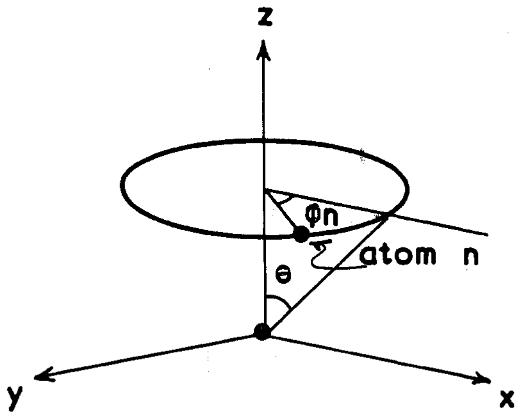

Figure 1.

TABLE I

GENERAL EXPRESSIONS FOR GROUP OVERLAP INTEGRALS[a]

σ_v—Symmetric Overlaps

$$G\,(s) = \sqrt{N}S_\sigma(s)$$

$$G\,(p_z) = \sqrt{N}\,[\cos\theta S_\sigma(p) - \sin\theta S_\pi(p)]$$

$$G\,(p_x) = [\sin\theta S_\sigma(p) - \cos\theta S_\pi(p)]\sum_N c_n\cos\phi_n$$

$$G\,(p_y) = [\sin\theta S_\sigma(p) - \cos\theta S_\pi(p)]\sum_N c_n\sin\phi_n$$

$$G\,(d_{z^2}) = \sqrt{N}\left[(\cos^2\theta - \frac{1}{2}\sin^2\theta)S_\sigma\,(d) - \frac{\sqrt{3}}{2}\sin 2\theta S_\pi\,(d) + \frac{\sqrt{3}}{2}\sin^2\theta S_\delta(d)\right]$$

$$G\,(d_{xz}) = \left[\frac{\sqrt{3}}{2}\sin 2\theta S_\sigma(d) + \cos 2\theta S_\pi(d) - \frac{1}{2}\sin 2\theta S_\delta(d)\right]\sum_N c_n\cos\phi_n$$

$$G\,(d_{yz}) = \left[\frac{\sqrt{3}}{2}\sin 2\theta S_\sigma(d) + \cos 2\theta S_\pi(d) - \frac{1}{2}\sin 2\theta S_\delta(d)\right]\sum_N c_n\cos\phi_n$$

$$G\,(d_{xy}) = \left[\frac{\sqrt{3}}{2}\sin^2\theta S_\sigma(d) + \frac{1}{2}\sin 2\theta S_\pi(d) + \frac{1}{2}(1 + \cos^2\theta)S_\delta(d)\right]\sum_N c_n\sin 2\phi_n$$

$$G\,(d_{x^2-y^2}) = \left[\frac{\sqrt{3}}{2}\sin^2\theta S_\sigma(d) + \frac{1}{2}\sin 2\theta S_\pi(d) + \frac{1}{2}(1 + \cos^2\theta)S_\delta(d)\right]\sum_N c_n\cos 2\phi_n$$

σ_v—Antisymmetric Overlaps

$$G'\,(p_x) = S_\pi(p)\sum_N c_n\sin\phi_n$$

$$G'\,(p_y) = S_\pi(p)\sum_N c_n\cos\phi_n$$

$$G'\,(d_{xz}) = [\cos\theta S_\pi(d) - \sin\theta S_\delta(d)]\sum_N c_n\sin\phi_n$$

$$G'\,(d_{yz}) = [\cos\theta S_\pi(d) - \sin\theta S_\delta(d)]\sum_N c_n\cos\phi_n$$

$$G'\,(d_{xy}) = [\sin\theta S_\pi(d) - \cos\theta S_\delta(d)]\sum_N c_n\cos 2\phi_n$$

$$G'\,(d_{x^2-y^2}) = [\sin\theta S_\pi(d) - \cos\theta S_\delta(d)]\sum_N c_n\sin 2\phi_n$$

[a] c_n is the coefficient associated with the *n*th orbital in the combination of surrounding-atom orbitals of correct symmetry to interact with the central atom orbital indicated.

are given as $S\rho(t)$ where ρ is the symmetry of the diatomic overlap and t the atomic orbital species on the central atom. It should be noted that only the symmetries of the orbitals on the surrounding atoms are specified. The formulas in the table will usually have to be applied to these orbitals as well.[8] For polyhedral molecules[6,9] it is best to obtain group overlap integrals within suitable fragments of the molecule using the expressions given in the table. The group overlap integrals appropriate to the whole molecule are then simply related to those of the fragments.

As an example in the use of this table we evaluate the group overlap integral between the ligand σ orbitals and the metal $d_{x^2-y^2}$ orbital in a ML_4 complex of S_4 symmetry. The ligand group orbital of B symmetry is

$$\psi(B) = \frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$$

the ligand orbitals being labeled cyclically viewed down the S_4 axis. The group overlap integral is then

$$\int d_{x^2-y^2}\psi(B)\,d\tau = \left[\frac{\sqrt{3}}{2}\sin^2\theta S_\sigma(d)\right]\left[\frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2}\right]$$
$$= 3\sin^2\theta S_\sigma(d)$$

In the limiting cases of square-planar complexes and tetrahedral complexes this expression reduces to $\sqrt{3}S_\sigma(d)$ and $(2/\sqrt{3})S_\sigma(d)$, respectively.

(8) For an example see D. A. Brown, *J. Inorg. Nucl. Chem.*, **10**, 39 (1959).

(9) J. D. Corbett and R. E. Rundle, *Inorg. Chem.*, **3**, 1408 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK

The Characterization of the Dimethylammoniate of Diborane

BY O. T. BEACHLEY

Received April 19, 1965

The literature contains many conflicting reports for the chemical and physical properties of a material called methylamine borane. One compound, a crystalline, volatile solid prepared from sodium borohydride and methylammonium chloride,[1] has been identified as $H_3B\text{-}NH_2CH_3$. Another material,[2] a nonvolatile liquid prepared from diborane and methylamine, has not been characterized completely. The n.m.r. spectrum[3] of this nonvolatile liquid is consistent with the ionic structure, $H_2B(NH_2CH_3)_2{}^+BH_4{}^-$. The following chemical and physical data provide more evidence that this compound is the dimethylammoniate of diborane, $H_2B(NH_2CH_3)_2{}^+BH_4{}^-$.

Experimental

Reaction of Diborane and Methylamine.—Diborane (1.10 mmoles) and methylamine (2.84 mmoles) were condensed on the

---

(1) H. Noth and H. Beyer, *Ber.*, **93**, 928 (1960).

(2) E. Wiberg, *Naturwissenschaften*, **35**, 182 (1948).

(3) S. G. Shore, C. W. Hickam, Jr., and D. Cowles, *J. Am. Chem. Soc.*, **87** 2755 (1965).

walls of a flask. The flask was then allowed to warm slowly to room temperature from −196° over a 1-hr. period and the excess amine (0.673 mmole) was removed. The product, a mobile, nonvolatile liquid which weighed 0.0986 g. and had a methylamine–diborane ratio of 1.97, can be assigned the empirical formula $B_2H_6 \cdot 2NH_2CH_3$.

Hydrolysis of $B_2H_6 \cdot 2NH_2CH_3$.—A sample of freshly prepared $B_2H_6 \cdot 2NH_2CH_3$ (0.865 mmole) was allowed to react immediately with excess 3 *M* hydrochloric acid. The initial vigor of the reaction was moderated by cooling the mixture with a −78° bath. The hydrogen (3.46 mmoles), measured with a Toepler pump–gas buret assembly, indicated the presence of 4.00 moles of easily hydrolyzable hydrogen atoms per mole of $B_2H_6 \cdot 2NH_2CH_3$. The aqueous solution was evaporated at 25°. The resultant solid was extracted with 50 ml. of dry chloroform and then the mixture was filtered. Removal of the chloroform from the solution left 0.093 g. of soluble material. The insoluble material, 0.0532 g. (0.862 mmole), was identified as boric acid. Methylammonium chloride was not observed as a hydrolysis product.

The chloroform-soluble material, a crystalline solid, softened to a transparent glass at 76–78°. The compound[4] $H_2B(NH_2CH_3)_2Cl$, observed to "melt" at 76–78°, would satisfy the stoichiometry of the hydrolysis reaction. Further evidence for the identification of this compound as $H_2B(NH_2CH_3)_2Cl$ was obtained by its elemental analysis, infrared spectrum, and characteristic stability[5] in acid solution.

Anal. Calcd. for $H_2B(NH_2CH_3)_2Cl$: B, 9.79; N, 25.4; Cl, 32.2. Found: B, 9.80; N, 24.8; Cl, 32.2.

Reaction of $B_2H_6 \cdot 2NH_2CH_3$ with Anhydrous Hydrogen Chloride.—Anhydrous hydrogen chloride (2.02 mmoles) and chloroform were condensed into a flask containing $B_2H_6 \cdot 2NH_2CH_3$ (1.10 mmoles). After the reaction at room temperature was complete, 1.47 mmoles of H_2 was collected. Diborane was identified by its infrared spectrum as another product of the reaction, but it could not be separated from unreacted hydrogen chloride. Therefore, this gaseous mixture was hydrolyzed and 2.32 mmoles of H_2 was found from 0.389 mmole of diborane. A chloride determination indicated 0.768 mmole of unreacted hydrogen chloride.

The chloroform solution resulting from the initial reaction was filtered and evaporated to dryness. There was 0.0220 g. of an unidentified insoluble material and 0.1109 g. of $H_2B(NH_2CH_3)_2Cl$. This sample of $H_2B(NH_2CH_3)_2Cl$ had an infrared spectrum and X-ray powder pattern which were identical with the sample of $H_2B(NH_2CH_3)_2Cl$ isolated from the hydrolysis reaction. Therefore, the compound with the empirical formula $B_2H_6 \cdot 2NH_2CH_3$ can be assigned the ionic formula $H_2B(NH_2CH_3)_2{}^+BH_4{}^-$.

Infrared Spectra and X-Ray Powder Pattern.—The infrared spectra of $H_2B(NH_2CH_3)_2BH_4$ as a liquid film and $H_2B(NH_2CH_3)_2Cl$ as a Nujol solution were recorded with a Perkin-Elmer 337 grating spectrometer.

$H_2B(NH_2CH_3)_2BH_4$.—Infrared spectrum (cm.$^{-1}$): 3200 (sh), 3178 (s), 3124 (s), 3016 (m), 2964 (m), 2950 (sh), 2900 (sh), 2700 (w), 2457 (s), 2450 (s), 2389 (m), 2350 (sh), 2334 (sh), 2322 (sh), 2289 (vs), 2222 (m), 1628 (sh), 1610 (m), 1600 (sh), 1478 (m), 1433 (w), 1366 (sh), 1350 (m), 1278 (w), 1198 (m), 1184 (m), 1168 (sh), 1130 (sh), 1119 (m), 1101 (m), 1089 (sh), 1028 (sh), 1021 (m), 980 (w), 942 (w), 923 (w), 843 (m), 826 (sh), 798 (w), 550 (m).

$H_2B(NH_2CH_3)_2Cl$.—Infrared spectrum (cm.$^{-1}$): 3205 (s), 3178 (s), 3160 (sh), 3060 (s), 2720 (m), 2430 (s), 2420 (s), 2380 (sh), 2340 (m), 2290 (s), 2228 (m), 1648 (m), 1630 (m), 1618 (m), 1482 (s), 1433 (w), 1362 (m), 1349 (m), 1278 (w), 1203 (m), 1195 (m), 1188 (s), 1169 (m), 1152 (m), 1129 (m), 1120 (m), 1070 (m), 1030 (m), 1008 (m), 982 (m), 944 (m), 923 (m), 875 (sh), 864 (m), 840 (m), 823 (m), 798 (w), 550 (m).

The X-ray powder pattern of $H_2B(NH_2CH_3)_2Cl$ was recorded with a 57.3-mm. diameter camera using Cu Kα radiation. The *d* spacings are reported in Ångstrom units: 7.66 (m), 5.89 (s), 5.08 (m), 4.58 (m), 3.71 (vs), 3.45 (vs), 3.29 (m), 3.07 (s), 2.84 (s), 2.68 (m), 2.56 (m), 2.43 (m), 2.35 (w), 2.24 (m), 2.17 (m), 1.97 (w), 1.80 (w), 1.72 (w).

Properties of $H_2B(NH_2CH_3)_2BH_4$.—The nonvolatile, liquid compound $H_2B(NH_2CH_3)_2BH_4$ very slowly decomposes at room temperature with the evolution of hydrogen. In addition to decomposition, $H_2B(NH_2CH_3)_2BH_4$ also slowly dissociates at room temperature to form the crystalline compound $H_3B–NH_2CH_3$, which was identified by its melting point, 57–58° (lit.[6] 57–58°), and infrared spectrum. A sample of freshly prepared $H_2B(NH_2CH_3)_2BH_4$ is a colorless, mobile liquid. However, upon standing for several months, the liquid changes into a predominantly crystalline mass of $H_3B–NH_2CH_3$ with only small deposits of the colorless liquid present. The dimethylammoniate of diborane is insoluble in chloroform, ether, and benzene but reacts with acetone, ethanol, and water.

Discussion

The reactions of the mobile, nonvolatile liquid prepared from diborane and methylamine are consistent with the ionic structure, $H_2B(NH_2CH_3)_2{}^+BH_4{}^-$. The proof of this structure requires evidence for the existence of the cation, $H_2B(NH_2CH_3)_2{}^+$, and the anion, $BH_4{}^-$. The reactions which identified these species are analogous to those used for the determination of the structure of the diammoniate of diborane,[7] $H_2B(NH_3)_2BH_4$.

The presence of the borohydride anion is suggested by the hydrolysis of $B_2H_6 \cdot 2NH_2CH_3$ and confirmed by its reaction with anhydrous hydrogen chloride according to the following equations. Metal borohydrides, such as $NaBH_4$, undergo comparable reactions.

$$H_2B(NH_2CH_3)_2BH_4 + 3H_2O + HCl(aq) \xrightarrow{3\,M\,HCl} H_2B(NH_2CH_3)_2Cl + H_3BO_3 + 4H_2$$

$$H_2B(NH_2CH_3)_2BH_4 + HCl(g) \longrightarrow H_2B(NH_2CH_3)_2Cl + H_2 + {}^1/_2B_2H_6$$

If the sample of $B_2H_6 \cdot 2NH_2CH_3$ were actually 2 moles of $H_3B–NH_2CH_3$, 6 moles of H_2, 2 moles of boric acid, and 2 moles of methylammonium chloride would be required as products for the hydrolysis reaction. Methylamine borane reacts with anhydrous hydrogen chloride[8] to form H_2 and $H_2ClB–NH_2CH_3$. None of these products was observed. The formation of $H_3B–NH_2CH_3$ from the reaction of $B_2H_6 \cdot 2NH_2CH_3$ with methylammonium chloride provides further evidence of the borohydride ion.

The cation of the dimethylammoniate of diborane was isolated as $H_2B(NH_2CH_3)_2{}^+Cl^-$ from the hydrolysis and anhydrous hydrogen chloride reactions. This type of boron hydride cation[5,8] has been identified in several investigations and is characteristically stable in aqueous solutions. The similarity between the infrared spectra of $H_2B(NH_2CH_3)_2Cl$ and $H_2B(t\text{-}C_4H_9NH_2)_2Cl$[4] lends more support for the identification of this cation. The presence of the $H_2B(NH_2CH_3)_2{}^+$ cation in $B_2H_6 \cdot 2NH_2CH_3$ is substantiated by the infrared spectrum as all of the absorptions of $H_2B(NH_2CH_3)_2Cl$ are present with small shifts and splitting of the bands in the spectra of $B_2H_6 \cdot 2NH_2CH_3$. It is very

---

(4) H. Noth, H. Beyer, and H. J. Vetter, *Ber.*, **97**, 110 (1964).

(5) N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).

(6) E. R. Alton, R. D. Brown, J. C. Carter, and R. C. Taylor, *ibid.*, **81**, 3550 (1959).

(7) R. W. Parry, D. R. Schultz, S. G. Shore, and P. P. Giradot, *ibid.*, **80**, 1 (1958); R. W. Parry, G. Kodama, and D. R. Schultz, *ibid.*, **80**, 24 (1958).

(8) H. Noth and H. Beyer, *Ber.*, **93**, 2251 (1960).

doubtful that this cation could be formed from the reactions which provided its isolation and identification.

The isolation of $H_2B(NH_2CH_3)_2BH_4$ provides another example in the growing list of reactions which initiate the unsymmetrical cleavage of diborane. The relative thermodynamic stability of $H_2B(NH_2CH_3)_2BH_4$ and $H_2B(NH_3)_2BH_4$ compared to the corresponding amine borane might be indicative of the probability of the occurrence of similar reactions with other donor systems. Ammonia borane, H_3B-NH_3, decomposes to form the more stable $H_2B(NH_3)_2BH_4$. However, methylamine borane is more stable than $H_2B(NH_2CH_3)_2BH_4$, as $H_2B(NH_2CH_3)_2BH_4$ slowly forms $H_3B-NH_2CH_3$ upon standing. Therefore, dimethylamine,[3] trimethylamine, and other donor molecules (DR'_3) might also initiate the unsymmetrical cleavage of diborane. Compounds of the type $H_2B(DR'_3)_2BH_4$ might be capable of isolation only at low temperatures because they will probably rapidly rearrange to corresponding compounds of the type $H_3B-DR'_3$ at room temperature. Thus, there might be only one type of reaction of donor systems with diborane, unsymmetrical cleavage. The compounds observed at room temperature would depend on the relative stabilities of the two systems, $H_2B(DR'_3)_2BH_4$ and $H_3B-DR'_3$, instead of the occurrence of symmetrical and unsymmetrical cleavage of diborane.

Acknowledgments.—The author wishes to thank Professor A. W. Laubengayer for his cooperation in making his research facilities available.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WAYNE STATE UNIVERSITY, DETROIT 2, MICHIGAN

Prediction of Stabilities of Trialkylgallium Addition Compounds

BY ALLAN LEIB,[1] MERLE T. EMERSON, AND JOHN P. OLIVER

Received May 10, 1965

The ability of group III derivatives to form addition compounds and the stability of these has been recognized as indicative of their chemical reactivity.[2] In the case of many of these compounds either direct gas phase dissociation measurements or calorimetric determinations provide the desired information; however, these standard techniques are not readily applicable to triethylgallium addition compounds because of their low volatility, small heat of formation, and tendency to undergo decomposition. Therefore, another suitable measure of stability is needed.

It has been shown that the chemical shift of the methyl group and the internal chemical shift of the ethyl group in CH_3X and CH_3CH_2X compounds have a direct dependence on the electronegativity of the attached group.[3,4] When considering the formation of an addition compound between a Lewis acid and base, a shift in electron density must take place upon formation of the coordinate bond. One would suppose that a large shift in electron density would correspond to the formation of a strong bond. This shift in electron density will be reflected in the chemical shift of neighboring protons in the moieties attached to the donor and acceptor. Therefore, the change in chemical shift of neighboring protons should reflect the stability of the addition compound. Studies of n.m.r. chemical shifts have been correlated with the stability of addition compounds of boron trihalides,[5] trimethylboron,[6] triethylboron,[7] and triethylaluminum.[8] Good agreements between chemical shift changes and independently determined stabilities were found. In this note we report a study of the change in chemical shift for a series of trimethyl- and triethylgallium addition compounds. The data are then used to obtain relative stabilities for these adducts.

Experimental

Trimethyl- and triethylgallium were prepared by reaction of the corresponding mercury compound with gallium metal[9] and were purified by repeated vacuum distillation or gas chromatography. Samples were prepared by distilling the gallium alkyl directly into the n.m.r. sample tube, adding excess base, and allowing the mixtures to warm to 0°. After standing for several hours to ensure complete reaction, the excess base was removed by low-temperature distillation. Alternately, to ensure the formation of 1:1 addition compounds a second series of samples was prepared by reaction of equimolar quantities of base with either trimethyl- or triethylgallium (determined by weight or gas volume). The samples were then dissolved in sufficient Freon 11 or Freon 113 to make a 20 to 30% solution and 1% of an internal standard was added. 1,1,1-Trichloroethane was used as an internal standard in the first experiments but was discarded because it underwent reaction in this system. Benzene or cyclopentane was used thereafter as internal standard. All reported line positions and chemical shifts were computed relative to cyclopentane with the results from the two series of samples within experimental error of each other. N.m.r. spectra were taken on a Varian D.P. 60 spectrometer and were calibrated by the audiofrequency side-band technique. Line frequencies were obtained by averaging the interpolated line positions from four or more spectra. The average deviation of line positions was ±0.2 c.p.s. The observed spectra of the addition compounds were analyzed as A_3B_2 systems,[10–12] and the resulting spectral parameters were used to calculate the theoretical line positions and intensities. These were then compared to the experimental spectra to check the validity of these parameters.

Discussion

The resulting chemical shifts, internal chemical shifts, and coupling constants are listed in Table I.

---

(1) Taken in part from the M.S. thesis of Allan Leib submitted to Wayne State University, 1965.

(2) F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958).

(3) B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

(4) C. R. McCoy and A. L. Allred, *J. Inorg. Nucl. Chem.*, **25**, 1219 (1963).

(5) J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, **42**, 1518 (1964).

(6) T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 4138 (1961).

(7) R. R. Holmes and R. P. Carter, Jr., *Inorg. Chem.*, **2**, 1146 (1963).

(8) H. E. Swift, C. P. Poole, Jr., and J. F. Itzel, Jr., *J. Phys. Chem.*, **68**, 2509 (1964).

(9) L. M. Dennis and W. Patnode, *J. Am. Chem. Soc.*, **54**, 182 (1932).

(10) P. T. Narasimhan and M. T. Rogers, *ibid.*, **82**, 34 (1960).

(11) P. T. Narasimhan and M. T. Rogers, *ibid.*, **82**, 5983 (1960).

(12) P. L. Corio, *Chem. Rev.*, **60**, 363 (1960).