turbidity had not changed after 6 months. The same relative behavior was observed at 50° where solution 4 precipitated in 5–8 hr. The reason for the earlier precipitation in the absence of excess electrolyte is probably related to the increased solubility of GaOOH in the ionic medium or to the competition between the polymerization and precipitation reactions.

Although the polymerization and variable behavior prior to equilibrium do not affect the nature of the final gallium species, the importance of the variables of time, temperature, and ionic strength in studies of polyionic systems is emphasized. A situation similar in several respects to this one arises in the case of iron(III) solutions where variable polymerization behavior is observed, but wherein the equilibrium data can be interpreted in terms of the solid hydroxide and Fe^{3+} ions in solution.[9,10]

Acknowledgment.—The authors are indebted to Professor Paul Schindler for very helpful discussions and encouragement in undertaking this research.

(9) W. Feitknecht and W. Michaelis, *Helv. Chim. Acta*, **45**, 212 (1962).

(10) P. Schindler, W. Michaelis, and W. Feitknecht, *ibid.*, **46**, 444 (1963).

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Transfer Reactions Involving Boron. XX. Disproportionation Reactions of Alkyl-, Alkoxy-, and Haloboranes[1]

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The solution redistribution equilibria of borane with alkylboranes, alkoxyboranes, haloboranes, and arylmercaptoboranes have been studied. The results obtained with the various systems are discussed individually and compared with each other and, when available, with gas-phase and other data appearing in the literature. The redistribution of trialkylboranes with borane in tetrahydrofuran produces a mixture of mono-, di-, and trialkylboranes and borane, the first two being the predominant products. Complicating the systems are the presence of five hydrogen-bridged monomer–dimer equilibria. The equilibrium constants for these equilibria have been determined for the *n*-propyl- and isopropylborane systems. The reaction of 1 or 2 mol of alcohols with 1 mol of borane produces dialkoxyboranes in kinetically controlled reactions. The dialkoxyboranes undergo slow redistribution reactions to give mixtures of borane and di- and trialkoxyboranes. Similarly, trialkyl borates and borane undergo slow disproportionation reactions. The redistribution equilibrium constants are identical, within experimental error, for primary and secondary alkoxyborane systems; however, the *t*-butoxyborane equilibrium constant is significantly different. The rate of attainment of equilibrium is markedly dependent on the structure of the alkoxy group. Boron trichloride reacts with borane to give either mono- or dichloroborane depending on the stoichiometry of the starting reagents, whereas boron trifluoride does not react with borane.

Borane–Trialkylboron Disproportionations

Schlesinger and coworkers[3,4] have observed that simple trialkylborons react with diborane, in the absence of solvent, to produce a complex equilibrium mixture of diborane and mono-, di-, tri-, and tetraalkyldiboranes. Brown and coworkers[5] have studied the disproportionation of tri-*n*-pentylboron with borane in tetrahydrofuran. They observed that the kinetically controlled (1 hr at 0°) product distribution formed in the hydroboration of 300 mmol of 1-pentene with 150 mmol of borane differs quite substantially (BH_3, 32.0%; RBH_2, 9.5%; R_2BH, 6.1%; R_3B, 52.4%) from the thermodynamically controlled product distribution formed on allowing the reaction mixture to stand at room temperature (BH_3, 2.7%; RBH_2, 24.0%; R_2BH, 61.3%; R_3B, 12%).[6]

Our studies on the mechanism of the hydroboration reaction required a more careful analysis of the disproportionation reactions (eq 1–3) which could conceivably compete with the hydroboration reaction.

$$R_3B + BH_3 \rightleftarrows R_2BH + RBH_2 \tag{1}$$

$$2R_2BH \rightleftarrows R_3B + RBH_2 \tag{2}$$

$$2RBH_2 \rightleftarrows R_2BH + BH_3 \tag{3}$$

The rate of the disproportionation of tri-*n*-propyl- and triisopropylboron with borane in tetrahydrofuran was followed by quenching aliquots of the reaction mixtures with *cis*-2-butene followed by glpc analysis of the resulting mixture of trialkyl-, dialkyl-*sec*-butyl-, alkyldi-

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[2] (a) Alfred P. Sloan Fellow, 1967–1969; (b) NDEA Fellow, 1967–1969.

[3] H. I. Schlesinger and A. O. Walker, *J. Amer. Chem. Soc.*, **57**, 621 (1935).

[4] H. I. Schlesinger, L. Horvitz, and A. B. Burg, *ibid.*, **58**, 407 (1936).

[5] H. C. Brown, A. Tsukamoto, and D. B. Bigley, *ibid.*, **82**, 4703 (1960).

[6] The analyses were carried out by quenching the reaction mixture with methanol and isolation of trimethyl borate, dimethyl *n*-pentylboronate, methyl di-*n*-pentylborinate, and tri-*n*-pentylboron by distillation.

sec-butyl-, and tri-*sec*-butylboron (corresponding to the concentrations of trialkyl-, dialkyl-, and monoalkylborane and borane). The glpc analyses, as well as oxidation of samples to the corresponding alcohols, showed that *no* alkyl isomerization occurred during the course of the reactions (maximum time followed was 10 days). The equilibrium compositions of the disproportion reaction mixtures at 25 and 40° are given in Table I.

TABLE I

COMPOSITION OF DISPROPORTIONATION EQUILIBRIUM MIXTURES[a]

R	Temp, °C	Concn, *M*			
		BH_3	RBH_2	R_2BH	R_3B
n-Propyl[b]	25	0.032	0.265	0.296	0.033
n-Propyl[b]	40	0.033	0.271	0.284	0.037
Isopropyl[c]	25	0.026	0.385	0.345	0.027
Isopropyl[c]	40	0.012	0.418	0.340	0.013

[a] Trialkylboron:borane initial ratio of 1:1. [b] Total boron concentration 0.626 *M*. [c] Total boron concentration 0.783 *M*.

The ^{11}B magnetic resonance spectra of the redistribution mixtures displayed only a very broad resonance band. Heteronuclear spin decoupling (H→B) or the use of perdeuterioborane caused the ^{11}B resonance spectra to become resolved into five peaks corresponding to borane ($\sim +3$ ppm relative to boron trifluoride etherate), alkylborane dimer (~ -17 ppm), dialkylborane dimer (~ -22 ppm), alkylborane monomer (~ -32 ppm), and dialkylborane monomer (~ -39 ppm). The trialkylboron appeared as a weak singlet at ~ -84 ppm.[7] The five following monomer–dimer equilibria (eq 4–8) were considered to be present

$$\mathrm{BH_3 + RBH_2 \rightleftharpoons BH_3 \cdot RBH_2} \tag{4}$$

$$\mathrm{BH_3 + R_2BH \rightleftharpoons BH_3 \cdot R_2BH} \tag{5}$$

$$\mathrm{2RBH_2 \rightleftharpoons RBH_2 \cdot RBH_2} \tag{6}$$

$$\mathrm{RBH_2 + R_2BH \rightleftharpoons RBH_2 \cdot R_2BH} \tag{7}$$

$$\mathrm{2R_2BH \rightleftharpoons R_2BH \cdot R_2BH} \tag{8}$$

in the equilibrium mixtures. The self-dimerization of borane does not occur in tetrahydrofuran as evidenced by the inability to detect diborane by ^{11}B magnetic resonance. However, the borane ^{11}B resonance peak of the disproportionation mixtures is badly distorted indicating a fast exchange of borane between the hydrogen-bridged complexes formed in eq 4 and 5. The trialkylboranes do not appear to be complexed with alkylboranes as indicated by ^{11}B resonance data. Although the reactants in eq 4–8 are written as uncomplexed species, they undoubtedly are complexed with solvent molecules. Studies in our laboratories have shown that borane complexes with tetrahydrofuran; however, trialkylboranes do not.[8] Pertinent, similar evidence could not be obtained for the mono- and dialkylboranes.

The equilibrium constants for eq 4–8 (R = *n*-propyl and isopropyl) have been calculated using computer techniques (see the Experimental Section for the details of the calculations) and are given in Table II.

TABLE II

MONOMER–DIMER EQUILIBRIUM CONSTANTS FOR EQ 4–8

R = *n*-propyl			R = isopropyl		
Eq	25°	40°	Eq	25°	40°
4	0.6	0.95	4	0.6	0.95
5	0.8	2.4	5	3.2	6.3
6	1.0	1.6	6	1.8	2.4
7	1.4	2.8	7	3.5	7.0
8	2.3	3.8	8	20	25

The experimental uncertainty of the equilibrium constants is believed to be better than ±15% of the values cited. The trends in the equilibrium constants are readily rationalized on the basis of two effects: (1) a simple electrostatic interaction between the polarized $B^{\delta+}$–$H^{\delta-}$ bonds of the complexing alkylboranes and (2) a steric effect imposed by the alkyl groups on the extent of complexing with solvent molecules.

TABLE III

ELECTRON DENSITIES CALCULATED BY THE EXTENDED HÜCKEL METHOD

	+ charge on B	− charge on H
BH_3	0.495	0.165
RBH_2[a]	0.65	0.184
R_2BH[a]	0.81	0.197
R_3B[a]	0.98	. . .

[a] The values cited are for *n*-alkylboranes; *sec*-alkylboranes give ~0.02 higher positive charge densities on boron.

The importance of the electrostatic interaction can be evaluated by consideration of the charge densities on boron and hydrogen as determined by extended Hückel calculations[9] which are given in Table III. If we simply sum the positive and negative charges on boron and hydrogen involved in the formation of the hydrogen-bridged dimers in eq 4–8, we find that the summed charges increase from eq 4 to 8 (eq 4, 1.59; eq 5, 1.67; eq 6, 1.67; eq 7, 1.84; eq 8, 2.01).[10] Superimposed on the readily apparent electrostatic effect is a steric effect. As the alkyl group becomes more bulky, *e.g.*, *n*-propyl to isopropyl, or as the number of alkyl groups increases, the ability of solvent molecules to coordinate with the central boron atom should decrease, thus increasing the necessity for stabilization by hydrogen-bridge dimer formation. This effect is quite apparent in the sequence of equilibrium constants for the R = isopropyl series and by comparison of the over-all *n*-propyl and isopropyl series.

The equilibrium constants for eq 1–3 (see Table IV) have been calculated both on the basis of total concentrations of borane and mono- and dialkylborane (monomer plus dimer) and on monomer concentration

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(7) The assignments were made by comparison of the ^{11}B magnetic resonance spectra of the hydroboration products of 2,3-dimethyl-2-butene and 2-methyl-2-butene which gave predominantly the mono- and dialkylboranes, respectively: H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, **81**, 6428 (1959).

(8) D. J. Pasto and P. Balasubramaniyan, *ibid.*, **89**, 295 (1967).

(9) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(10) The suggestion of such a correlation is not without precedent. We have observed previously that the Lewis acidity of a number of chloroboron derivatives as determined by nmr techniques gives a linear correlation with the calculated charge density on the central boron atom (see ref 8).

only, the latter being calculated from ^{11}B magnetic resonance data.[11] The latter values are less precise than the former because of the method of analysis. Comparison of the two sets of values indicates the importance of hydrogen-bridge dimer formation. The equilibrium constants for the isopropyl series are in general larger than those for the *n*-propyl series, the result of the greater steric demands of the isopropyl group in the higher alkylated boranes affecting both the ground-state energy and the ability for stabilization by complexing with the solvent molecules.

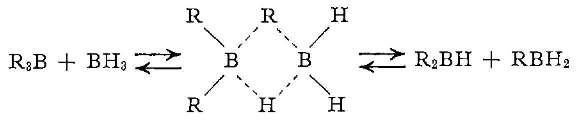
TABLE IV

EQUILIBRIUM CONSTANTS FOR EQ 1–3

R = *n*-propyl			R = isopropyl		
Eq	25°	40°	Eq	25°	40°
1	82[a] (31)[b]	63 (20)	1	189 (165)	840 (160)
2	0.098 (0.33)	0.12 (0.43)	2	0.87 (1.65)	0.47 (1.4)
3	0.13 (0.10)	0.13 (0.12)	3	0.60 (0.04)	0.23 (0.02)

[a] Calculated on the basis of total (monomer plus dimer) borane and mono- and dialkylborane concentrations. [b] Values in parentheses are calculated on the basis of free monomer concentrations.

The *n*-propyl system approaches equilibrium significantly faster than the isopropyl system. (A complete analysis of the kinetics of eq 1–3 is being attempted and will be reported separately later.) The disproportionation reactions are believed to proceed *via* a four-centered transition state illustrated below.



An elimination–readdition sequence cannot be occurring as evidenced by the complete lack of isomerization of the alkyl groups attached to boron, particularly in the case of the isopropyl system. The slower rate of disproportionation of the isopropyl system reflects the increased steric demands of the R group in the transition state.

Alkoxyborane Equilibrations

Burg and Schlesinger[12] in 1933 observed that diborane reacts with methanol to give dimethoxyborane as a distillable liquid which, however, undergoes slow reversible decomposition to give diborane and trimethyl borate. Monomethoxyborane and monomethoxydiborane were not detected as intermediates. Dimethoxyborane also undergoes disproportionation in the gas phase giving diborane and trimethyl borate.[13] Alkyl–alkoxy exchange between alkylalkoxyboranes requires several days at relatively high temperatures (160–200°).[14]

The reaction of an alcohol with borane in tetrahydrofuran in a 1:1 or 0.5:1 mole ratio, followed by immediate analysis by ^{11}B nmr, produces a mixture of borane and dialkoxyborane. No monoalkoxyborane (<5%) could be detected. Upon standing, the dialkoxyboranes underwent disproportionation to produce borane and trialkyl borate (eq 9). The same equilibrium is slowly established by treating borane with trialkyl borates.

$$3(RO)_2BH \rightleftarrows 2(RO)_3B + BH_3 \qquad (9)$$

The equilibrium constants for the *n*-propoxy-, *n*-butoxy-, isobutyoxy-, and *sec*-butoxyborane systems are the same within experimental error (see Table V); however, the equilibrium constant for the *t*-butoxyborane system is significantly lower. This trend reflects a significantly increased steric interaction in the tri-*t*-butyl borate compared with the other trialkyl borates encountered in this study. The ^{11}B magnetic resonance parameters also indicate that the tri-*t*-butyl system is somewhat different, the chemical shifts of di-*t*-butoxyborane and tri-*t*-butyl borate being −25.8 ppm (J = 166 Hz) and −15.8 ppm, whereas the other dialkoxyboranes and trialkyl borates appear at −27 ± 0.2 ppm (J = 168 Hz) and −18.0 ± 0.7 ppm.

TABLE V

EQUILIBRIUM CONSTANTS FOR THE REACTION

$3(RO)_2BH \rightleftarrows 2(RO)_3B + BH_3$

R	K
n-Propyl	3.3[a]
n-Butyl	5.7,[a] 6.1[b]
Isobutyl	3.2,[a] 7.3[b]
sec-Butyl	3.8,[a] 2.9[b]
t-Butyl	0.17,[a] 0.13[c]

[a] Derived from a 1:1 alcohol–borane mixture. [b] Derived from a 0.5:1 alcohol–borane mixture. [c] Derived from disproportionation of tri-*t*-butyl borate with borane.

The rate of attainment of equilibrium varies significantly as a function of the structure of the alkoxy group. Primary, straight-chain dialkoxyboranes (*n*-propoxy and *n*-butoxy) attain equilibrium in approximately 2 days at 25°, whereas the isobutoxy-, *sec*-butoxy-, and *t*-butoxyborane systems require 7, 18, and 35 days, respectively, to reach equilibrium.[15] The trend in the rates of disproportionation reflect increased steric demands in the four-centered transition states for alkoxy transfer, similar to those observed with the alkyl-transfer reactions discussed earlier in this paper.

The chemical behavior of alkoxyboranes derived from glycols is very similar. Rose and Shore[16] have prepared 1,3,2-dioxaboralane by treating diborane with ethylene glycol in diethyl ether. 1,3,2-Dioxaboralane is a distillable liquid; however, it undergoes disproportionation in the gas phase (K_{eq} = 25 ± 3 at 25°) and in tetrahydrofuran solution according to eq 10.

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(11) The equilibrium constants for the *n*-propyl system based on the total concentration of the various species compares reasonably well with equilibrium constants calculated for the *n*-pentyl system based on the work of Brown and Subba Rao:[7] $K_{Eq_1} = 45$; $K_{Eq_2} = 0.08$; $K_{Eq_3} = 0.29$.

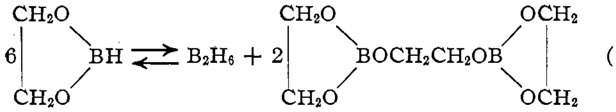
(12) A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **55**, 4020 (1933).

(13) W. J. Lehmann, T. P. Onak, and I. Shapiro, *J. Chem. Phys.*, **30**, 1215 (1959).

(14) P. L. Pennaritz, Ph.D. Dissertation, University of Notre Dame, 1963.

(15) The very slow rate of disproportionation of di-*t*-butoxyborane makes it possible to prepare di-*t*-butoxyborane quantitatively for other studies by treating a slight excess of *t*-butyl alcohol with 1 mol of borane.

(16) S. H. Rose and S. G. Shore, *Inorg. Chem.*, **1**, 744 (1962).


(10)

The ^{11}B magnetic resonance spectrum of a freshly prepared reaction mixture of borane and ethylene glycol shows the presence of borane, dialkoxyborane, and trialkoxyborane similar to the other alkoxyborane systems studied.

The lack of formation of monoalkoxyborane in the reactions of alcohols with borane and the disproportionations of dialkoxyboranes and trialkyl borates with borane appears to be thermodynamically controlled and not due to kinetic factors. The formation of dialkoxyborane in the reactions of alcohols with borane may occur by the rapid consecutive reactions of borane and monoalkoxyborane with the alcohol (eq 11) or the rapid disproportionation of an intermediate monoalkoxyborane (eq 12). The distinction between these two

$$\mathrm{ROH} + \mathrm{BH_3} \longrightarrow \mathrm{ROBH_2} + \mathrm{ROH} \longrightarrow \mathrm{(RO)_2BH} \quad (11)$$

$$2\mathrm{ROBH_2} \rightleftharpoons \mathrm{(RO)_2BH} + \mathrm{BH_3} \quad (12)$$

processes cannot be made on the basis of the present experimental data.

The reasons for the thermodynamic instability of the monoalkoxyboranes are not obvious. The thermodynamic instability of dialkoxyboranes in the gas phase or in nondonor solvents can be attributed to the apparently greater thermodynamic stability of diborane (see later discussion). However, in tetrahydrofuran the thermodynamic stability gained by the formation of diborane does not apply, and other factors must be operating. Perhaps the tendency of borane, and not the dialkoxyborane, to complex with the donor solvent leads to the greater thermodynamic stability of borane.

Borane-Boron Trihalide Disproportionations

The disproportionation of borane and boron trichloride in tetrahydrofuran produces only the mono- or dichloroborane (eq 13 and 14) depending on the stoichiometry of the reagents.[8] The rates of formation of the mono- and dichloroboranes are very rapid, the equilibrium being established essentially as fast as the reagents are mixed. The rate constants of the reverse reactions in eq 13 and 14 must be very small as indicated by the complete absence of borane and boron trichloride in the reaction mixture (by ^{11}B magnetic resonance) and from kinetic and product formation evidence derived from the hydroboration of olefins with mono- and dichloroborane.[17] In contrast, borane and boron trifluoride do not react in tetrahydrofuran solution.

$$2\mathrm{BH_3} + \mathrm{BCl_3} \rightleftharpoons 3\mathrm{BH_2Cl} \quad (13)$$

$$\mathrm{BH_3} + 2\mathrm{BCl_3} \rightleftharpoons 3\mathrm{BHCl_2} \quad (14)$$

The thermodynamic stability of mono- and dichloroboranes in a donor solvent sharply contrasts the chemical behavior of the mono- and dihaloboranes in nondonor solvents or in the gas phase. Lynds and Bass[18] reported that dichloroborane in the gas phase disproportionates essentially quantitatively to diborane and boron trichloride (eq 15) with an equilibrium constant of 532 ± 15 atm^{-1}. No monochloroborane or monochlorodiborane was observed as an intermediate. Murib, Horvitz, and Bonecutter[19] have measured both the liquid-phase (neat liquid mixture) and gas-phase equilibrium constants for eq 15, deriving values of $K_{\mathrm{gas}} = 872.3\ \mathrm{atm}^{-1}$ and $K_{\mathrm{liq}} = 12.52 \times 10^3\ \mathrm{l.\ mol}^{-1}$. Monochloroborane appears not to have been observed. Similar trends have been noted with the bromo-[20] and fluoroboranes.[21]

$$6\mathrm{BHCl_2} \rightleftharpoons \mathrm{B_2H_6} + 4\mathrm{BCl_3} \quad (15)$$

The reasons for the different behavior of the chloro- and fluoroborane systems in tetrahydrofuran is not readily apparent. Borane, monochloroborane, dichloroborane, boron trichloride, and boron trifluoride all complex with tetrahydrofuran. The strength of the complexing interaction, as indicated by the difference in chemical shifts of the α-hydrogens of tetrahydrofuran in a 1:1 complex *vs.* pure tetrahydrofuran,[22] increases in the order $\mathrm{BH_3}$ (14 Hz) < $\mathrm{BF_3}$ (39.1 Hz) < $\mathrm{BH_2Cl}$ (40.7 Hz) < $\mathrm{BHCl_2}$ (47.3 Hz) < $\mathrm{BCl_3}$ (64 Hz). As all of the species complex with tetrahydrofuran, the complexing interaction would not appear to be responsible for the difference in behavior. The predominant factor must be manifest in the different types of bonding involved in the boron-halogen bond, the boron-fluorine bond possessing considerable double-bond character owing to back-bonding of the electrons on fluorine (2p→2p), whereas with chlorine this interaction (3p→2p) is not as favorable. In the case of fluorine, the greater the number of fluorines bonded to boron, the more stable the species relative to a solvent-complexed mono- or difluoroborane. It is interesting to note that triphenylmercaptoborane behaves like boron trichloride in tetrahydrofuran reacting with borane to give only mono- or diphenylmercaptoborane depending on the stoichiometry of the reagents[23]

$$\mathrm{(C_6H_5S)_3B} + 2\mathrm{BH_3} \longrightarrow 3\mathrm{C_6H_5SBH_2} \quad (16)$$

$$2\mathrm{(C_6H_5S)_3B} + \mathrm{BH_3} \longrightarrow 3\mathrm{(C_6H_5S)_2BH} \quad (17)$$

The difference in the behavior of mono- and dichloroborane in an oxygen-donor solvent (tetrahydrofuran) *vs.* the gas phase or a nondonor solvent is more readily rationalized on the basis of the greater thermodynamic stability of diborane in the absence of a donor solvent. In terms of bonding, the diborane structure must provide a thermodynamically more favorable situation (all

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[17] D. J. Pasto and S.-Z. Kang, *J. Amer. Chem. Soc.*, **90**, 3797 (1968).

[18] L. Lynds and C. D. Bass, *Inorg. Chem.*, **3**, 1147 (1964).

[19] J. H. Murib, D. Horvitz, and C. A. Bonecutter, *Ind. Eng. Chem. Prod. Res. Develop.*, **4** (4), 273 (1965).

[20] L. Lynds, T. Wolfram, and C. D. Bass, *J. Chem. Phys.*, **43**, 3775 (1965).

[21] L. Lynds and C. D. Bass, *ibid.*, **43**, 4357 (1965); R. F. Porter and S. K. Wason, *J. Phys. Chem.*, **69**, 2208 (1965).

[22] Taken from ref 8 and J. F. Deters, P. A. McCusker, and R. C. Pilger, Jr., *J. Amer. Chem. Soc.*, **90**, 4583 (1968).

[23] D. J. Pasto, C. C. Cumbo, and P. Balasubramaniyan, *ibid.*, **88**, 2187 (1966).

orbitals of boron being occupied by σ bonds) compared to the dihaloboranes, which exist as monomers, in which back-bonding by the nonbonded electrons on the halogen must occur. The fact that borane exists as a monomer in tetrahydrofuran denies the system the added thermodynamic stability gained by forming a diborane structure, and the reactions in donor solvents must be controlled by solvent stabilization of the species (which should increase as the Lewis acidity of the boron species increases) and the bonding properties of the boron–halogen bond.

Experimental Section

Borane–Trialkylborane Disproportionations.—A carefully weighed portion of trialkylborane was added to a quantity of standardized borane (~0.35 *M*) in tetrahydrofuran (approximate mole ratio of 0.5:1 to 2:1) maintained under a nitrogen atmosphere. The reaction mixtures were maintained at 25 ± 0.1 and 40 ± 0.1° and aliquots were periodically removed by a syringe and added to a great excess of *cis*-2-butene in tetrahydrofuran. The quenched reaction mixtures were analyzed by glpc on a silicone oil column at 100° with the injector block maintained at 90–125°. The response ratios for the mixed *n*-propyl-*sec*-butylboranes were calculated by interpolation from the response ratio of tri-*n*-propyl- to tri-*sec*-butylborane.

The fully equilibrated reaction mixtures were analyzed by ^{11}B magnetic resonance using heteronuclear spin decoupling ($H \rightarrow ^{11}B$). The resulting spectra showed peaks near +3, −17, −22, −32, and −39 ppm (relative to boron trifluoride etherate internal capillary). The peaks were identified as borane (A), monoalkylborane dimer (B), dialkylborane dimer (C), monoalkylborane monomer (D), and dialkylborane monomer (E). Peak B represents the total amount of monoalkylborane appearing in the $RBH_2 \cdot BH_3$, $RBH_2 \cdot RBH_2$, and $RBH_2 \cdot R_2BH$ dimers, and peak C represents the total dialkylborane appearing in the $R_2BH \cdot BH_3$, $RBH \cdot RBH_2$, and $R_2BH \cdot R_2BH$ dimers. The relative areas of the five peaks were measured and converted to molar concentrations. A computer program was designed to calculate sets of possible equilibrium constants. An assumed low concentration of $RBH_2 \cdot BH_3$ in peak B and $R_2BH \cdot RBH_2$ in peak C was specified and the concentrations of the remaining species in solution were calculated from stoichiometric relationships governing the system. From these concentrations the first set of five equilibrium constants was calculated. The $RBH_2 \cdot BH_3$ concentration was then incremented to the maximum value defined by stoichiometric considerations, a set of five equilibrium constants being calculated after each incrementation. When $RBH_2 \cdot BH_3$ reached its maximum allowed value, the concentration of $R_2BH \cdot RBH_2$ was incremented once and the concentration of $RBH_2 \cdot BH_3$ was again incremented from its specified low value to its maximum value determined by the new stoichiometric restrictions. These calculations generate a matrix of sets of five equilibrium constants plus an indicator number to position the concentrations employed to calculate a given set of equilibrium constants. Each set of equilibrium constants from one matrix is compared in five-dimensional space with each set of equilibrium constants of a matrix derived from a different starting mole ratio of trialkylborane to borane. Values of equilibrium constants were printed only when the difference in the five-dimensional space distance was below a specified value. Refinements in the calculations could be made by specifying small incrementations within limited concentration ranges. Although a single set of equilibrium constants representing the absolute minimum could not be achieved, the final equilibrium constants were selected from an average of those values appearing in the region where the greatest number of minimum distances was obtained.

Borane–Alcohol Reactions.—To carefully weighed portions of the alcohols were added aliquots of standardized borane in tetrahydrofuran (approximately 1 *M*) under nitrogen at 0°. After the hydrogen evolution had ceased (30 min), the reaction mixtures were stirred at room temperature for 1 hr and portions of the reaction mixtures were sealed in nmr tubes and the ^{11}B magnetic resonane spectra were recorded. The ^{11}B resonance parameters are given in Table VI. The nmr tubes were allowed to stand at room temperature and the ^{11}B spectra were periodically recorded until no further changes in composition were noted (see Table VII).

The equilibrium constant (eq 9) for the *t*-butoxyborane system was also determined starting with tri-*t*-butoxyborane and borane. The rate of attainment of the final equilibrium distribution approximated that for the alcohol plus borane reaction mixture.

Table VI

^{11}B Magnetic Resonance Parameters of Alkoxyboranes

	δ, ppm (relative to $BF_3 \cdot (C_2H_5)_2O$)	
Alkoxy group	$(RO)_2BH$ (*J*, Hz)	$(RO)_3B$
n-Propoxy	−27.5 (165)	−17.5
n-Butoxy	−27.2 (160)	−18.8
Isobutoxy	−27.0 (168)	−17.3
sec-Butoxy	−26.8 (168)	−17.8
t-Butoxy	−25.8 (166)	−15.8

Table VII

Alkoxyborane Reaction Mixture Equilibrium Compositions

		Per cent		
Alkoxy group	BH_3:ROH ratio	BH_3	$(RO)_2BH$	$(RO)_3B$
n-Propoxy	1:0.5	52	22	26
n-Butoxy	1:1	39	22	39
n-Butoxy	1:0.5	53	19	28
Isobutoxy	1:1	39	22	39
Isobutoxy	1:0.5	54	18	28
sec-Butoxy	1:1	40	24	36
sec-Butoxy	1:0.5	47	24	29
t-Butoxy	1:1	23	48	29
t-Butoxy	. . .[a]	18	56	36

[a] Derived by disproportionation of tri-*t*-butyl borate with borane.

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