Dipole Moment of Ammonia-Borane

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The dipole moment of ammonia-borane, H₃NBH₃, has been measured as 4.9 debye units in dioxane solution; the results are discussed briefly.

CRYSTALLINE ammonia-borane, H₃NBH₃, has a highly ordered boron-nitrogen arrangement and almost negligible vapor pressure at room temperature. Such properties suggest a high dipole moment for the molecule, since the isoelectronic C₂H₆ is a gas at room temperature and boils at -88°C. Quantitative information regarding the size of the dipole is of considerable interest.

Because of low volatility and thermal instability of the compound at elevated temperatures, dipole moment measurements have been made in dilute dioxane solution using a heterodyne beat method. A value of 4.9 debye units has been obtained. This value is of the proper magnitude for the dipoles to make a significant contribution to the observed physical properties. The rather similar solid Me₂OB₃F₂ has a moment of 4.35 debyes, melts at -14°C and boils at 128°C.

The value for H₃NBH₃ is of some interest in connection with earlier arguments relative to the structure of the “diammoniate of diborane.” It has been suggested that the dimeric character of the “diammoniate of diborane,” B₃H₆·2NH₃, in liquid ammonia is an experimental illusion which results from strong dipole-dipole interaction between monomeric H₃NBH₃ units. Although the dipole moment of H₃NBH₃ is indeed high, it has been demonstrated recently that H₃NBH₃ is monomeric in liquid ammonia. Such behavior is consistent with an earlier observation to the effect that salts such as NH₄Br and NaBH₄ have molecular weights corresponding to ion pairs in liquid ammonia even though the strongly polar M⁺X⁻ units have a high over-all moment. [e.g., the moment for the gaseous KCl molecule is 6.30 (5b).]

The ion pair observation is indeed consistent with behavior expected from theoretical considerations of salts in a solvent such as liquid ammonia.

EXPERIMENTAL

1. Apparatus

The precision heterodyne beat apparatus was built in the Central Physical Chemistry Research Laboratory of the Chrysler Corporation of Detroit, Michigan, and was generously donated to the University of Michigan by the Chrysler Corporation. The unit consists of a fixed frequency oscillator which is controlled at one megacycle by a quartz crystal. The output of a variable frequency oscillator, having the dielectric cell as part of its tank circuit, is combined in

1 (a) E. L. Lippert and W. N. Lipscomb, J. Am. Chem. Soc. 78, 503 (1956); (b) E. Hughes, ibid. 78, 502 (1956); (c) S. G. Shore and R. W. Parry, ibid. 77, (1955).
3 L. E. Agromonov, J. Gen. Chem. (U. S. S. R.) 9, 1389 (1939); ibid. 10, 1120 (1940); Chem. Abstracts 34, 1267 (1940); ibid. 38, 1333 (1944); E. Wiberg, A. Bole, and P. Buchheit, Z. anorg. Chem. 256, 287, 301 (1948).
a vacuum tube mixer with the output of the fixed frequency unit. The output of the mixer is equal to the difference between the frequencies of the two inputs. The variable oscillator is then tuned until this frequency, as indicated on the frequency meter, becomes zero. Frequencies can be compared with an error of less than one cycle per second. More detailed design details are available upon request.

The cell used was of a standard type with a capacitance of about 30 μfarads. The dielectric constant of pure dioxane at 25°C was taken from Bureau of Standards tables as 2.209; the value was used for calibration.

The index of refraction of solutions was determined using a Bausch and Lomb precision Abbe refractometer. The data obtained showed rather bad scatter, but the effect of the deviations on the final value of the dipole moment was trivial.

2. Reagents

Reagent grade dioxane was purified by refluxing with dilute hydrochloric acid for 6 hours, washing with potassium hydroxide solution and drying with potassium hydroxide pellets. Final drying was effected by storing the liquid in contact with LiAlH₄ for several days; the dry reagent was distilled in the vacuum line directly onto H₃NBH₃ as described below.

Ammonia-borane, prepared as previously described, was placed on the frit of a special vacuum line filtration assembly and leached with pure dry dioxane into a special narrow neck, high precision density cell. The solution was transferred from the density cell into the dielectric cell under dry nitrogen. Special precautions to avoid exposure to water vapor were taken. The ammonia-borane concentration was obtained after completion of the physical measurements by hydrolyzing the solution with 3M HCl in a sealed tube at 100°C for about 5 days. The liberated hydrogen was measured; nitrogen was determined by a micro-Kjeldahl procedure, and boron by titration of boric acid with NaOH in the presence of mannitol. The consistency of the analytical data served as a cross check on the identity and purity of the solute. Typical hydridic H/B/N ratios were: 2.97/0.98/1.00; 3.01/1.03/1.00; •••/0.95/1.00; 2.92/0.93/1.00.

3. Data and Interpretations

All measurements were taken at or corrected to 25°C. Density and dielectric constant measurements on 8 dioxane solutions, ranging in concentration from 0.0201 mole fraction H₃NBH₃ to pure dioxane gave values of \( \langle \alpha d/\alpha e \rangle_e = -0.2 \) and \( \alpha e/\alpha x = 34.0 \). Detailed data are shown in Table I. These values, when used in the Hedestrand equation, gave a value of 506 cm³ for the apparent total polarization of the solute. Values of the refractive index of the pure solvent (1.4194) and for the solution of mole fraction 0.0156 and 0.0159 (1.4206 and 1.4209) indicated values of \( dn/dx \) (i.e., the change in refractive index with mole fraction) of 0.09 from which the sum of the electronic and atomic polarizations was estimated as about 15 cm³. The orientation polarization was thus 491 cm³ giving a value of 4.88±0.1D for the dipole moment.

It is perhaps somewhat fortuitous that a value of 4.8D was obtained from the temperature coefficients of the dielectric constants of the solution and pure dioxane over the temperature range of 21°C to 41°C. The temperature coefficient of the molar polarization of ammonia-borane was 1.60 cm³/moleXdeg.

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\[^{10}\text{See reference 5(b), p. 301. Other methods of treating the data, such as that of Onsager, gave values ranging from 4.7 to 4.9D.}\]