be considered as an E′ mode, while no other explanation than E″ can be given for the 798 cm^{-1} line. Also, in the spectrum of B-trichloroborazine, the γNH(E″) mode is observed at 817 cm^{-1}.

Based on these assignments, the BH and NH deformational modes of species A_2'' and E″ show an appreciable correspondence in their frequency shifts upon deuteration, thus tending to support the validity of the assignments.

	γBH, cm^{-1}	γBD, cm^{-1}	γNH, cm^{-1}	γND, cm^{-1}
A_2''	~915	~795	~715	~545
E″	~965	~725	~790	~550

Conclusion

Table VII depicts the proposed assignments and the isotopic shifts of the borazine fundamentals. All other observed frequencies not assigned to fundamentals can be attributed to overtone and combination bands without making assumptions about the inactive A_1' vibrations or even those fundamentals which have some inherent uncertainty. From the data in Table VII it is apparent that most of the proposed assignment revisions of the vibrational frequencies of borazine are adequately substantiated by isotopic data, which are in agreement with the product rule. Nevertheless some minor uncertainties remain which should be clarified by a subsequent study of the vibrational spectra of substituted borazines. Also, a full mathematical treatment based on the present experimental data, which should permit more detailed descriptions of the vibrational character of the various modes, will be reported later.

The revised assignments of ν_{13} and ν_{14} should result in a lower B–N valence force constant of borazine than that heretofore assumed. It is apparent that the cited assignments of the two ring stretching modes of species E′ demand a reconsideration of the assignments made for the vibrational spectra of substituted borazines. The necessity for such study has already been indicated previously when these two modes of $(-BF-NH-)_3$ were identified at 1510 and 1401 cm^{-1}, respectively.[22] An examination of the available spectra of a large number of variously substituted borazines indicates that the strongest band of nearly all spectra (corresponding to the revised value of ν_{13} of the parent borazine) is always accompanied by a weaker absorption having a lower frequency of approximately 50–100 cm^{-1}. Such data are illustrated in Table VIII. B-Trifluoroborazine has the highest BN ring vibration of all borazines that have been studied to date.

TABLE VIII

THE TWO BN RING MODES (SPECIES E′) OF SOME BORAZINES

Borazine	BN ring modes, cm^{-1}	Borazine	BN ring modes, cm^{-1}
$(-BF-NH-)_3$	1510/1401	$(-BCl-NH-)_3$	1442/1334
$(-BCD_3-NH-)_3$	1485–1362	$(-BCH_3-ND-)_3$	1441/1322
$(-BCH_3-NH-)_3$	1482–1378	$(-BBr-NH-)_3$	1436/1327
$(-BH-NH-)_3$	1465/1406	$(-BH-NCH_3-)_3$	1412/1314

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(22) H. Beyer, H. Jenne, J. B. Hynes, and K. Niedenzu, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 266.

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Lewis Acidity of Alanes. Interactions of Trimethylalane with Sulfides

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Solution calorimetric techniques have been employed to determine the enthalpies of formation of a number of sulfide–trimethylalane adducts in hexane. The enthalpies (in kcal/mole) found are: $S(CH_3)_2$, -16.69 ± 0.18; $(C_2H_5)_2S$, -16.75 ± 0.17; $H_2\overline{CSC}HCH_3$, -15.24 ± 0.17; $(CH_2)_3S$, -16.04 ± 0.18; $(CH_2)_4S$, -16.95 ± 0.18; $(CH_2)_5S$, -16.99 ± 0.20. Tensimetric determinations of the enthalpies of vaporization and dimerization of trimethylalane yielded $+9.88 \pm 0.06$ and -20.40 ± 0.34 kcal/mole, respectively. The enthalpy of vaporization of $(CH_3)_3Al \cdot S(CH_3)_2$ was found to be $+10.99 \pm 0.36$ kcal/mole. These values were used along with enthalpies of solution to correct the solution enthalpy of formation of $(CH_3)_3Al \cdot S(CH_3)_2$ to the gas phase, yielding $\Delta H_f(g) = -18.05 \pm 0.50$ kcal/mole.

Introduction

Although alkylalanes have been established as relatively strong Lewis acids, the literature contains only a limited amount of data on the enthalpies of molecular adduct formation. The gas-phase enthalpies of formation of adducts of trimethylalane with dimethyl sulfide[2] and dimethyl selenide[3] have been reported but adducts of amines, ethers, and phosphines were found to be too stable to study by this technique.[2] Toward trimethylalane the relative donor abilities of several Lewis bases have been assigned using the results of displacement reactions.[2,3] Calorimetric investigations of triethylalane interactions with amines, ethers, and sulfides have been reported,[4-6] but with the

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[1] National Aeronautics and Space Administration Predoctoral Fellow, 1966–1967.

(2) N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316 (1942).

(3) G. E. Coates, *J. Chem. Soc.*, 2003 (1951).

(4) E. Bonitz, *Chem. Ber.*, **88**, 742 (1955).

(5) E. G. Hoffmann and W. Tornau, *Z. Anal. Chem.*, **188**, 321 (1962).

(6) W. L. Everson and E. W. Rameriz, *Anal. Chem.*, **37**, 806 (1965).

exception of triethylamine[4] only approximate values have been reported for the interaction of trimethylalane with various bases.[6]

The studies reported in this paper were undertaken to determine the validity of using solution calorimetric enthalpies as approximations of gas-phase enthalpies for alane systems. The system trimethylalane–dimethyl sulfide was studied in detail so that the solution calorimetric enthalpy could be corrected to a gas-phase enthalpy allowing comparison with the datum which is in the literature.[2] The solution calorimetric technique was used to determine the relative Lewis basicities of several aliphatic and alicyclic sulfides. Establishment that the enthalpies of adduct formation in solution are good approximations of the gas-phase enthalpies would suggest that the basicities of phosphines, ethers, amines, and other strong bases toward trimethylalane can be determined using a calorimetric technique.

Experimental Section

Materials.—Trimethylalane was kindly provided by the Ethyl Corp. at a stated purity of 97.6% minimum. The sample required for each experiment was distilled just prior to use. All samples were used within 18 hr of distillation (observed bp 124.5–126° (750 mm); lit.[7] value, 125–126° (760 mm).

Commercial reagent grade hexane obtained from J. T. Baker Chemical Co. was stirred with several fresh quantities of concentrated sulfuric acid, washed three times with 5% potassium hydroxide solution and twice with distilled water, and dried over anhydrous magnesium sulfate. It was then distilled, purged with nitrogen, and stored over Linde 4A Molecular Sieves (observed bp 67.8–67.9° (734.5 mm); lit.[8] value, 67.7° (734.5 mm); observed $n^{20}\text{D}$ 1.3742; lit.[9] value, 1.3749).

All of the liquid sulfides were analyzed using gas chromatography on a 5-ft 20% SE-30 on 60–80 Chromosorb W column. In all cases impurities were less than 0.1%. Dimethyl sulfide, $(CH_3)_2S$, was obtained from K & K Laboratories and used as received (observed $n^{20}\text{D}$ 1.4353; lit.[9] value, 1.4354). Diethyl sulfide, $(C_2H_5)_2S$, was obtained from Eastman Organic Chemicals and used as received (observed $n^{20}\text{D}$ 1.4430; lit.[9] value, 1.4430). Tetrahydro-1-thiapyran, $(CH_2)_5S$, was obtained from Eastman Organic Chemicals and used as received (observed $n^{20}\text{D}$ 1.5070; lit.[9] value, 1.5067). Tetrahydrothiophene, $(CH_2)_4S$, was purchased from Eastman Organic Chemicals and purified by heating under reflux over CaH_2 and then distilled from $LiAlH_4$ under nitrogen (observed bp 118° (746 mm); lit.[10] value, 120.9° (760 mm); observed $n^{20}\text{D}$ 1.5048; lit. value, 1.5048). Propylene sulfide, $H_2\overline{CSC}HCH_3$, was prepared by the method of Snyder, *et al.*,[11] and was distilled just prior to use (observed bp 74° (747.0 mm); lit.[9] value, 74.4° (760 mm); observed $n^{20}\text{D}$ 1.4760; lit.[9] value, 1.475). Thietane, $(CH_2)_3S$, was obtained from Eastman Organic Chemicals and used as received (observed $n^{20}\text{D}$ 1.5095; lit.[10] value, 1.5102).

Preparation of the Trimethylalane–Dimethyl Sulfide Adduct.—To 4.0 g (0.055 mole) of solid trimethylalane at 0°, under nitrogen, was added 3.85 g (0.055 mole) of dimethyl sulfide. The liquid adduct was stirred at room temperature for 3 hr and then distilled three times at reduced pressure. The equation expressing our vapor pressure data agreed well with that calculated from the data of Davidson and Brown[2] (observed bp 48.7° (11.9 mm); lit.[2] value, 48.7° (12.0 mm)). Our observed equation was $\log P = (-2497/T) + 8.8352$ (Davidson and Brown:[2] $\log P = (-2488/T) + 8.8084$).

Vapor Pressures of Trimethylalane.—The equilibrium vapor pressures of triply distilled trimethylalane were measured using an isoteniscope which was thermostated in an oil bath. The mercury height readings taken using a Griffen and George cathetometer (Model B-2035) and corrected for capillarity were assigned a precision of ±0.01 mm. Temperatures regulated to ±0.05° by the thermostating bath were measured to ±0.1°. The data were taken using a random variation of the temperature.

Gas-Phase Dissociation of Trimethylalane.—The gas-phase dissociation of trimethylalane was studied in a tensimeter of known volume (559.2 cc) which was suspended inside an insulated jacket with a double-walled window for viewing the manometer. Constant temperature was maintained by the vapors of a liquid which was refluxed from a flask attached to the bottom of the jacket. The temperature was varied by changing the pressure on the boiling liquid with an associated manostat assembly capable of maintaining any pressure setting from 100 to 725 mm to within ±0.2 mm.[12] The mercury heights, which were measured using a Gaertner cathetometer and short-focus telescope, were corrected for capillarity and the thermal density variation of mercury. These measurements were assigned a precision of ±0.005 mm. The temperatures were measured to ±0.01° using a total immersion thermometer which had been calibrated using an NBS thermometer as reference. In each experiment a sample of known mass was transferred into the tensimeter and pressure measurements were made with random variation of temperature. Measurements at lower temperatures were taken after each high-temperature measurement in order to check for possible nonreversible decomposition of the sample. The theoretical pressure of trimethylalane dimer, P_{D_0}, and the observed pressure, P_{obsd}, were used in the expression to calculate the dissociation equilibrium constant, K_D.

$$K_D(\text{atm}) = \frac{4(P_{\text{obsd}} - P_{D_0})^2}{(2P_{D_0} - P_{\text{obsd}})760} \qquad (1)$$

Calorimeter.—The calorimeter used in this study is similar to that described by Arnett[13] although different sample introduction and base line compensation techniques are employed. In order to achieve a base line of convenient slope, a second thermistor, nearly identical with that used in the reaction calorimeter, was connected in one arm of the thermistor bridge circuit and placed in a second calorimeter similar to the reaction calorimeter, but containing only pure solvent. The slope of the base line was changed by manipulation of the stirring rates of the two stirrers. In this manner the heat of stirring and the cooling effect of nitrogen introduction in the reaction calorimeter can be nullified. The reactant was introduced into the solution by breaking a thin-walled bulb at the end of a glass tube which extends below the surface of the solution. The tubes used were thoroughly cleaned, dried, and treated to remove oxygen before they were loaded with reactant in an inert-atmosphere box. Through a rubber septum on one end of the tube was thrust a wire plunger which was used to break the thin-walled bulb. This ejected the limiting reactant into the solution containing the other reactant in excess. Tubes prepared in this manner were kept in the dark to retard photodecomposition of the alane. In this manner, the alane was quantitatively introduced in a reproducible fashion. In a typical calorimeter experiment 100 ml of hexane solvent was introduced into the 200-ml reaction calorimeter dewar flask, which was then fitted with a machined Teflon plug, through which a screw design stirrer, heater coil, thermistor, and nitrogen gas inlet were passed.

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(7) A. V. Grosse and J. M. Mavity, *J. Org. Chem.*, **5**, 106 (1940).

(8) "International Critical Tables," Vol. III, McGraw-Hill Book Co. Inc., New York N. Y., 1928, pp 199–246.

(9) "Selected Values of Properties of Hydrocarbons," American Petroleum Research Institute, Project 44, Vol. VII.

(10) W. E. Haines, R. V. Helm, G. W. Bailey, and J. S. Ball, *J. Phys. Chem.*, **58**, 270 (1954).

(11) H. R. Snyder, J. M. Stewart, and J. B. Zregler, *J. Am. Chem. Soc.*, **69**, 2672 (1947).

(12) (a) D. E. McLaughlin, Ph.D. Thesis, University of Michigan, 1959; (b) L. J. Sachs, Ph.D. Thesis, University of Illinois, 1964.

(13) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. MacDuggleby, *J. Am. Chem. Soc.*, **87**, 1541 (1965).

TABLE I

ΔH_{vap} DATA OF $[Al(CH_3)_3]_2$

Temp, °C	17.60	20.05	21.72	25.50	28.65	33.50	36.7	43.6	47.7
P, mm	7.86	9.38	10.13	12.60	15.00	19.01	23.02	32.49	40.61

A nitrogen atmosphere was maintained over the solution. A measured quantity of base was introduced into the hexane with a syringe and a small sample of trimethylalane was ejected into the solution to remove any reactive reagents. A previously prepared tube containing trimethylalane was then placed in the calorimeter through the Teflon plug and the system was allowed to come to thermal equilibrium. The equilibrated base line compensating device was engaged and the stirring rate was adjusted to produce a usable base line on the recorder. The techniques and calculations used in determining the actual heats associated with the various processes were virtually identical with those outlined in the literature.[13] After a calibration, the alane was ejected into the solution and a second calibration was recorded. The temperature of the calorimeter was held at 28.5 ± 1.5°.

Successive determinations were carried out in the same solution until one-half to two-thirds of the initial quantity of sulfide had reacted. In this manner the effect of changing the concentrations of adduct and base were determined. If an equilibrium prevails or other than a 1:1 adduct exists, progressively lower enthalpies should be observed with each reaction. Some trials were done using all of the initial quantity of sulfide with no significant change in the successively observed enthalpies. In the case of propylene sulfide and dimethyl sulfide, reverse reactions were also studied with the sulfide being ejected into the hexane containing excess trimethylalane. Enthalpies observed in these experiments were identical with those determined in the forward direction for the solution reaction. Enthalpies of solution were determined by simply ejecting the various solutes into hexane.

The accuracy of the calorimetric equipment was checked by determining the heat of the neutralization reaction

$$HCl\cdot 70H_2O + NaOH\cdot 8400H_2O = H_2O(l) + NaCl\cdot 8470H_2O \qquad (2)$$

The average of five determinations was $\Delta H_f = -13.86 \pm 0.25$ kcal/mole. The value calculated from heat of formation data at 298°K is -13.72 kcal/mole.[14] The standard deviations of the enthalpies are lower in hexane than in water as is reflected in the data in Table V.

Results

The data from which the enthalpy of vaporization of trimethylalane were determined are given in Table I. Least-squares analysis of these data give the vapor pressure equation: $\log P = (-2159/T) + 8.3287$. Regression analysis of these data at the 99% confidence level yields: $\Delta H_{vap}[Al(CH_3)_3]_2 = +9.88 \pm 0.06$ kcal/mole.

Calculation of the enthalpy of dimerization of trimethylalane was based on two determinations, both of which are given in Table II along with previously reported data. Least-squares analysis of our data yields the equation: $\log K_D = (-4457.9/T) + 9.4395$. Application of regression analysis provides at the 99% confidence level: $\Delta H_{dim}[Al(CH_3)_3]_2 = -20.40 \pm 0.34$ kcal/mole.

The enthalpy of vaporization of the trimethylalane–dimethyl sulfide adduct was calculated from equilibrium vapor pressure data of the adduct using the following relationship, which takes into account the partial dissociation of the adduct into monomer and dimer alane and dimethyl sulfide.

$$P_{AB} = \frac{3\sqrt{K_D}\,(\sqrt{K_D + 3P_T - 3P_{AB}} - \sqrt{K_D})^2 + 2(\sqrt{K_D + 3P_T - 3P_{AB}} - \sqrt{K_D})^3}{27K_{diss}} \qquad (3)$$

The dissociation constant, K_D, of the dimer alane is determined using the previously described relationship. The dissociation constant, K_{diss}, for the reaction $A\cdot B \rightleftharpoons {}^1/_2A_2 + B$, was determined using Davidson and Brown's[2] value of 8.5 kcal/mole as the enthalpy of dissociation. Their data yielded the following relationship, which was used to calculate K_{diss} at 10° intervals: $\log K_{diss} = (-1857.5/T) + 3.5404$. The partial pressure of the adduct is P_{AB}. The total pressure, P_T, used in the calculations of P_{AB}, is calculated from the experimentally determined relationship found in the Experimental Section. Least-squares and regression analysis of these data give the following value at the 99% confidence level: $\Delta H_{vap} = [(CH_3)_3Al\cdot S(CH_3)_2] = +10.99 \pm 0.36$ kcal/mole.

In the case of trimethylalane–dimethyl sulfide adduct the enthalpy measured in solution was corrected to the gas phase using the thermodynamic cycle

$$\begin{tikzcd}
A(g) \arrow[d, "{}^1/_2\Delta H_{dim}(A_2)"] & + & B(g) \arrow[d, "-\Delta H_{vap}(B)"] \arrow[r, "\Delta H_f{[AB(g)]}"] & AB(g) \\
{}^1/_2A_2(g) \arrow[d, "-{}^1/_2\Delta H_{vap}(A_2)"] & & B(l) \arrow[dd, "\Delta H_{soln}(B)"] & AB(l) \arrow[u, "\Delta H_{vap}(AB)"'] \\
{}^1/_2A_2(l) \arrow[d, "{}^1/_2\Delta H_{soln}(A_2)"] & & & \\
{}^1/_2A_2(soln) & + & B(soln) \arrow[r, "\Delta H_f{[AB(obsd\ soln)]}"] & AB(soln) \arrow[uu, "-\Delta H_{soln}(AB)"']
\end{tikzcd} \qquad (4)$$

The gaseous enthalpy of formation was calculated using the data given in Table IV and the expression

$$\Delta H_f[AB(g)] = \Delta H_{obsd\ soln} + \Delta H_{soln}(B) + \Delta H_{vap}(AB) + {}^1/_2\Delta H_{soln}(A_2) - \Delta H_{vap}(B) - \Delta H_{soln}(AB) - {}^1/_2\Delta H_{vap}(A_2) + {}^1/_2\Delta H_{dim}(A_2) \qquad (5)$$

This yields a value: $\Delta H_{f,calcd}(g) = -18.05 \pm 0.50$ kcal/mole. $\Delta H_{f,cor}$(soln) were determined using the thermodynamic cycle

$$\begin{tikzcd}
A(soln) \arrow[d, "``{}^1/_2\Delta H_{dim}(A_2)''"] & + & sulfide(soln) \arrow[dd] \arrow[r, "\Delta H_{f,cor}(soln)"] & A\cdot(sulfide)(soln) \\
{}^1/_2A_2(soln) \arrow[d, "-{}^1/_2\Delta H_{soln}(A_2)"] & & & \\
{}^1/_2A_2(l) & + & sulfide(soln) \arrow[r, "\Delta H_{f,obsd}"] & A\cdot(sulfide)(soln) \arrow[uu]
\end{tikzcd} \qquad (6)$$

The expression which arises from this thermodynamic cycle was used to calculate the corrected enthalpies

$$\Delta H_{f,cor}(soln) = -{}^1/_2\Delta H_{soln}(A_2) + ``{}^1/_2\Delta H_{dim}(A_2)'' + \Delta H_{f,obsd} \qquad (7)$$

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(14) National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

TABLE II

ΔH_{dim} DATA FOR $[Al(CH_3)_3]_2$

Temp, °C	P_{obsd}, mm	K, atm	Calcd mol wt
Determination I: $P_{D_0} = (4.8500 \times 10^{-2})T$			
140.18	29.585	4.322×10^{-2}	98.4
120.52	25.026	1.323×10^{-2}	110.6
130.27	27.167	2.404×10^{-2}	104.5
150.18	32.388	8.083×10^{-2}	92.05
70.12	17.655	2.670×10^{-4}	136.9
90.19	19.898	1.576×10^{-3}	128.6
100.27	21.287	3.242×10^{-3}	123.5
110.39	22.978	6.582×10^{-3}	117.5
80.04	18.678	6.856×10^{-4}	133.1
Determination II: $P_{D_0} = (6.1970 \times 10^{-2})T$			
69.86	22.259	2.610×10^{-4}	138.0
79.64	23.438	6.445×10^{-4}	134.7
90.22	24.950	1.550×10^{-3}	130.4
100.09	26.544	3.111×10^{-3}	125.9
110.31	28.575	6.431×10^{-3}	120.2
Laubengayer Data:[a] $P_{D_0} = (2.354 \times 10^{-1})T$			
100.3	94.5	2.8199×10^{-3}	134.0
115.0	102.2	7.6165×10^{-3}	128.9
155.7	135.2	9.2291×10^{-3}	107.6

[a] A. W. Laubengayer and W. F. Gilliam, *J. Am. Chem. Soc.*, **63**, 477 (1941).

TABLE III

OBSERVED VAPOR PRESSURE DATA AND CALCULATED VAPOR PRESSURE DATA FOR $(CH_3)_3Al \cdot S(CH_3)_2$

Temp, °C	Obsd P_T, mm	Calcd P_{AB}, mm
40.0	7.29	5.79
50.0	12.80	9.90
60.0	21.99	16.65
70.0	36.00	26.50
80.0	59.84	43.10

TABLE IV

THERMODYNAMIC CYCLE ENTHALPY VALUES FOR $(CH_3)_3Al \cdot S(CH_3)_2$ IN HEXANE

Quantity	Value, kcal/mole
$\Delta H_{\mathrm{soln}}(\mathrm{adduct})$	$+1.65 \pm 0.03$
$\Delta H_{\mathrm{soln}}[(CH_3)_2S]$	$+0.760 \pm 0.004$
$^1/_2\Delta H_{\mathrm{soln}}[(CH_3)_3Al)_2]$	$+0.223 \pm 0.025$
$\Delta H_{\mathrm{f,obsd\ soln}}$	-6.49 ± 0.06
$\Delta H_{\mathrm{vap}}(\mathrm{adduct})$	$+10.99 \pm 0.36$
$^1/_2\Delta H_{\mathrm{dim}}[((CH_3)_3Al)_2]$	-10.20 ± 0.17
$^1/_2\Delta H_{\mathrm{vap}}[((CH_3)_3Al)_2]$	$+4.94 \pm 0.03$
$\Delta H_{\mathrm{vap}}[(CH_3)_2S]$	$+6.74 \pm 0.20$[a]

[a] Calculated from data found by A. Berthoud and R. Brum, *J. Chim. Phys.*, **21**, 143 (1924).

In this treatment it was assumed that the enthalpy of dimerization of trimethylalane in hexane is equivalent to that in the gas phase. This may not be so since hexane solvation may favor the monomer form which would alter the enthalpy of dimerization. However, the deviation is expected to be small, since hexane solvation is thought to be minimal.

Discussion

The equilibrium constants for the gas-phase dissociation of trimethylalane and the calculated enthalpy of dimerization reported here are in good agreement with those of Laubengayer.[15] The enthalpy of vaporization of trimethylalane agrees well with that reported by McCullough.[16]

TABLE V

MEASURED ENTHALPIES OF $(CH_3)_3Al \cdot (\mathrm{sulfide})$ IN HEXANE

Base	No. of determn	$\Delta H_{\mathrm{f,obsd}}$, kcal/mole	$\Delta H_{\mathrm{f,cor}}(\mathrm{soln})$, kcal/mole
$(C_2H_5)_2S$	3	-6.33 ± 0.02	-16.75 ± 0.17
$(CH_3)_2S$	9	-6.27 ± 0.06	-16.69 ± 0.18
$H_2\overline{CSC}HCH_3$	4	-4.82 ± 0.02	-15.24 ± 0.17
$(CH_2)_3S$	7	-5.62 ± 0.05	-16.04 ± 0.18
$(CH_2)_4S$	4	-6.53 ± 0.06	-16.95 ± 0.18
$(CH_2)_5S$	5	-6.57 ± 0.10	-16.99 ± 0.20

The gas-phase enthalpy of formation of the trimethylalane–dimethyl sulfide adduct determined by correction of the solution enthalpy is in good agreement with the gas-phase value found in the literature (*i.e.*, corrected solution, -18.05 ± 0.50 kcal/mole; lit.,[17] -18.7 ± 2.0 kcal/mole). The solution enthalpy, -16.69 ± 0.18 kcal/mole, deviates from the corrected solution enthalpy by about 7% suggesting that for trimethylalane systems calorimetric measurements in hexane are good approximations of the gas phase. The observed differences may be explained by considering two of the enthalpy terms used in the thermodynamic cycle. The calculation of the enthalpy of vaporization of the adduct is based on 8.5 ± 2.0 kcal/mole, the value reported by Brown[2] as the enthalpy of adduct dissociation into dimer alane and dimethyl sulfide. This number is of very low precision and we suspect that it is too large. Also the assumption that the gas-phase enthalpy of dimerization of trimethylalane is equal to that in solution may not be valid.

Comparison of the solution enthalpy of formation values for the six sulfides examined reveals a similar magnitude in all and a relatively small difference between any two. Tetrahydrothiophene and tetrahydro-1-thiapyran are the strongest donors and are virtually indistinguishable in donor strength. The dialkyl sulfides, both weaker donors than the five- and six-membered ring sulfides, are nearly equal in donor strength with diethyl sulfide being perhaps a bit stronger. Thietane and propylene sulfide are the weakest donors with propylene sulfide being the weakest.

The order of donor strength observed in this study (*i.e.*, $(CH_2)_5S \sim (CH_2)_4S > (C_2H_5)_2S \sim (CH_3)_2S > (CH_2)_3S > H_2\overline{CSC}HCH_3$) is somewhat different from that observed for iodine,[18] where the order varies depending on the type of measurement used. In both of these studies the order is assigned on the basis of small differences in the enthalpies of interaction. However, the results are unlike those recently reported for BCl_3[19] where the observed order of donor ability of sulfides was $(CH_2)_4S >> (CH_2)_5S \sim (C_2H_5)_2S > (CH_3)_2S$.

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(15) See footnote *a* of Table II.

(16) J. P. McCullough, J. F. Messerly, R. T. Moore, and S. S. Todd, *J. Phys. Chem.*, **67**, 677 (1963).

(17) This number involves the enthalpy of dimerization of trimethylalane and is stated using the value reported in this paper.

(18) M. Tamres and S. Searles, *J. Phys. Chem.*, **66**, 1099 (1962).

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The differences in the observed enthalpies of $Al(CH_3)_3$ and BCl_3 interactions with $(CH_2)_5S$ and $(CH_2)_4S$ suggest that ring-size effects are involved in the BCl_3 adducts. These ring-size effects are probably steric in nature. This type of effect has been established in BF_3 interactions with cyclic ethers where $(CH_2)_4O$ has a greater enthalpy of interaction than $(CH_2)_5O$.[20] If this effect in the sulfides were not steric, one would expect that trimethylalane should also differentiate the donor abilities of $(CH_2)_5S$ and $(CH_2)_4S$. These results are not inconsistent with other studies which have established that the steric requirements in alane adducts are much less severe than those in corresponding borane adducts. The 2,6-lutidine–trimethylalane adduct is quite stable[21] whereas the corresponding trimethylborane adduct does not exist, apparently for steric reasons.[22] The tetrahedral covalent radius of aluminum, which is approximately 43% larger than that of boron, apparently results in the formation of sufficiently long dative bonds so that the alane methyl groups are adequately removed from the sphere of steric influence of substituents on the donor atom.

The small differences in the observed solution enthalpies suggest that steric effects are minimal. The observed differences are probably best explained by considering the influence of inductive effects and ring strain upon the sulfur lone-pair availability.

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Reactions of Pentaborane(9) and Pentaborane Derivatives

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The preparations of a number of pentaborane derivatives are described and ^{11}B and ^{1}H nmr spectra recorded and correlated. Assessments of alternative preparative schemes are given. An extension of the apex to base rearrangement reaction to polyalkyl pentaboranes reveals the following trends: the rate of rearrangement decreases with increasing number of alkyl substituents on the pentaborane framework; the rate increases with the use of stronger and less sterically hindered bases. Mechanistic inferences are discussed.

Introduction

Although a number of reports on reactions of pentaborane and on the preparation of pentaborane derivatives appear in the literature,[1–24] there is a need for a study which correlates the reactivities and properties of such compounds. It is, in part, an attempt to pave the way for a systematized examination of this sort that accounts for the present work. The preparations of several new derivatives are described and assessments of presently known synthetic routes are made. In addition, both ^{1}H and ^{11}B nmr spectra are gathered and correlated.

Experimental Section

Materials.—Methyl chloride, ethylene, hydrogen chloride, and trimethylamine were obtained from The Matheson Co., Inc., and used without further purification. Chlorine (Matheson) was freed from HCl by a single distillation. Pentaborane and decaborane were obtained from Olin Mathieson Chemical Co., Inc., aluminum chloride from J. T. Baker Chemical Co., and metal hydrides from Metal Hydrides, Inc. Diglyme (Ansul), ethyl ether, and tetrahydrofuran were distilled from lithium aluminum hydride before use. 1-Methyl-,[3,4,8] 1-bromo-,[2,5,16] 2-bromo-,[17] 1-chloro-[25], and 2-chloropentaboranes[15,26] were pre-

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