $(CH_3)_2NH$, at −78°, and the excess reactant was distilled off *in vacuo*. In one case 22.0 cc.[8] of the complex was heated for 3 hours in a closed bulb, yielding 20.0 cc. of H_2 (calcd., 22.0 cc.). In another case, 27.2 cc. of the complex was similarly heated, yielding 22.9 cc. of H_2 (calcd., 27.2 cc.). In each case the desired product contained important proportions of impurities later identified as the disproportionation products $(CH_3)_2NBH_2$ and $(CH_3)_2NB(CH_3)_2$—present in spite of attempts to minimize them by hourly removal of all volatile products. However, it was possible to remove these impurities by fractional condensation at −78°, and then to recognize the reversible formation of the dimer form of $(CH_3)_2NBHCH_3$.

Purification of Monomeric Dimethylaminodimethylborine.—The monomeric $(CH_3)_2NBHCH_3$ was largely converted to the dimer form by allowing the sample to stand at room temperature under an initial pressure near 250 mm., decreasing as the liquid dimer condensed out. After a half-hour the dimer was isolated by fractional condensation *in vacuo* (passed a trap at 0° but condensed at −25°) and the remaining monomer was further converted in the same manner. Then the dimer, slightly contaminated with dimeric

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[1] E. Wiberg, A. Bolz and P. Buchheit, *Z. anorg. Chem.*, **256**, 285 (1948).

[2] A. B. Burg and C. L. Randolph, Jr., THIS JOURNAL, **73**, 955 (1951).

[3] E. Wiberg and P. Buchheit, quoted by J. Goubeau, *FIAT Rev. Ger. Sci.*, Inorg. Part I, 228 (1948).

[4] A. B. Burg and J. Banus, THIS JOURNAL, **76**, 3903 (1954).

[5] H. I. Schlesinger, N. W. Flodin and A. B. Burg, *ibid.*, **61**, 1078 (1939).

[6] This modification was suggested by Professor David M. Ritter of the University of Washington.

[7] J. R. Elliot, W. L. Roth, G. F. Roedel and E. M. Boldebuck, THIS JOURNAL, **74**, 5212 (1952).

[8] Throughout this paper the abbreviation cc. refers to gases or vapors at standard conditions, in accord with usage related to the high-vacuum methods here employed.

TABLE I

VAPOR TENSIONS OF PURIFIED $(CH_3)_2NBHCH_3$

t (°C.)	−58.9	−49.9	−42.9	−40.8	−36.4	−29.5	−26.8	−22.8
$p_{mm.}$ (obsd.)	4.6	9.3	15.5	18.0	23.9	36.9	43.2	53.9
$p_{mm.}$ (calcd.)	4.6	9.3	15.5	17.9	23.9	36.8	43.2	54.2

$(CH_3)_2NBH_2$, was left overnight in a 500-ml. bulb at room temperature, dissociating almost entirely into the monomer, without appreciable disproportionation. Now the pure monomer was isolated by passage at low pressure through a trap at −78°.

Physical Properties of the Monomer.—The highly purified monomer $(CH_3)_2NBHCH_3$ melted in the range −136.4 to −136.2°. Vapor density determinations gave the molecular weight as 70.5 or 70.7 (calcd., 70.91). The vapor tensions, measured on individually repurified samples, appear in Table I. They determine the equation $\log_{10}P_{mm} = -(1947/T) + 1.75 \log_{10}T - 0.009815T + 7.771$, according to which the normal boiling point would be near 44° and the Trouton constant only about 17.2 cal./deg. mole. By a simpler method of extrapolation—assumption of a normal Trouton constant of 21.0 and projecting a Clapeyron–Clausius curve from the average of the middle points of Table I—the b.p. would be estimated as 42°.

Proof of Formula of the Monomer.—The purified monomer was hydrolyzed in the presence of a known quantity of hydrogen chloride and the amine content was determined by titrating the excess acid. A 6.65-cc. sample yielded 6.59 cc. of H_2 (one B–H link) and 6.3 cc. of amine. The CH_3–B bond was destroyed by H_2O_2, the excess of which was decomposed by boiling; then the boric acid was titrated as equivalent to 6.4 cc. of gas. These values, taken with the molecular weight and the source of the material, left no doubt of the formula $(CH_3)_2NBHCH_3$.

The Dimer Form.—The highly purified dimer of $(CH_3)_2NBHCH_3$ had vapor tensions of 1.2 mm. at 0° and 3.5 mm. at 25°; but its dissociation to the monomer was too rapid to permit a full range of dependable measurements. At −23°, however, its volatility was low enough and its stability sufficient for a determination of its molecular weight by the vapor-tension lowering of dimethyl ether. For this purpose the usual differential manometer system[9] was employed, using a bath of melting carbon tetrachloride (−22.8°) for temperature constancy. The results, for two samples at mole fractions of 0.016 and 0.014, averaged 146 ± 8 (calcd., 142 for dimer).

The pure dimer is a white solid melting above room temperature, but the m.p. could not be determined on account of the dissociation to monomer. When it forms from the gaseous monomer, it condenses as a liquid which evidently contains some dissolved monomer.

The Monomer–Dimer Equilibrium.—An 11.8-cc. sample of pure monomeric $(CH_3)_2NBHCH_3$ was allowed to stand at 23° for 95 minutes, during which the pressure decreased from 45.0 to 44.2 mm. The monomer was again isolated and measured as 11.4 cc., and the condensate at −78° was evaporated and measured as 0.22 cc. This evidently was the dimer, for its gas-volume doubled on standing at room temperature. Although these observations indicated an easy reversibility in the monomer–dimer system, it would be difficult to obtain a full set of gas-phase equilibrium constants—partly because there is too little association, but also because of the tendency of the substance to disproportionate on standing. However, it was possible to obtain some fairly useful data on the equilibria between the liquid and gas phases.

For this purpose the pressure established by samples of the monomer were observed in a small-volume immersible tensimeter,[10] held at constant temperature within 0.05°. Equilibration usually required about five hours, and since the disproportionation reaction became evident in 12 to 24 hours, it was necessary to repurify the sample before each trial. The typical pressure values below 40° (above which disproportionation became too rapid) are given by Table II. They determine the equation $\log_{10}P_{mm} = 8.124 - 1800/T$. The meaning of this equation is complex, but a rough interpretation can be made by assuming that Raoult's law is applicable and that the sole source of the pressure is the monomer, in equilibrium with its solution in the relatively involatile liquid dimer. Then the liquid-phase mole fractions of the monomer (fourth line of Table II) are calculated by dividing the observed pressures by the vapor tensions of the pure monomer as calculated from the equation related to Table I. From the results it appears that the standard free energy of the liquid-phase dissociation is slightly above zero. It is also noted that the vaporization is a composite process, for at 21.65° only 18% of the vapor is directly evaporated monomer, and 82% of it comes from the dissociation of the liquid dimer. Since these percentages change sharply with temperature, there would be little significance in a free energy equation derived from the Clapeyron–Clausius equation related to Table II. In any case, it is difficult to be sure of establishing the monomer–dimer equilibrium without permitting some disproportionation to occur, and the effects of the products cannot be judged. Hence a strictly quantitative description of the energetics is not possible, but it is sure that the dissociation of dimeric $(CH_3)_2NBHCH_3$ sharply exceeds that of dimeric $(CH_3)_2NBH_2$ under comparable conditions.

TABLE II

LIQUID–VAPOR EQUILIBRIA OF $(CH_3)_2NBHCH_3$

t (°C.)	21.65	29.48	34.38	38.56
p (obsd.)	104.5	151.0	185.3	224.0
p (calcd.)	104.5	150.0	186.6	224.0
Apparent mole fraction of monomer (liq. phase)	0.266	0.295	0.311	0.343

The Disproportionation Reaction.—Pure $(CH_3)_2NBHCH_3$ (15.1 cc.) was placed at 20 mm. pressure and room temperature for about 25 days, after which the monomer form was isolated as before and measured as 8.14 cc. The yield of $(CH_3)_2NB(CH_3)_2$ (vapor tension 15.5 mm. at −21.2°; calcd., 15.3 mm.) was 3.03 cc., implying a 40% disproportionation of $(CH_3)_2NBHCH_3$ according to the equation

$$2(CH_3)_2NBHCH_3 \rightleftarrows (CH_3)_2NB(CH_3)_2 + (CH_3)_2NBH_2$$

The remixed sample showed no further change during two weeks.

The Reverse of the Disproportionation.—The above disproportionation reaction proved to be sufficiently reversible for possible use in the synthesis of $(CH_3)_2NBHCH_3$. In one experiment 1.20 mmoles of $(CH_3)_2NB(CH_3)_2$ was allowed to react with 1.27 mmoles of $(CH_3)_2NBH_2$ in the liquid state at 100° during three hours, giving a 35% yield of $(CH_3)_2NBHCH_3$, the monomer and dimer forms of which were separately isolated and measured. The monomer was identified by its vapor tension of 23.9 mm. at −36.4° (calcd., 23.9 mm.) and its melting point, −135.5° (known, −136.5°).

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LOS ANGELES 7, CALIFORNIA

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[9] A. B. Burg, THIS JOURNAL, **65**, 1630 (1943).

[10] A. B. Burg and H. I. Schlesinger, *ibid.*, **59**, 785 (1937).