from the low-temperature side, but the use of this method would tend to increase the transitional entropy increment by 0.1 to 0.3 e.u.

The transitional entropy increment of 4.0 e.u. is quite comparable with that in the ammonia–triborane (4.15), and the slow approach to equilibrium is also very suggestive of a similar process despite the fact that this transition occurs at a temperature 90° lower. Further elucidation of the mechanism of the presumed disordering in the molecular orientation awaits the availability of X-ray diffractional data on both forms.

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

Vapor Pressures of the Methylamine–Boranes and Ammonia–Triborane[1]

BY E. R. ALTON, R. D. BROWN, J. C. CARTER AND R. C. TAYLOR

Vapor pressures of the solid compounds, $CH_3NH_2BH_3$, $(CH_3)_2NHBH_3$, $(CH_3)_3NBH_3$ and $NH_3B_3H_7$, have been measured between 0° and their melting points by the Knudsen method. Vapor pressure equations and the heats of sublimation have been derived from a least squares analysis of the data. An upper limit has been set for the vapor pressure of NH_3BH_3 at 25°.

In connection with a program of study of the physical and chemical properties of boron hydride derivatives, the vapor pressures of ammonia–borane, mono-, di- and trimethylamine–borane and of ammonia–triborane have been measured in the neighborhood of room temperature by the Knudsen method. No vapor pressure data for these compounds have appeared previously in the literature with the exception of the trimethylamine compound.[2] In the latter case the data were determined manometrically from 23° to the melting point and cover a different range than the present measurements.

Experimental

Ammonia–borane,[3] trimethylamine–borane[2] and ammonia–triborane[4] were prepared by the methods described in the literature and purified by sublimation or, in the case of the triborane, recrystallization. Methylamine–borane and dimethylamine–borane were prepared by slightly modified procedures for ammonia–borane.[5] Contrary to reports in the literature,[6,7] these two methylamine–boranes are odorless, stable white solids with sharply defined melting points of 54 and 36°, respectively, and no tendency to evolve hydrogen when maintained *in vacuo*. In this respect they resemble many other boron hydride derivatives whose apparent properties and stability depend markedly upon the method of preparation and the resulting purity. Since the weight of material effusing was determined by the decrease in weight of the container, precautions were necessary to eliminate spurious weight loss. Where a solvent had been used in purification, the material was held *in vacuo* for several hours before measurement to ensure the absence of volatile

impurities. Transfers were made in a dry box to prevent contamination by water with subsequent decomposition. Before weighing and again after the experiment and before reweighing, the vaporization chamber was filled with dry nitrogen. After each series of measurements, the sample was inspected and if an amine odor was detectable, the data were discarded. Tests carried out by sealing a sample in a small evacuated system with an attached manometer showed that decomposition with permanent gas (H_2) evolution under the conditions of the measurements was negligible.

The vaporization chamber consisted of a small monel cylinder with an i.d. of 15 mm. and a depth of 20 mm. It was fitted with an open cap at the top which compressed the platinum sheet containing the orifice between two thin copper gaskets to complete the closure. The orifices were carefully drilled, inspected under the microscope for imperfections and burrs and their diameters measured by a comparator. The two used had diameters of 0.0374 and 0.0776 cm. and ratios of thickness to radius of 0.163 and 0.314, respectively.

Effusion took place from the chamber into a vacuum of approximately 10^{-5} mm. of Hg, a surface maintained at liquid nitrogen temperature some 8 cm. above the orifice trapping most of the effused material. The vaporization chamber was recessed into a closely fitting 0.8 kg. block of copper to provide a large thermal reservoir and the latter was enclosed by a double walled section of the vacuum system through which constant temperature water was circulated. The temperature of the copper block immediately adjacent to the vaporization chamber was monitored by a copper–constantan thermocouple. In general, the loss in weight per run was of the order of 10–50 mg.

Experimental Results

Vapor pressures were calculated from the relationship[8]

$$P_{mm} = 17.14 \frac{W}{KAt} \left(\frac{T}{M}\right)^{1/2}$$

where W is the weight of the substance in grams effusing in time t seconds through an orifice of A cm.[2] area. M is the molecular weight, assumed that of the simple 1:1 complex, T is the absolute temperature and K is the Clausing correction factor

(1) This research was supported by the United States Air Force under Contracts No. AF 33(616)-3343 and AF 33(616)-5874 monitored by the Aeronautical Research Laboratory, Wright Air Development Center, Ohio.

(2) A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 780 (1937).

(3) S. G. Shore and R. W. Parry, *ibid.*, **80**, 8 (1958).

(4) G. Kodama, R. W. Parry and J. C. Carter, *ibid.*, **81**, 3534 (1959).

(5) R. W. Parry, R. C. Taylor, C. E. Nordman and Staff, Wright Air Development Center Technical Report, 1959 (in preparation).

(6) E. Wiberg, A. Bolz and P. Buckheil, Z. anorg. Chem., **256**, 285 (1948).

(7) R. E. McCoy and S. H. Bauer, THIS JOURNAL, **78**, 2061 (1956).

(8) S. Dushman, "Scientific Foundations of Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949.

for orifice thickness. The data obtained are shown in Fig. 1 where the solid lines are derived from a least squares analysis of the data. The corresponding equations, temperature ranges and heats of vaporization derived from the simple Clausius–Clapeyron equation are shown below. The uncertainties in the constants represent standard deviations calculated from the residuals of the experimental data. The data of Burg and Schlesinger for trimethylamine–borane did not overlap the present data but appeared consistent on a log P vs. $1/T$ plot. They were consequently included in the least squares determination of the vapor pressure equation which as a result covers the longest temperature range of the four compounds.

Two measurements were carried out on ammonia-borane, NH_3BH_3 but, because of the small weight loss, their precision is low. They are sufficient to set an upper limit of one micron for the vapor pressure at $25°$.

Methylamine–borane, $(CH_3)NH_2:BH_3$

$$\log P \text{ (mm.)} = - \frac{4114(1 \pm 0.053)}{T} + 11.411(1 \pm 0.063)$$

Range $= 0$ to $45°$ $\Delta H = 18.8 \pm 1.0$ kcal./mole

Dimethylamine–borane, $(CH_3)_2NH:BH_3$

$$\log P \text{ (mm.)} = - \frac{4034(1 \pm 0.038)}{T} + 12.544(1 \pm 0.042)$$

Range $= 0$ to $35°$ $\Delta H = 18.5 \pm 0.7$ kcal./mole

Trimethylamine–borane, $(CH_3)_3N:BH_3$

$$\log P \text{ (mm.)} = - \frac{2962(1 \pm 0.014)}{T} + 9.894(1 \pm 0.014)$$

Range $= 0$ to $90°$ $\Delta H = 13.6 \pm 0.2$ kcal./mole

Ammonia triborane, $NH_3B_3H_7$

$$\log P \text{ (mm.)} = - \frac{3739(1 \pm 0.0075)}{T} + 9.200(1 \pm 0.0096)$$

Range $= 30$ to $55°$ $\Delta H = 17.1 \pm 0.1$ kcal./mole

Inspection of the heats of sublimation shows that the values for the monomethyl- and dimethylamine compounds are approximately the same and are
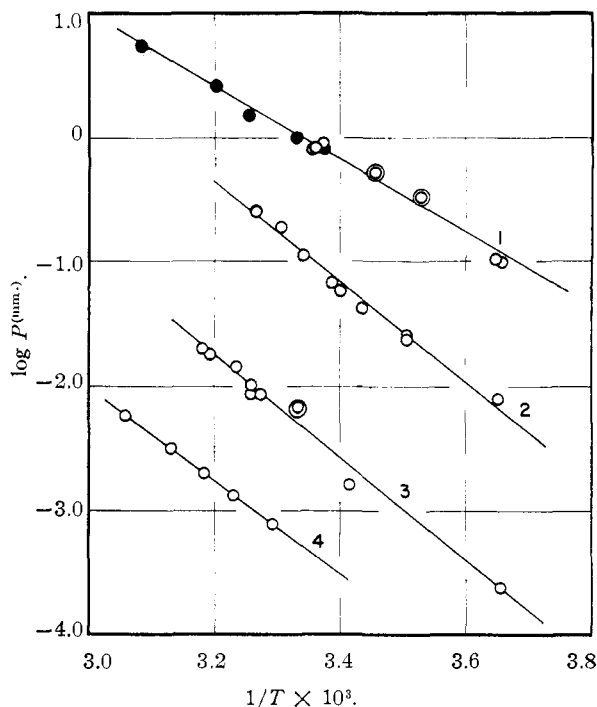

Fig. 1.—Vapor pressure–temperature relationships for some amine–boranes: 1, $(CH_3)_3N:BH_3$; 2, $(CH_3)_2NH:BH_3$; 3, $(CH_3)NH_2:BH_3$; 4, $NH_3:B_3H_7$ (●, ref. 1).

appreciably higher than the value for the trimethyl-amine compound. This observation agrees with the greater polar nature to be expected for these substances despite their lower melting points. The magnitude of the difference, approximately 5 kcal./mole, suggests that hydrogen bonding may be of importance in the crystal structure of the first two compounds.

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The Crystal Structure of $(NH_3)_2BH_2Cl$[1]

BY C. E. NORDMAN AND CHARLES R. PETERS

An X-ray diffraction study of $(NH_3)_2BH_2Cl$ indicates that the compound forms orthorhombic crystals, $a = 10.20 \pm 0.04$ Å., $b = 10.20 \pm 0.04$ Å., $c = 17.42 \pm 0.08$ Å. A very prominent subcell exists, for which $a = b = 10.20$ Å., $c = 8.71$ Å. The approximate structure based on the subcell is consistent with the space group $D_{2h}{}^{18}$-Bbcm and consists of puckered layers of chloride ions interleaved with layers of $(NH_3)_2BH_2{}^+$ ions. The latter contain two B–N bonds of nearly equal length, 1.58 ± 0.02 Å. forming a nearly tetrahedral N–B–N angle.

Introduction

The compound $(NH_3)_2BH_2Cl$ was first prepared by Schultz and Parry[2] by allowing $B_2H_6·2NH_3$ ("diammoniate of diborane") to react with NH_4Cl. More recently it has been obtained as a product of the reaction of $B_4H_{10}·2NH_3$ with HCl.[3] In a recent

(1) Presented, in part, at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

(2) D. R. Schultz and R. W. Parry, THIS JOURNAL, 80, 4 (1958).

(3) R. W. Parry and G. Kodama, Proc. XVI Congress, IUPAC, Inorganic Section, Paris, 1957, p. 483; G. Kodama and R. W. Parry, THIS JOURNAL, in press.

series of papers[2,4] Parry and co-workers already have presented strong chemical evidence that the structure of the "diammoniate of diborane," long the subject of conflicting theories, is $[H_2B(NH_3)_2][BH_4]$ and that the structure of the corresponding halide salts is $[H_2B(NH_3)_2]X$, where $X = Cl^-$ or Br^-. These conclusions have been supported by the results of Raman spectroscopic

(4) S. G. Shore and R. W. Parry, THIS JOURNAL, 80, 8 (1958); 80, 12 (1958); R. W. Parry and S. G. Shore, ibid., 80, 15 (1958); S. G. Shore, P. R. Girardot and R. W. Parry, ibid., 80, 20 (1958).