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Lewis Acidity of Alanes. Interactions of Trimethylalane with Amines, Ethers, and Phosphines

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Solution calorimetric techniques in hexane have been employed to determine the enthalpy of formation of a number of trimethylalane adducts with phosphorus, nitrogen, and oxygen donors. The enthalpies (in kcal/mole) found are: $P(CH_3)_3$, -21.02 ± 0.28; $P(C_2H_5)_3$, -22.12 ± 0.33; $P(C_6H_5)_3$, -17.63 ± 0.18; $N(CH_3)_3$, -29.96 ± 0.19; $HN(CH_3)_2$, -30.84 ± 0.26; H_2NCH_3, -30.02 ± 0.31; NH_3, -27.55 ± 0.25; pyridine, -27.56 ± 0.17; 2-picoline, -26.13 ± 0.24; 2,6-lutidine, -19.87 ± 0.21; $(C_2H_5)_3N$, -26.47 ± 0.18; $HN(C_2H_5)_2$, -27.33 ± 0.18; $O(CH_3)_2$, -20.29 ± 0.20; $O(C_2H_5)_2$, -20.21 ± 0.23; tetrahydrofuran, -22.90 ± 0.19; 2-methyltetrahydrofuran, -22.94 ± 0.18; 2,5-dimethyltetrahydrofuran, -22.95 ± 0.17. For the trimethylalane–trimethylamine and trimethylalane–dimethyl ether systems appropriate vapor-phase data were used with the calorimetric data to calculate a gas-phase enthalpy. For $(CH_3)_3Al \cdot N(CH_3)_3$, $\Delta H_f(g) = -32.29 \pm 0.29$. For $(CH_3)_3Al \cdot O(CH_3)_2$, $\Delta H_f(g) = -21.92 \pm 0.18$ kcal/mole. The general sequence of basicities toward trimethylalane, $N > P \geq O > S$, is established.

Introduction

The literature contains little quantitative data describing the stability of trimethylalane adduct systems, probably because the extreme stabilities of these adducts do not permit study in the gas phase. Consequently the literature contains only relative donor abilities of some Lewis bases toward trimethylalane based on the results of displacement reactions[3,4] and a few approximate values of the interaction of trimethylalane with various bases.[5]

Solution calorimetric studies of trimethylalane–sulfide adduct formation in hexane[6] have been found to provide good approximations of the gas-phase enthalpies of adduct formation. Subsequent calorimetric studies have been made of the donor strengths of sulfoxides, sulfinamides, and thionylamides[7] toward trimethylalane in hexane. This work has now been extended to nitrogen, oxygen, and phosphorus donors. In order to establish the value of using calorimetry in hexane to approximate the gas-phase enthalpies of amine and ether interactions with trimethylalane, detailed examination of the $(CH_3)_3Al \cdot N(CH_3)_3$ and $(CH_3)_3Al \cdot O(CH_3)_2$ systems was performed. Available vaporization data were used in thermodynamic cycles to convert solution data to the gas phase.

Experimental Section

Materials.—Trimethylalane and hexane were obtained and purified as previously described.[6] All of the liquid bases were analyzed using gas chromatography on a 20% SE-30 on 60–80 Chromosorb W 5-ft column. In all cases impurities were less than 0.1%.

Reagent grade triethylamine obtained from Matheson Coleman and Bell was stirred 12 hr with $LiAlH_4$, distilled onto fresh CaH_2, and used immediately (observed bp 88° (744.5 mm), lit.[8] value 89.5° (759 mm)). Fisher reagent grade diethylamine was stirred 4 hr with solid KOH and distilled from fresh KOH onto CaH_2 just prior to use (observed bp 54.2° (745 mm), lit.[8] value 55° (756 mm)). Trimethylamine, dimethylamine, monomethylamine, and ammonia obtained from Matheson were passed through an $18 \times {}^5/_8$ in. KOH drying tower. Trimethylamine was further purified by passing through a P_2O_5 tower.

Baker reagent grade pyridine and 2-picoline obtained from Eastman Organic Chemicals were stirred 12 hr with $LiAlH_4$ and distilled, and the middle third was collected over CaH_2 just prior to use. For pyridine: observed bp 113° (743.4 mm), lit.[8] value 115.5° (760 mm). For 2-picoline: observed bp 127° (743.9 mm), lit.[9] value 129.4° (760 mm). Reagent grade 2,6-lutidine obtained from Eastman Organic Chemicals was stirred 12 hr with $AlCl_3$, refluxed 0.5 hr, and distilled onto CaH_2 (observed bp 139–140° (741.4 mm), lit.[10] value 140–141° (760 mm)).

Dimethyl ether obtained from Matheson was slowly passed through a $6 \times {}^5/_8$ in. CaH_2 drying column and used immedi-

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ately without further purification. Diethyl ether, obtained from J. T. Baker Co., was dried over Linde 4A Molecular Sieves, refluxed 12 hr over $LiAlH_4$, and distilled onto CaH_2 (observed bp 34° (736.9 mm), lit.[8] value 34.6° (760 mm)). Eastman reagent grade tetrahydrofuran, 2-methyltetrahydrofuran, and Aldrich practical grade 2,5-dimethyltetrahydrofuran were stirred with $LiAlH_4$ for 12 hr and distilled onto CaH_2 just prior to use. For tetrahydrofuran: observed bp 64–65° (736.7 mm), lit.[11] value 64–65° (760 mm). For 2-methyltetrahydrofuran: observed bp 77–77.5° (735.8 mm), lit.[12] value 77–78° (716 mm). For 2,5-dimethyltetrahydrofuran: observed bp 88.7° (738.3 mm), lit.[13] value 92° (742 mm).

Triethylphosphine was prepared by addition of phosphorus trichloride to ethyl bromide Grignard reagent in diethyl ether. The product was purified by distillation (observed bp 57.5–59.5° (70.8 mm), lit.[14] value, 128.5-120° (762 mm)). Trimethylphosphine was prepared in the manner described by Rothstein,[15] except that the trimethylphosphine was isolated as the trimethylphosphine–silver iodide tetramer as described by Burg and Wagner.[16] Pyrolysis of the adduct in an inert atmosphere produced the desired product in about 5% yield. Eastman practical grade triphenylphosphine was recrystallized twice from hexane, dried under vacuum, and stored over P_2O_5 in a vacuum desiccator (observed mp 79.5–80°, lit.[17] value, 79°).

Preparation of the Trimethylalane–Trimethylamine Adduct.—To 2.47 g (0.0343 mol) of trimethylalane in 7 ml of dry benzene at 25° under nitrogen was added with stirring 0.0343 mol of gaseous trimethylamine, purified as previously described. The benzene was removed at reduced pressure and the adduct was recrystallized from hexane at −78° in an inert atmosphere. The adduct was then dried at reduced pressure. The white crystals could not be further purified *via* vacuum sublimation without some decomposition. Two independently prepared samples produced similar melting points (observed mp 87–94°, lit.[3] value 105°). *Anal.* Calcd for $C_6H_{18}AlN$: active alkyl, 34.38; Al, 20.56. Found: active alkyl, 35.27; Al, 20.70. The active alkyl analysis entails measuring the volume of methane evolved in hydrolysis of the adduct.

Preparation of the Trimethylalane–Dimethyl Ether Adduct.—After condensing 6 ml of dimethyl ether into a nitrogen-filled flask cooled to −78°, 2.25 g (0.31 mol) of trimethylalane was added slowly with stirring. The reaction mixture was allowed to warm to room temperature with the expulsion of the excess dimethyl ether. The adduct was then vacuum distilled (observed bp 56–57° (20 mm), lit.[3] value 56° (20 mm)).

Gaseous materials were handled in a 10-cm³ gas buret which was flushed 8–10 times before a sample was taken. The number of moles of gaseous reactant was calculated using the ideal gas law. The calorimeter used in this work is described elsewhere.[6]

The calorimetric procedure involved measuring the enthalpy associated with each of six to eight successive additions of 0.04–0.06 g of trimethylalane to excess base in *n*-hexane. In each experiment the initial base concentration was approximately 1.5 times the trimethylalane accumulated over all of the successive additions. It was observed experimentally that, even though with each successive addition of trimethylalane the base concentration decreased and the adduct concentrations increased, there was virtually no variation of the observed molar enthalpies over the entire concentration range. These results indicate that the reaction goes to completion over the trimethylalane concentration range of 0.010–0.060 *M*.

All measurements were made at a solution temperature of 25–28° and under a blanket of nitrogen. Enthalpies of solution were measured by addition of the solute to pure hexane.

All enthalpies are based on the defined thermochemical calorie; *i.e.*, 1 cal = 4.1840 abs J.

Results

Detailed analysis of the trimethylalane–trimethylamine and the trimethylalane–dimethyl ether systems were carried out to calculate the gas-phase enthalpy for the adduct formation. Each system was examined in two ways: first the reaction of pure trimethylalane with excess base in hexane solution and, second, adding the gaseous base to excess trimethylalane in hexane solution. Thermodynamic cycle 1 describes the first case, trimethylalane reacting with excess base in hexane solution. This cycle yields the equation used

$$\begin{tikzcd}
\mathrm{A(g)} \arrow[d, "{}^1/_2\Delta H_{\mathrm{dim}}(\mathrm{A_2})"] & + & \mathrm{B(g)} \arrow[rr, "\Delta H(\mathrm{g})"] \arrow[dd, "\Delta H_{\mathrm{soln}}(\mathrm{B})"] & & \mathrm{AB(g)} & \\
{}^1/_2\mathrm{A_2(g)} \arrow[d, "-{}^1/_2\Delta H_{\mathrm{vap}}(\mathrm{A_2})"] & & & \mathrm{AB(l)} \arrow[ur, "\Delta H_{\mathrm{vap}}(\mathrm{AB})"] & \text{or} & \mathrm{AB(s)} \arrow[ul, "\Delta H_{\mathrm{subl}}(\mathrm{AB})"'] \\
{}^1/_2\mathrm{A_2(l)} & + & \mathrm{B(soln)} \arrow[rr, "\Delta H_{\mathrm{obsd}}"] & & \mathrm{AB(soln)} \arrow[u, "-\Delta H_{\mathrm{soln}}(\mathrm{AB})"'] &
\end{tikzcd} \tag{1}$$

to calculate the gas-phase enthalpy. With $(CH_3)_3Al \cdot O(CH_3)_2$, a liquid adduct, the value $\Delta H_{\mathrm{vap}}(\mathrm{AB})$ is used, whereas with $(CH_3)_3Al \cdot N(CH_3)_3$, a solid adduct, $\Delta H_{\mathrm{subl}}(\mathrm{AB})$ is used

$$\Delta H(\mathrm{g}) = \Delta H_{\mathrm{obsd}} - \Delta H_{\mathrm{soln}}(\mathrm{AB}) + [\Delta H_{\mathrm{subl}}(\mathrm{AB}) \text{ or } \Delta H_{\mathrm{vap}}(\mathrm{AB})] + {}^1/_2\Delta H_{\mathrm{dim}}(\mathrm{A_2}) - {}^1/_2\Delta H_{\mathrm{vap}}(\mathrm{A_2}) + \Delta H_{\mathrm{soln}}(\mathrm{B}) \tag{2}$$

The values used in eq 2 for both systems are given in Table I.

TABLE I

ENTHALPY VALUES FOR $(CH_3)_3Al \cdot N(CH_3)_3$ AND $(CH_3)_3Al \cdot O(CH_3)_2$[a]

Quantity	Value, kcal/mole
${}^1/_2\Delta H_{\mathrm{dim}}[(Al(CH_3)_3)_2]$	-10.20 ± 0.17[b]
${}^1/_2\Delta H_{\mathrm{vap}}[(Al(CH_3)_3)_2]$	$+4.94 \pm 0.03$[b]
$\Delta H_{\mathrm{subl}}[(CH_3)_3Al \cdot N(CH_3)_3]$	$+10.9$[c]
$\Delta H_{\mathrm{vap}}[(CH_3)_3Al \cdot O(CH_3)_2]$	$+9.85$[c]
$\Delta H_{\mathrm{soln}}[(CH_3)_2O]$	-4.18 ± 0.01
$\Delta H_{\mathrm{soln}}[N(CH_3)_3]$	-5.31 ± 0.06
$\Delta H_{\mathrm{soln}}[(CH_3)_3Al \cdot N(CH_3)_3]$	$+4.11 \pm 0.09$
$\Delta H_{\mathrm{soln}}[(CH_3)_3Al \cdot O(CH_3)_2]$	$+1.99 \pm 0.03$
$\Delta H_{\mathrm{obsd}}[(CH_3)_3Al \cdot O(CH_3)_2]$	-10.46 ± 0.04
$\Delta H_{\mathrm{obsd}}[(CH_3)_3Al \cdot N(CH_3)_3]$	-18.63 ± 0.20

[a] Adding $[(CH_3)_3Al]_2$ to excess base in hexane. [b] See ref 6. [c] See ref 3.

The gas-phase enthalpies calculated for cycle 1 are: $(CH_3)_3Al \cdot N(CH_3)_3$, -32.29 ± 0.29 kcal/mole; $(CH_3)_3Al \cdot O(CH_3)_2$, -21.92 ± 0.18 kcal/mole.

The gas-phase enthalpy for the reaction of gaseous base with excess trimethylalane in hexane can be found utilizing a thermodynamic cycle which is similar to (1) but which includes the enthalpy of solution of the alane $[-{}^1/_2\Delta H_{\mathrm{soln}}(\mathrm{A_2})]$, instead of that of the base $[-\Delta H_{\mathrm{soln}}(\mathrm{B})]$, along with the proper observed enthalpies for this case. The gas-phase enthalpy of this second thermodynamic cycle is then calculated using

$$\Delta H(\mathrm{g}) = \Delta H_{\mathrm{obsd}} - \Delta H_{\mathrm{soln}}(\mathrm{AB}) + [\Delta H_{\mathrm{vap}}(\mathrm{AB}) \text{ or } \Delta H_{\mathrm{subl}}(\mathrm{AB})] + {}^1/_2\Delta H_{\mathrm{dim}}(\mathrm{A_2}) - {}^1/_2\Delta H_{\mathrm{vap}}(\mathrm{A_2}) + {}^1/_2\Delta H_{\mathrm{soln}}(\mathrm{A_2}) \tag{3}$$

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The thermodynamic values required in eq 3 which are not already given in Table I are found in Table II.

TABLE II

ENTHALPY VALUES FOR $(CH_3)_3Al \cdot N(CH_3)_3$ AND $(CH_3)_3Al \cdot O(CH_3)_2$[a]

Quantity	Value kcal/mole
$^1/_2\Delta H_{soln}[(CH_3)_3Al)_2]$	+0.223 ± 0.025
$\Delta H_{obsd}[(CH_3)_3Al \cdot N(CH_3)_3]$	−25.02 ± 0.06
$\Delta H_{obsd}[(CH_3)_3Al \cdot O(CH_3)_2]$	−15.72 ± 0.09

[a] Adding gaseous bases to excess $[(CH_3)_3Al]_2$ in hexane.

The gas-phase enthalpies calculated from the second cycle are then: $(CH_3)_3Al \cdot N(CH_3)_3$, −33.15 ± 0.20 kcal/mole; $(CH_3)_3Al \cdot O(CH_3)_2$, −22.78 ± 0.20 kcal/mole.

The total solution enthalpy for the case of adding alane to excess base in solution can be calculated from the thermodynamic cycle

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

The relationship defining the total solution enthalpy is given by

$$\Delta H_{tot\,soln} = \Delta H_{obsd} + ``^1/_2\Delta H_{dim}(A_2)\text{''} - {^1/_2}\Delta H_{soln}(A_2) \quad (5)$$

In these thermodynamic cycles it is assumed that trimethylalane is an undissociated dimer in hexane. It has been established that trimethylalane exists as an undissociated dimer in hydrocarbon solvents in the concentration range of 0.05–0.25 *M*.[18,19] Partial dissociation of even 1% of the dimeric liquid trimethylalane upon dissolution in hexane would be expected to increase the enthalpy of solution by approximately +0.2 kcal/mole dimer (1% of the enthalpy of dissociation of dimeric trimethylalane). It was observed that the molar heats of solution of trimethylalane in hexane show a random deviation of ±0.02 kcal/mole of dimer over the concentration range 0.015–0.060 *M*. This observation suggests that trimethylalane exists as an undissociated dimer at concentrations as low as 0.015 *M* in hexane.

The use of the value "$\Delta H_{dim}(A_2)$" in eq 5 and 6 involves the assumption that the enthalpy of dimerization is the same in hexane solution as in the gas phase. This is probably not exactly true, but the deviation from the gas phase is probably small, since hexane solvation is thought to be small as reflected by the very small enthalpy of solution.

The following total solution enthalpies were found for the first case: $(CH_3)_3Al \cdot N(CH_3)_3$, −29.05 ± 0.26 kcal/mole; $(CH_3)_3Al \cdot O(CH_3)_2$, −20.88 ± 0.18 kcal/mole.

The total solution enthalpies for the second case, adding gaseous amine to excess alane in hexane, can be calculated with the aid of a thermodynamic cycle which is similar to (4) but which includes the enthalpy of solution of the base and not the enthalpy of solution of the alane, along with the proper observed enthalpies for this case.

The following equation defines the total solution enthalpy for the second case

$$\Delta H_{tot\,soln} = \Delta H_{obsd} + ``^1/_2\Delta H_{dim}(A_2)\text{''} - \Delta H_{soln}(B) \quad (6)$$

The values found were: $(CH_3)_3Al \cdot N(CH_3)_3$, −29.91 ± 0.19 kcal/mole; $(CH_3)_3Al \cdot O(CH_3)_2$, −21.74 ± 0.19 kcal/mol.

The enthalpies of adduct formation with trimethylamine, dimethylamine, methylamine, and ammonia were found by adding a known amount of the gas to excess trimethylalane in hexane. In no case was there any difficulty with a secondary reaction involving condensation with an amino proton. The total solution enthalpies for all gaseous bases were determined using the thermodynamic cycle defined by eq 3. Data for the gaseous amines are found in Table III.

TABLE III

ENTHALPIES OF $[(CH_3)_3Al]_2$ INTERACTION WITH METHYLAMINES AND AMMONIA

Base	ΔH_{obsd}, kcal/mole	ΔH_{soln}, (base), kcal/mole	$\Delta H_{tot\,soln}$, kcal/mole
$(CH_3)_3N$	−25.02 ± 0.06	−5.31 ± 0.07	−29.96 ± 0.19
$(CH_3)_2NH$	−25.38 ± 0.19	−4.75 ± 0.05	−30.84 ± 0.26
$(CH_3)NH_2$	−23.67 ± 0.22	−3.86 ± 0.13	−30.02 ± 0.31
NH_3	−19.17 ± 0.15	−1.82 ± 0.11	−27.55 ± 0.25

An attempt was made to determine the enthalpy of adduct formation in the reverse manner, adding trimethylalane to excess gaseous amine dissolved in hexane. In all cases other than trimethylamine, there was evidence for adduct stoichiometry greater than 1:1. The interaction of the 1:1 adduct with excess amine is presently under study.

The results of the adduct formation between trimethylalane and pyridine, 2-picoline, 2,6-lutidine, triethylamine, and diethylamine are found in Table IV. The total solution values of all liquid and solid bases were determined by adding the pure alane to the base dissolved in hexane.

TABLE IV

ENTHALPIES OF $[(CH_3)_3Al]_2$ INTERACTION WITH PYRIDINES AND ETHYLAMINES

Base	ΔH_{obsd}, kcal/mole	$\Delta H_{tot\,soln}$, kcal/mole
Pyridine	−17.14 ± 0.02	−27.56 ± 0.17
2-Picoline	−15.71 ± 0.17	−26.13 ± 0.24
2,6-Lutidine	−9.45 ± 0.12	−19.87 ± 0.21
$(C_2H_5)_3N$	−16.05 ± 0.05	−26.47 ± 0.18
$(C_2H_5)_2NH$	−16.91 ± 0.06	−27.33 ± 0.18

The enthalpies of reaction of the dialkyl ethers and the tetrahydrofuran (THF) derivatives with trimethylalane are given in Table V. In each instance the alane was added to excess base in hexane solution.

The results of the phosphine studies are given in

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TABLE V
ENTHALPIES OF $[(CH_3)_3Al]_2$ INTERACTION WITH OXYGEN DONORS

Base	ΔH_{obsd}, kcal/mole	$\Delta H_{tot\,soln}$, kcal/mole
THF	-12.48 ± 0.08	-22.90 ± 0.19
2-Methyl THF	-12.52 ± 0.07	-22.94 ± 0.18
2,5-Dimethyl THF	-12.53 ± 0.03	-22.95 ± 0.17
$(C_2H_5)_2O$	-9.79 ± 0.15	-20.21 ± 0.23
$(CH_3)_2O$	-9.87 ± 0.10	-20.29 ± 0.20

Table VI. Care was taken to ensure that the solubilities of the reactants and products were not exceeded in each case. Again, the base was in excess in hexane solution.

TABLE VI
ENTHALPIES OF $[(CH_3)_3Al]_2$ INTERACTION WITH PHOSPHORUS DONORS

Base	ΔH_{obsd}, kcal/mole	$\Delta H_{tot\,soln}$, kcal/mole
$P(C_6H_5)_3$	-7.21 ± 0.07	-17.63 ± 0.18
$P(CH_3)_3$	-10.60 ± 0.23	-21.02 ± 0.28
$P(C_2H_5)_3$	-11.70 ± 0.28	-22.12 ± 0.33

Discussion

The calculated gas-phase enthalpies found for the trimethylalane–trimethylamine and trimethylalane–dimethyl ether adducts reveal that these are very stable adducts with trimethylamine being a stronger donor than dimethyl ether. In both trimethylalane–trimethylamine and trimethylalane–dimethyl ether systems some disagreement exists in the calculated gas phase enthalpies depending on the manner in which the reaction is observed. This same disagreement is correspondingly seen in the total solution values. The reaction of gaseous amine with alane in solution produces an enthalpy 0.86 kcal/mole more negative than the same reaction being run in the reverse manner. Similarly, the reaction of gaseous dimethyl ether with alane in solution is 0.86 kcal/mole more negative than that found in the reverse reaction. A detailed reexamination of these systems did not reveal the source of this discrepancy.

In the trimethylalane–trimethylamine case, agreement between the total solution enthalpy and the calculated gas-phase enthalpy is fair, the total solution value being about 10% less than the gas-phase value (−29.91 *vs.* −33.15 kcal/mole). In the trimethylalane–dimethyl ether case, agreement is within about 5%, and again the total solution value is less than that in the gas phase (−21.74 *vs.* −22.78 kcal/mole). Part of the difference between the total solution and gas-phase values can perhaps be attributed to the assumption that the enthalpy of dimerization of trimethylalane is the same in hexane solution and in the gas phase. It is concluded that solution calorimetry in hexane can be used as an approximation of the gas phase for amines and ethers. (In the trimethylalane–dimethyl sulfide system the total solution value was −16.69 kcal/mole as compared to a calculated gas-phase value of −18.05 kcal/mole.)

Nitrogen Donors.—Toward trimethylalane the following total solution enthalpy sequence was found: $(CH_3)_2NH > CH_3NH_2 \sim (CH_3)_3N > NH_3$. Toward trimethylborane in gas-phase studies the same sequence has been reported.[20]

Examination of a molecular model of the trimethylamine–trimethylalane adduct reveals the existence of a small frontal steric interaction, when the aluminum and nitrogen atoms are tetrahedrally coordinated. Atwood and Stucky[21] have found in the bis(trimethylalane)–dioxane adduct an O–Al–C bond angle of ~100°, substantially less than the tetrahedral angle of 109°. If the corresponding angle (N–Al–C) is smaller than 109° in the trimethylamine–trimethylalane adduct, frontal steric interactions would be even larger than the molecular model indicates. Consequently, the enthalpy of adduct formation of the trimethylamine–trimethylalane adduct should be decreased accounting for the position of trimethylamine in the above sequence. It is interesting to note that the enthalpy difference between the trimethylamine and dimethylamine adducts in the trimethylalane systems is much less than that found in the trimethylborane system (0.88 kcal in 30 kcal/mole *vs.* 1.7 kcal in 20 kcal/mole). This is indicative of a smaller influence of steric contributions in determining the enthalpy of adduct formation in the alane system. In the phosphorus and sulfur systems, the dative bond is long enough to exclude essentially frontal steric interactions.

Triethylamine has a weaker interaction with trimethylalane than any of the other amines studied, suggesting significant frontal steric interaction. Since it is not possible to rotate simultaneously all three of the ethyl groups away from the acceptor molecule, a frontal steric effect is expected. Hoffman and Tornau[22] reported for the trimethylalane–triethylamine system an observed enthalpy of −15.4 ± 0.2 kcal/mole in the solvent cyclohexane. Corrected for the enthalpy of dimerization of trimethylalane, this becomes −25.6 ± 0.3 kcal/mole. This compares well with −26.47 ± 0.18 kcal/mole found in this study in the solvent *n*-hexane.

The difference in the donor abilities of triethylamine and diethylamine is much greater in the trimethylborane systems [$(C_2H_5)_2NH$, −16.93 kcal/mole; $(C_2H_5)_3N$, −10 kcal/mole[20]] where the dative bond is shorter than in the trimethylalane adducts [$(C_2H_5)_2NH$, −27.33 kcal/mole; $(C_2H_5)_3N$, −26.47 kcal/mole].

Pyridine and the methyl-substituted pyridines yield the following enthalpy sequence with trimethylalane: pyridine > 2-picoline > 2,6-lutidine. The sequence can be readily explained by frontal strain effects overriding the inductive effect of the methyl substituents. Brown[23] has reported the same sequence toward trimethylborane with the 2,6-lutidine adduct not forming presumably for steric reasons. This is to be expected in view of the shorter dative bond in the borane systems. The enthalpies of interaction of pyridine and 2,6-

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lutidine with triethylalane have been reported as calorimetrically determined in *n*-decane.[24] For $(C_2H_5)_3Al \cdot NC_5H_5$, $\Delta H_f = -21.2$ kcal/mole, and for $(C_2H_5)_3Al \cdot NC_5H_3(CH_3)_2$, $\Delta H_f = -18.0$ kcal/mole. These enthalpy values do not include a correction for the enthalpy of dimerization of triethylalane. This value has been reported as -16.93 ± 0.23 kcal/mole in hexadecane.[25] Since triethylalane is about 10–11% dissociated in a hydrocarbon solvent at ambient temperatures, one can only calculate the maximum enthalpy value by making the correction based on 100% dimerization of the triethylalane. Corrected in this way, these enthalpies become -29.7 kcal/mole for pyridine and -26.5 kcal/mole for 2,6-lutidine. These are surprising results since it is expected that triethylalane would have significantly larger frontal interaction than trimethylalane. The pyridines are generally weaker donors toward trimethylalane than the methylamines or ammonia but are comparable to the ethylamines.

Phosphorus Donors.—Toward trimethylalane the sequence of interaction of phosphines is: $P(C_2H_5)_3 > P(CH_3)_2 > P(C_6H_5)_3$. The enthalpy reported for the trimethylborane–trimethylphosphine adduct is much less than that observed here for trimethylalane.[20] The difference is probably due to larger steric interactions in the borane case. Steric requirements in the trimethylalane–phosphine adducts seem to be small since the greater inductive effect of the ethyl group is manifested in a larger enthalpy. The much lower enthalpy of the trimethylalane–triphenylphosphine adduct is probably due to inductive effects since the frontal strain effect is not expected to be much larger than that in the triethylphosphine adduct. The observation of little or no frontal steric interaction in trimethylalane–phosphine adducts is most likely ascribable to the comparatively long dative bond. This is to be expected in view of previous studies which indicate little or no frontal steric effects in trimethylalane–sulfide adducts.[6]

Oxygen Donors.—The donor abilities of the three tetrahydrofurans are virtually indistinguishable toward trimethylalane. Examination of molecular models reveals the methyl substituents are pinned away from the alane acceptor greatly reducing steric interaction. Diethyl ether and dimethyl ether are indistinguishable in their interaction with trimethylalane. The trimethylborane–dimethyl ether adduct does not exist for steric reasons,[26] but apparently the lower steric requirement of trimethylalane allows the quite stable adduct to form. A substantial difference is observed in the enthalpy of adduct formation of diethyl and dimethyl ethers with the acid boron trifluoride, with dimethyl ether being the stronger base.[27] Also tetrahydrofuran is a stronger base than dimethyl ether toward boron trifluoride[28] as is found in this study with trimethylalane.

The enthalpies of adduct formation of a number of aliphatic and alicyclic sulfides with trimethylalane in hexane have been reported.[6] The sulfides as a class were observed to be weaker donors toward trimethylalane than the ethers. The order of donor strengths $O > S$ and $N > P$ is found in previous work with trimethylborane and is observed in this work with trimethylalane. Over-all, the following sequence of decreasing basicity of the alkylated donors toward trimethylalane in hexane is observed: $N > P \geq O > S$.

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Transition Metal Borohydride Complexes. II.[1] The Reaction of Copper(I) Compounds with Boron Hydride Anions

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The reaction between solutions containing $(R_3Y)_nCuCl$ and $NaBH_4$, where R is an alkyl or aryl group and Y is P, As, or Sb, has been investigated. In those cases where Y is phosphorus and R an aryl group (C_6H_5, *p*-$CH_3C_6H_4$, *m*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$), stable crystalline borohydride complexes of composition $(R_3Y)_2Cu(BH_4)$ could be isolated. With trialkylphosphine, triphenylarsine, and triphenylstibine ligands under identical conditions, decomposition, rather than complex formation, occurred. Similar studies of the reaction between $[(C_6H_5)_3Y]_mCuCl$ compounds and CsB_3H_8 yielded complexes $[(C_6H_5)_3Y]_nCu(B_3H_8)$ for Y = P ($n = 2$), As ($n = 2$), and Sb ($n = 3$). The results of infrared spectral and other physical studies of the new complexes are presented and discussed in terms of their molecular structures. Possible factors influencing the course of the reaction of copper(I) compounds with the borohydride ion are set forth.

Introduction

The borohydride ion, BH_4^-, is one of the more common inorganic reducing agents. It is therefore of considerable interest to establish the stereochemical and electronic principles which are operative when

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