that ionization of B_2F_4 occurs through removal of an electron much more closely associated with the B–B skeleton than with the B–F bond.

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Strong Hydrogen Bonds. IV. The $B_2H_7^-$ Species[1,2]

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Tetraethylammonium borohydride reacts at −78.5° with diborane to form $(C_2H_5)_4NB_2H_7$. At 0° hydrogen is also produced in a 1:10 mol ratio of H_2 to $(C_2H_5)_4BH_4$. Calorimetric studies allow an estimate of -31 ± 8 kcal/mol to be made for the minimum enthalpy of formation of the hydrogen bond in $B_2H_7^-$. This large enthalpy for an electron-deficient hydrogen bond is interpreted as showing that the lone pair usually deemed necessary for hydrogen-bond formation may actually be antibonding in character.

The $B_2H_7^-$ species was first postulated by Brown, Tierney, and Stehle[3] to account for the deviation from Henry's law of the pressure of B_2H_6 in contact with a solution of $NaBH_4$ in diglyme.[4] They proposed a structure for this anion involving a single hydrogen bridge bond. This is the only structure consistent with the equations of balance[5] for this species.

Our interest in the $B_2H_7^-$ species centered about the hydrogen-bond energy of the electron-deficient BHB bond. In order to obtain a value for this energy, a first requirement is a simple borohydride salt which reacts with diborane with no solvent present. A solid $NaB_2H_7 \cdot$diglyme had previously been isolated but attempts to remove the diglyme had been unsuccessful.[6] Lipscomb[7] had suggested that the $B_2H_7^-$ ion may not exist in the absence of solvent stabilization.

If the role of the diglyme is to solvate the sodium ion, rather than the $B_2H_7^-$ ion, removal of the diglyme should produce a salt which could increase its lattice energy greatly through the loss of diborane

$$NaB_2H_7(s) \longrightarrow NaBH_4(s) + 0.5B_2H_6(g)$$

According to this viewpoint, the reverse of the above reaction does not occur (in the absence of solvent), because the energy needed to expand the $NaBH_4$ lattice in order to accommodate the $B_2H_7^-$ species which would be formed is greater than the energy which is released through the formation of the $B_2H_7^-$ species. The situation appears to be analogous to the failure of NaBr to add HBr or NaI to add HI although such reactions do occur when tetraalkylammonium salts are used instead of sodium salts. The ionic radius[8] of BH_4^- is 2.03 Å, compared to 1.95 Å for Br^- and 2.16 Å for I^-.

Adams[9] was unable to prepare KB_2H_7 either in solution or as a solid, probably because the difference in lattice energies of KBH_4 and KB_2H_7 is large and the energy of coordination of potassium ion with diglyme is small.

It would appear that stable compounds containing the $B_2H_7^-$ species could be synthesized if the size of the cation were adjusted so that the lattice energies of MBH_4 and MB_2H_7 were comparable. The tetraalkylammonium cation seemed to be most suitable for this purpose. It was expected that very little lattice expansion would be needed to insert a "BH_3" unit into the lattice of a tetraalkylammonium borohydride. The preparation of a $B_2H_7^-$ compound under these circumstances would indicate that stabilization by solvation is not essential.

Experimental Section

Tetraethylammonium borohydride (Aldrich Chemical Co.), reported purity 97.5%, was used as received. Diborane was prepared from the reaction of concentrated H_2SO_4 with KBH_4 (Callery Chemical Co.) under conditions described by Jolly.[10]

Pressure–composition isotherms were obtained at −78.5 and 0° in a greaseless section of the vacuum line.[11] At −78.5° (see Figure 1) the reaction between B_2H_6 and $(C_2H_5)_4NBH_4$ evolved a

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[1] Taken in part from the Ph.D. thesis of W. G. Evans, 1964.

[2] Paper III: D. H. McDaniel and W. G. Evans, *Inorg. Chem.*, **5**, 2180 (1966).

[3] H. C. Brown, P. F. Stehle, and P. A. Tierney, *J. Am. Chem. Soc.*, **79**, 2020 (1957).

[4] Dimethyl ether of diethylene glycol.

[5] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1964, p 43.

[6] E. B. Baker, R. B. Ellis, and W. S. Wilcox, *J. Inorg. Nucl. Chem.*, **23**, 41 (1961).

[7] See ref 5, p 130.

[8] S. C. Abrahams and J. Kalnajs, *J. Chem. Phys.*, **22**, 434 (1954); the Br^- and I^- radii are from L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 514.

[9] R. M. Adams, "Borax to Boranes," Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, p 67.

[10] W. J. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1960, p 158.

[11] For a general discussion of vacuum-line techniques see R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

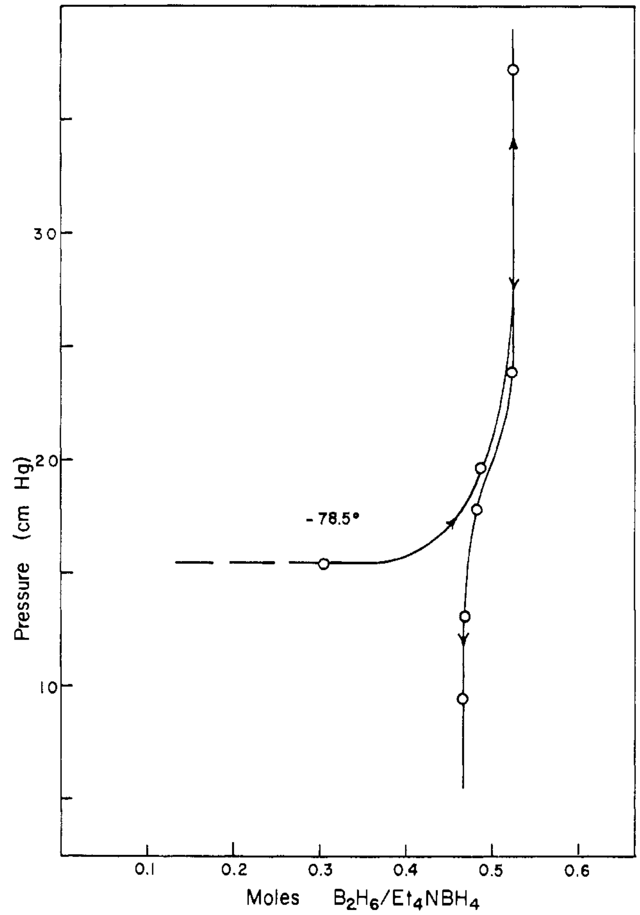

Figure 1.—Pressure–composition behavior of B_2H_6 and $(C_2H_5)_4NBH_4$ at −78.5°.

small amount of hydrogen, equal to about 1% of the diborane absorbed. The plateau pressure up to the 0.5:1 mol ratio of B_2H_6 to $(C_2H_5)_4NBH_4$ should not be regarded as an equilibrium pressure since the diborane which has been absorbed cannot be recovered. The $(C_2H_5)_4NB_2H_7$ produced is stable in a dry atmosphere. Addition of aqueous mineral acid separately to $(C_2H_5)_4NB_2H_7$ and $(C_2H_5)_4NBH_4$ gave volumes of H_2 in the ratio of 1.74 (calculated ratio of 1.75, *i.e.*, $7H_2/4H_2$). Although $(C_2H_5)_4NBH_4$ reacts only slowly with water, $(C_2H_5)_4NB_2H_7$ reacts vigorously with water evolving 3 mol of hydrogen

The phase behavior at 0° is very similar to that obtained at −78.5° except that hydrogen is produced in a 1:10 mol ratio of H_2 to $(C_2H_5)_4NBH_4$. Solution studies[12,13] of the reaction of B_2H_6 with BH_4^- ion have shown that, at temperatures above 25° and B_2H_6 pressures above 1 atm, $B_3H_8^-$ and H_2 are produced in very high yield. At still higher temperatures polyhedral borane ions are produced, the products being highly dependent on the basicity of the solvent.[13] Accordingly, the solid products obtained at 0° in this study were assumed to be a 9:1 mixture of $(C_2H_5)_4NB_2H_7$ and $(C_2H_5)_4NB_3H_8$.

Since the enthalpy change of the reaction could not be obtained from a study of decomposition pressure with temperature, a direct calorimetric approach was attempted. The ice calorimeter developed in our laboratories by Valleé[14] was selected for this purpose owing to the low heat loss of this calorimeter over long time periods. Preliminary studies revealed that complete absorption of diborane by the borohydride could not be achieved even after a 20-hr period. In the calorimetric run, the reaction was followed over a 2–3-hr period or to about 25% completion of the stoichiometric reaction. The diborane absorbed was calculated from the pressure drop in the calorimeter system after appropriate corrections were made for the side reaction occurring at 0°. Three separate calorimetric determinations gave values of −16.2, −16.5, and −17.2 kcal/mol of B_2H_6. Since an independent study of noncondensable gases in the system revealed that, under the conditions of the calorimetric experiments, an amount of noncondensable gas equivalent to 20% of the initial diborane was produced, it appears that two competing reactions are proceeding simultaneously in the calorimeter

$$B_2H_6(g) + 2(C_2H_5)_4NBH_4(s) \longrightarrow 2(C_2H_5)_4NB_2H_7(s) \qquad (1)$$

$$B_2H_6(g) + (C_2H_5)_4NBH_4(s) \longrightarrow (C_2H_5)_4NB_3H_8(s) + H_2(g) \qquad (2)$$

Reaction 2 is inferred from the hydrogen evolution and solution behavior[12,13] of B_2H_6 with BH_4^- at 25° and higher temperatures. This interpretation indicates the enthalpy change for 80% of reaction 1 and 20% of reaction 2 is −16.5 kcal/mol of B_2H_6.

Discussion

The phase studies carried out, particularly the one at −78.5°, clearly show the existence of the compound $(C_2H_5)_4NB_2H_7$. This suggests that the role of diglyme in the reaction of $NaBH_4$ with B_2H_6 is to solvate the Na^+ ion rather than the $B_2H_7^-$ ion.

The enthalpy datum at 0° is complicated by the simultaneous occurrence of a side reaction which is assumed to be reaction 2. The enthalpy change for reaction 2 is not known; however, it might be expected to be close to that of the formally similar reaction

$$2B_2H_6(g) \longrightarrow B_4H_{10}(g) + H_2(g) \qquad (3)$$

Both reactions 2 and 3 have a net effect of converting two B–H bonds into one B–B and one H–H bond. Using the heat of atomization reported[15] for B_2H_6 and B_4H_{10} and the value of 104.2 kcal/mol for the dissociation energy of H_2, the enthalpy change of reaction 3 is calculated as −1.6 kcal. If this value is used for the enthalpy change of reaction 2, the value for reaction 1 becomes 20.2 kcal.

The enthalpy change of reaction 4 has been determined to be +35.0 kcal.[16] Combining the enthalpies of (1) and (4) gives an enthalpy of −27.6 kcal for the reaction

$$B_2H_6(g) \longrightarrow 2BH_3(g) \qquad (4)$$

$$(C_2H_5)_4NBH_4(s) + BH_3(g) \longrightarrow (C_2H_4)_4NB_2H_7(s) \qquad (5)$$

The hydrogen-bond energy of $B_2H_7^-$ is defined by the enthalpy change for the reaction

$$BH_4^-(g) + BH_3(g) \longrightarrow B_2H_7^-(g) \qquad (6)$$

Reaction 6 differs from reaction 5 by the difference in lattice energy of $(C_2H_5)_4NBH_4$ and $(C_2H_5)_4B_2H_7$. The lattice energy difference for $(C_2H_5)_4NBr$ and $(C_2H_5)_4NBrHBr$ is ≥1.2 kcal; for $(C_2H_5)_4NI$ and $(C_2H_5)_4NIHI$ it is ≥5.1 kcal.[17] Since the BH_4^- ion is intermediate in size between Br^- and I^-, by interpolation the lattice energy difference may be taken to be ≥3 ± 2 kcal. Accordingly the enthalpy change for reaction 6 may be set at a minimum value of −30.6 kcal. The major source of uncertainty in this value is the estimate of the enthalpy change for reaction 2. A value of ±50 kcal for the enthalpy change of reaction 2 would cause

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(12) D. F. Gaines, R. Schaeffer, and F. Tebbe, *Inorg. Chem.*, **2**, 526 (1963).

(13) H. C. Miller, N. E. Miller, and E. L. Muetterties, *ibid.*, **3**, 1436 (1964).

(14) R. E. Valleé, *Rev. Sci. Instr.*, **33**, 856 (1962).

(15) See ref 5, p 109.

(16) A. B. Burg and Y. C. Fu, *J. Am. Chem. Soc.*, **88**, 1147 (1966).

(17) D. H. McDaniel and R. E. Valleé, *Inorg. Chem.*, **2**, 996 (1963).

a variation in the enthalpy change of reaction 6 from −25 to −37 kcal. Such limits appear to be reasonably cautious. Combining these with the uncertainty in the energy expended in lattice expansion, it appears appropriate to set limits of about ±8 kcal on this value of −31 kcal/mol for the minimum hydrogen-bond energy of $B_2H_7^-$.

The large magnitude of the $B_2H_7^-$ hydrogen-bond energy (second only to the FHF^- at −37 kcal)[18] may be taken to mean that the lone pair of electrons usually considered to be necessary for hydrogen bonding may actually be destabilizing in their effect on the hydrogen-bond energy. In the molecular orbital approach to hydrogen bonding,[19] only an orbital, either vacant or filled, is necessary for the hydrogen-acceptor atom. If the available orbital is filled with an electron pair, this pair will end up in a nonbonding molecular orbital. The present datum for the H-bond energy of the $B_2H_7^-$ species makes it appear that the "nonbonding" orbital may actually be antibonding in character. The only other hydrogen-bond energies for electron-deficient systems which are currently available are −17.5 kcal/H bond for diborane[16] and an estimate by Coates[20] of −15 to −20 kcal/H bond for the $(C_2H_5)_2AlH$ polymer. These values are much larger than the value for other H bonds in neutral species and again imply that the lone electron pairs contributed to hydrogen bonds may be antibonding in character.

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(18) S. A. Harrell and D. H. McDaniel, *J. Am. Chem. Soc.*, **86**, 4497 (1964).

(19) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

(20) G. E. Coates, "Organo-Metallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1960, p 142.

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High-Yield Synthesis of the Smaller *closo*-Carboranes $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$

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Under conditions of relatively high temperature, low pressure, and short residence time the *nido*-carborane 4,5-$C_2B_4H_8$ is converted in nearly 100% yield to the three *closo*-carboranes 1,5-$C_2B_3H_5$, 1,6- (and a little 1,2-) $C_2B_4H_6$, and 2,4-$C_2B_5H_7$. Conditions have not yet been completely optimized, but at 450–460° at 10 mm pressure for 1–3 sec (continuous flow system) 25–30% of the $C_2B_4H_8$ is converted approximately as follows: 40% $C_2B_3H_5$, 20% $C_2B_4H_6$, and 40% $C_2B_5H_7$, based on moles of $C_2B_4H_8$ consumed. The mechanism of formation of $C_2B_3H_5$ and $C_2B_5H_7$ appears to be *via* disproportionation of two $C_2B_4H_8$ molecules, while $C_2B_4H_6$ probably forms by simple loss of hydrogen from the $C_2B_4H_8$ parent.

Introduction

The first *closo*-carboranes discovered,[1-4] 1,5-$C_2B_3H_5$, 1,6- (and 1,2-) $C_2B_4H_6$, and 2,4-$C_2B_5H_7$, with the respective systematic names *closo*-1,5-dicarbapentaborane-5, *closo*-1,6-dicarbahexaborane-6, and *closo*-2,4-dicarbaheptaborane-7, were initially produced only in trace amounts from B_5H_9 and HCCH in a silent electric-discharge apparatus, and their derivative chemistry consequently has suffered from the lack of ready availability. In striking contrast the initially realized yields of the icosahedral *closo*-dicarbadodecaborane-12 $C_2B_{10}H_{12}$, which was discovered and characterized[5-16] independently of the small *closo*-carboranes, were much greater. Consequently its derivative chemistry, including the production of superior polymers by incorporation of $-C_2B_{10}H_{10}-$ moieties into silicones, has far outdistanced the derivative chemistry of $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$.[17] As to the compounds in the $C_2B_nH_{n+2}$ *closo*-carborane series lying between $C_2B_5H_7$ and $C_2B_{10}H_{12}$, routes to at least one isomer of each species have been discovered within the past 5 years. These include $C_2B_6H_8$,[18,19]

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(1) C. D. Good and R. E. Williams, U. S. Patent 3,030,289 (1959); *Chem. Abstr.*, **57**, 12534*b* (1962).

(2) R. E. Williams, C. D. Good, and I. Shapiro, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 14N.

(3) I. Shapiro, C. D. Good, and R. E. Williams, *J. Am. Chem. Soc.*, **84**, 3837 (1962).

(4) I. Shapiro, B. Keilin, R. E. Williams, and C. D. Good, *ibid.*, **85**, 3167 (1963).

(5) T. L. Heying, J. W. Ager, S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963).

(6) T. L. Heying, J. W. Ager, S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *ibid.*, **2**, 1097 (1963).

(7) M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1111 (1963).

(8) M. M. Fein, D. Grafstein, J. E. Paustian, J. Bobinski, B. M. Lichstein, N. Mayes, N. N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1115 (1963).

(9) D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *ibid.*, **2**, 1120 (1963).

(10) D. Grafstein, J. Bobinski, J. Dvorak, J. E. Paustian, H. F. Smith, S. Karlin, C. Vogel, and M. M. Fein, *ibid.*, **2**, 1125 (1963).

(11) D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963); U. S. Patent 3,226,429 (1961).

(12) H. Schroeder, T. L. Heying, and J. R. Reiner, *ibid.*, **2**, 1092 (1963).

(13) H. Schroeder and G. D. Vickers, *ibid.*, **2**, 1317 (1963).

(14) S. Papetti and T. L. Heying, *ibid.*, **2**, 1105 (1963).

(15) L. I. Zakharkin, V. I. Stanko, V. A. Brattsev, Yu. A. Chapovskii, and O. Yu. Ochlobystin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2238 (1963); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2074 (1963).

(16) V. I. Stanko, Yu. A. Chapovskii, V. A. Brattsev, and L. I. Zakharkin, *Usp. Khim.*, **34**, 1011 (1965); *Russ. Chem. Rev.*, 424 (1965); *Chem. Abstr.*, **63**, 9429*c* (1965).

(17) S. Papetti, B. B. Schaeffer, A. P. Gray, and T. L. Heying, *J. Polymer Sci.*, **4**, 1623 (1966).

(18) R. E. Williams and F. J. Gerhart, *J. Am. Chem. Soc.*, **87**, 3513 (1965).

(19) F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *ibid.*, **88**, 609 (1966).