(19) V. J. Bartuska, T. T. Nakashima, and G. E. Maciel, *Rev. Sci. Instrum.*, **41**, 1458 (1972).
(20) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N.Y., 1969.
(21) T. P. Onak and F. J. Gerhart, *Inorg. Chem.*, **1**, 742 (1962).
(22) G. E. Ryschkewitsch, S. W. Harris, E. J. Mezey, H. H. Sisler, E. A. Weilmuenster, and A. B. Garrett, *Inorg. Chem.*, **2**, 890 (1963).
(23) H. I. Schlesinger and A. O. Walker, *J. Amer. Chem. Soc.*, **57**, 621 (1935).
(24) A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **59**, 780 (1937).
(25) J. R. Spielman and A. B. Burg, *Inorg. Chem.*, **2**, 1139 (1963).
(26) J. D. Odom, L. W. Hall, S. Riethmiller, and J. R. Durig, *Inorg. Chem.*, **13**, 170 (1974).
(27) J. Dobson and R. Schaeffer, *Inorg. Chem.*, **9**, 2183 (1970).
(28) C. D. Good and D. M. Ritter, *J. Amer. Chem. Soc.*, **84**, 1162 (1962); *J. Chem. Eng. Data*, **7**, 416 (1962).
(29) J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).
(30) J. Bacon, R. J. Gillespie, and J. W. Quail, *Can. J. Chem.*, **41**, 3063 (1963).
(31) M. Suzuki and R. Kubo, *Mol. Phys.*, **7**, 201 (1963).
(32) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 11 (1970).
(33) A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, **55**, 950 (1971).
(34) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).
(35) W. Gordy, H. Ring, and A. B. Burg, *Phys. Rev.*, **78**, 512 (1950).

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Existence of Complexes of $LiAlH_4$ and AlH_3 in Ether Solvents and in the Solid State

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The reaction between $LiAlH_4$ and AlH_3 in 1:1, 1:2, 1:3, and 1:4 molar ratios in both diethyl ether and THF has been investigated by infrared spectroscopy. Also solutions of $LiAlH_4$ and AlH_3 in diethyl ether were evaporated to dryness and the resulting solids were examined by dta–tga and X-ray powder diffraction methods. Previous reports claiming the preparation of $LiAl_2H_7$ and $LiAl_3H_{10}$ by the reaction of $LiAlH_4$ with $BeCl_2$ in ether and also the reaction of LiH with AlH_3 were studied in detail and attempts were made to prepare the complexes by exactly the same procedure reported. Contrary to previous reports, in no case was any evidence found to indicate the existence of $LiAl_2H_7$, $LiAl_3H_{10}$, or any complex between $LiAlH_4$ and AlH_3 in ether or THF solution or in the solid state as products in the reactions studied.

Introduction

Recently we found that diethyl ether soluble aluminum hydride can be prepared by a number of different methods.[1,2] (See eq 1–3.) This finding allows a convenient study of the

$$2LiAlH_4 + BeCl_2 \xrightarrow{Et_2O} Li_2BeH_2Cl_2\downarrow + 2AlH_3 \quad (1)$$

$$2LiAlH_4 + H_2SO_4 \xrightarrow{Et_2O} H_2\uparrow + Li_2SO_4\downarrow + 2AlH_3 \quad (2)$$

$$2LiAlH_4 + ZnCl_2 \xrightarrow{Et_2O} 2LiCl\downarrow + ZnH_2\downarrow + 2AlH_3 \quad (3)$$

interaction between $LiAlH_4$ and AlH_3 in diethyl ether which has been reported by a number of laboratories to be strong enough so as to produce stable complexes ($LiAlH_4 \cdot nAlH_3$, where $n = 1$–4). Although aluminum hydride can be prepared in tetrahydrofuran,[3] complexes between $LiAlH_4$ and AlH_3 would not be expected to be stable due to the strong aluminum–oxygen bond in H_3Al–OC_4H_8.

Recent Russian work[4] claims the preparation of $LiAl_2H_7$ ($LiAlH_4 \cdot AlH_3$) and $LiAl_3H_{10}$ ($LiAlH_4 \cdot 2AlH_3$) in diethyl ether; however, the compounds were reported to be more stable in the solid state than in ether solution. Also a recent study concerning the structure and properties of $LiAl_2H_7$ has appeared in the French literature.[5] These workers reported $LiAl_2H_7$ to be stable in the solid state but unstable in diethyl ether solution. In addition, other French workers[6] have reported the preparation of the compound $LiAl_4H_{13}$ ($LiAlH_4 \cdot 3AlH_3$) by the reaction of LiH with AlH_3 in ether solvent. In each case the reports claim solid-state stability of the complexes but report diethyl ether solutions as being unstable.

On the other hand, several reports have appeared that claim the formation of complexes of the type $LiAlH_4 \cdot nAlH_3$ in ether solvent. It has been reported that the electrical conductivity of solutions of $LiAlH_4$ and AlH_3 in diethyl ether indicates the formation of ions alternate to those arising from $LiAlH_4$ and AlH_3 separately.[7,8] Because of these reports and because of the analogy to the $MAlH_4 \cdot nAlR_3$ systems,[9] further claims for the existence of $MAlH_4 \cdot nAlH_3$ complexes have been made, in particular, $LiAl_2H_7$.[10]

We have been evaluating new hydrides as stereoselective reducing agents and felt that $LiAlH_4 \cdot AlH_3$ compounds would behave differently from either $LiAlH_4$ or AlH_3. Reduction studies in this laboratory have shown that a mixture of $LiAlH_4$ and AlH_3 in ether solvent gives the same stereochemistry of reduction of 4-*tert*-butylcyclohexanone and 3,3,5-trimethylcyclohexanone as would be expected for a simple physical mixture of $LiAlH_4$ and AlH_3. At this point we decided to take a closer look at the so-called complexes "$LiAlH_4 \cdot nAlH_3$" both in ether solution by infrared spectroscopy and in the solid state by dta–tga and powder diffraction.

Experimental Section

Apparatus. Reactions were performed under nitrogen at the bench using Schlenk tube techniques.[11] Filtrations and other manipulations were carried out in a glove box equipped with a recirculating system using manganese oxide columns to remove oxygen and Dry Ice–acetone traps to remove solvent vapors.[12]

Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Solids were run as Nujol mulls between CsI plates. Solutions were run in matched 0.10-mm path length NaCl cells. X-Ray powder data were obtained on a Philips-Norelco X-ray unit using a 114.6-mm camera with nickel-filtered Cu $K\alpha$ radiation. Samples were sealed in 0.5-mm capillaries and exposed to X-rays for 6 hr. *d* spacings were read on a precalibrated scale equipped with viewing apparatus. Intensities were estimated visually. Dta–tga data were obtained under vacuum with a modified Mettler thermoanalyzer, Model II. A more detailed description of this apparatus has been given elsewhere.[13,14]

Analytical Work. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[11] Alkali metals were determined by flame photometry. Aluminum was determined by EDTA titration.

Materials. $LiAlH_4$ was obtained as gray, lumpy solids from Ventron, Metal Hydrides Division. Solutions of $LiAlH_4$ in diethyl ether and THF were prepared by stirring the solid hydride for 24 hr with freshly distilled solvent, followed by filtration, to yield a clear, colorless solution. Lithium hydride was prepared by the hydrogenation of *tert*-butyllithium at room temperature at 3000 psi for 24 hr. A slurry of LiH in diethyl ether was used. Aluminum hydride in diethyl ether was prepared by the reaction of $LiAlH_4$ with $BeCl_2$ in a 2:1 molar ratio.[1,2] The white solid was removed by filtration leaving a nearly lithium-free clear solution of aluminum hydride. The molar ratios of Al to H to Li in this solution were 1.00:3.13:0.043. Aluminum hydride in THF was prepared by the reaction of 100% H_2SO_4 with $LiAlH_4$ in THF according to the procedure of Brown.[3] Li_2SO_4 was

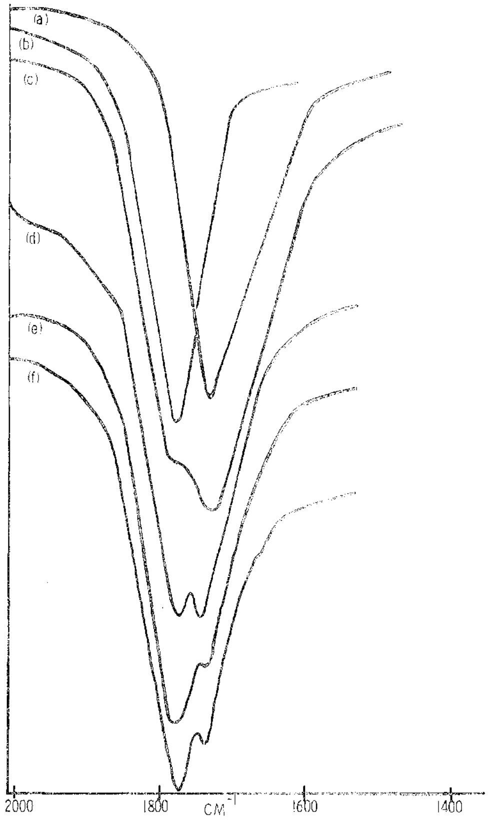

Figure 1. Infrared spectra of mixtures of LiAlH$_4$ and AlH$_3$ in diethyl ether: (a) LiAlH$_4$; (b) AlH$_3$; (c) 1:1 LiAlH$_4$ + AlH$_3$; (d) 1:2 LiAlH$_4$ + AlH$_3$; (e) 1:3 LiAlH$_4$ + AlH$_3$; (f) 1:4 LiAlH$_4$ + AlH$_3$.

Table I. Elemental Analysis of Mixtures of LiAlH$_4$ and AlH$_4$ in 1:1, 1:2, 1:3, and 1:4 Ratios in Diethyl Ether

LiAlH$_4$:AlH$_3$	Analysis, %				Mole ratio Li:Al:H:Et$_2$O
	Li	Al	H	Et$_2$O	
1:1	7.45	56.79	7.45	28.31	1.02:2.00:7.08:0.35
1:2	4.91	55.58	6.97	32.54	1.03:3.00:10.13:0.64
1:3	3.58	53.20	6.52	36.70	1.05:4.00:13.22:1.01
1:4	2.65	51.08	6.17	40.10	1.01:5.00:16.31:1.43

removed by filtration and a nearly lithium-free solution of AlH$_3$ in THF was obtained. The molar ratios of Al to H to Li in this solution were 1.00:3.06:0.016. These reactant solutions were standardized by aluminum analysis and transferred volumetrically. All solvents were distilled at atmospheric pressure from LiAlH$_4$ (diethyl ether) or NaAlH$_4$ (THF) immediately before use.

Reactions Involving LiAlH$_4$ and AlH$_3$ in Diethyl Ether. Reaction of LiAlH$_4$ and AlH$_3$ in 1:1, 1:2, 1:3, and 1:4 Molar Ratios. In four separate experiments, 2.5 mmol of LiAlH$_4$ in diethyl ether was added to 2.5, 5.0, 7.5, and 10 mmol of AlH$_3$ in diethyl ether. The resulting clear solutions were stirred for 1 hr and the infrared spectra were recorded (Figure 1). The solvent was then removed from the solution under vacuum until a dry white solid resulted. Elemental analyses of the solid products are given in Table I, the X-ray powder diffraction patterns are recorded in Table II, and the vacuum dta–tga curves of the resulting solids are recorded in Figures 2–5. In all cases the infrared spectrum of the solids (Nujol mulls) yielded broad, nondistinct bands.

Reaction of LiAlH$_4$ and AlH$_3$ in 1:1, 1:2, 1:3, and 1:4 Molar Ratios in THF. Five-millimole amounts of LiAlH$_4$ in THF were added to each of the following quantities of AlH$_3$ in THF: (1) 5 mmol, (2) 10 mmol, (3) 15 mmol, and (4) 20 mmol. In each case the resulting solution was stirred for 1 hr and then the infrared spectrum was recorded. The infrared spectra for these solutions are shown in Figure 6.

Reaction of LiH and AlH$_3$ in 1:4 Molar Ratio in Diethyl Ether. A slurry of 5 mmol of LiH in ether was added to 20 mmol of AlH$_3$ in ether. The resulting clear solution was stirred for 1 hr and the infrared spectrum was recorded (Figure 7). The solvent was then removed from the solution under vacuum producing a dry white solid. Elemental analysis of the solid showed Li, Al, H, and ether in the molar ratio of 1.00:4.02:13.22:1.16. The X-ray powder diffraction patterns are recorded in Table II and the dta–tga diagram of the resulting solid under argon atmosphere is recorded in Figure 8.

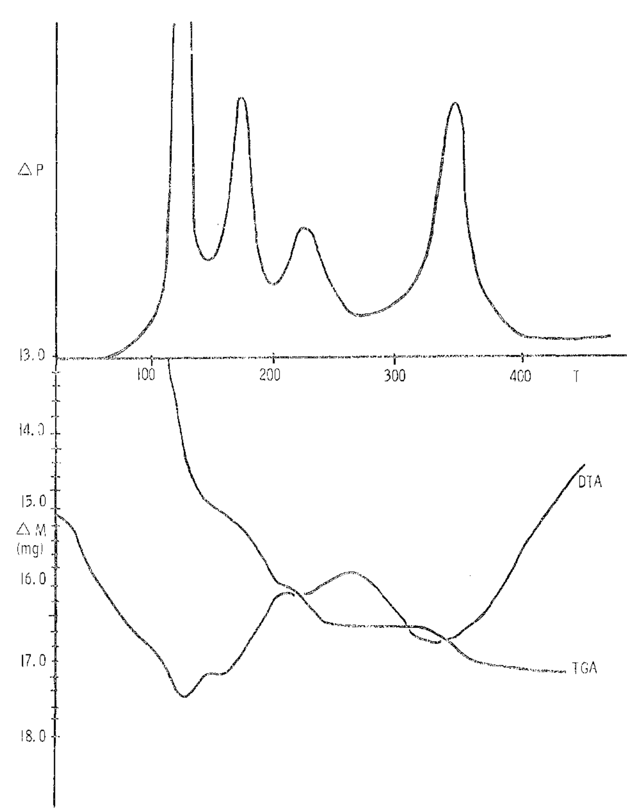

Figure 2. Vacuum dta–tga of proposed "LiAl$_2$H$_7$."

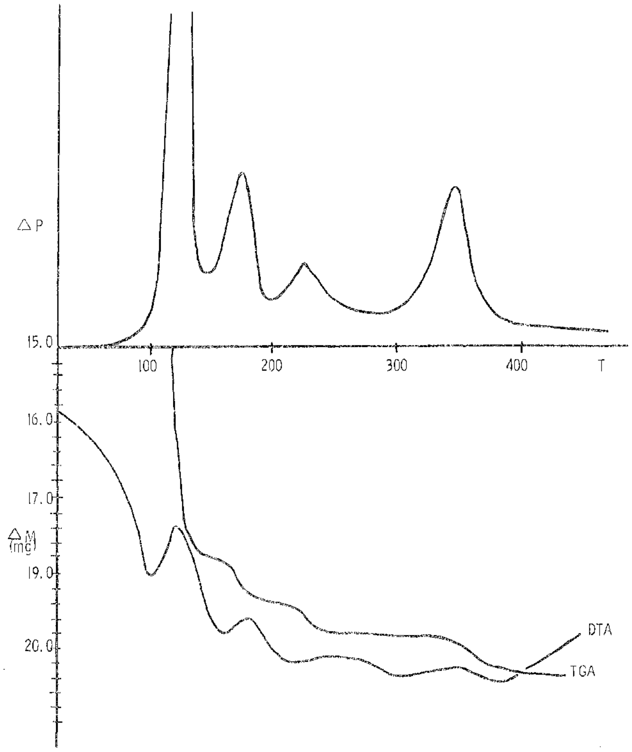

Figure 3. Vacuum dta–tga of LiAl$_3$H$_{10}$.

Reaction of LiAlH$_4$ with BeCl$_2$ in 4:1 Molar Ratio in Diethyl Ether. A 20-mmol amount of LiAlH$_4$ in diethyl ether was added to 5 mmol of BeCl$_2$ in diethyl ether. A white precipitate appeared immediately. After 30 min of stirring the precipitate was allowed to settle. An

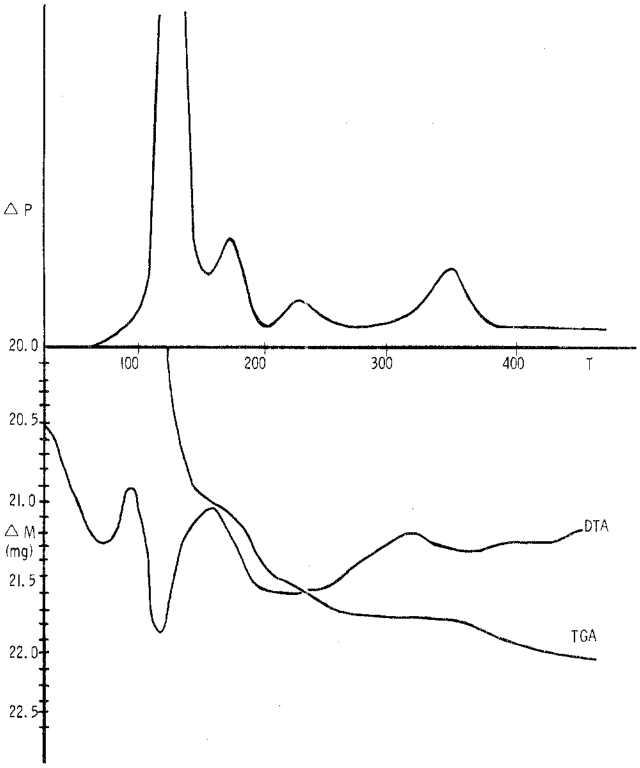

Figure 4. Vacuum dta–tga of $LiAl_4H_{13}$.

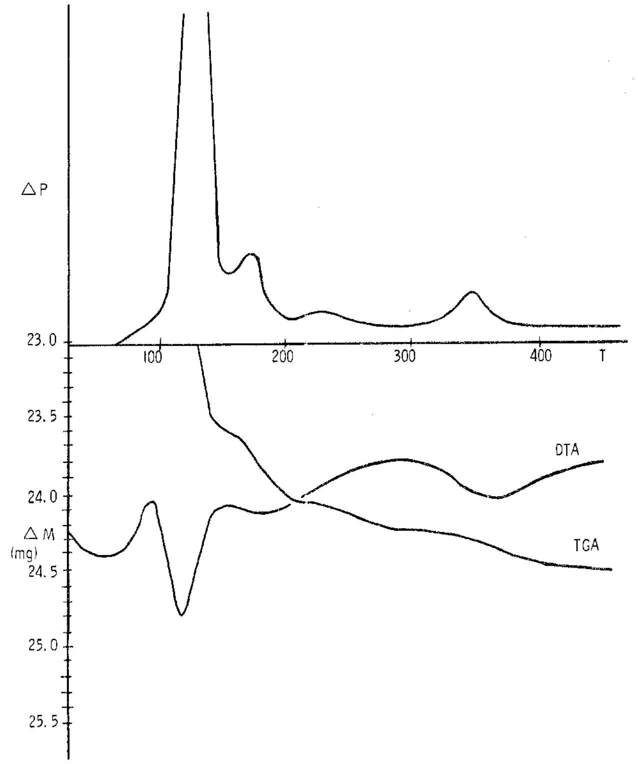

Figure 5. Vacuum dta–tga of $LiAl_5H_{16}$.

infrared spectrum was then run on the clear solution. The spectrum is shown in Figure 9.

Reaction of $LiAlH_4$ with $BeCl_2$ in 2:1 Molar Ratio in Diethyl Ether. Formation of "$LiAl_2H_7$." A 10-mmol amount of $BeCl_2$ in diethyl ether was added slowly with stirring to 20 mmol of $LiAlH_4$ in diethyl ether cooled at −5°. A white precipitate appeared immediately. The mixture was stirred for 1 hr and the precipitate was allowed to settle. The infrared spectrum of the clear solution was identical with the infrared spectrum of AlH_3.

Reaction of $LiAlH_4$ with $BeCl_2$ in 3:1 Molar Ratio. Formation of "$LiAl_3H_{10}$." A 15-mmol amount of $LiAlH_4$ in diethyl ether was added to 5 mmol of $BeCl_2$ in diethyl ether. A white precipitate appeared immediately. After 30 min of stirring, the precipitate was allowed to settle. An infrared spectrum was then run on the clear solution. The spectrum is shown in Figure 9.

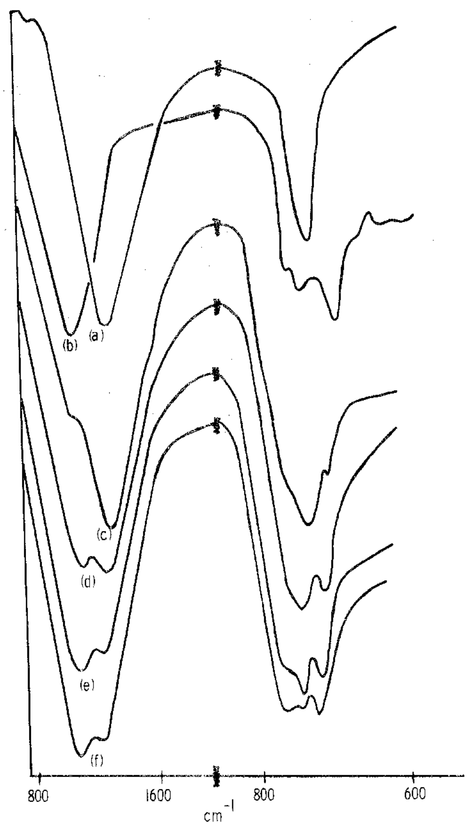

Figure 6. Infrared spectra of mixtures of $LiAlH_4$ and AlH_3 in THF: (a) $LiAlH_4$; (b) AlH_3; (c) 1:1 $LiAlH_4$ + AlH_3; (d) 1:2 $LiAlH_4$ + AlH_3; (e) 1:3 $LiAlH_4$ + AlH_3; (f) 1:4 $LiAlH_4$ + AlH_3.

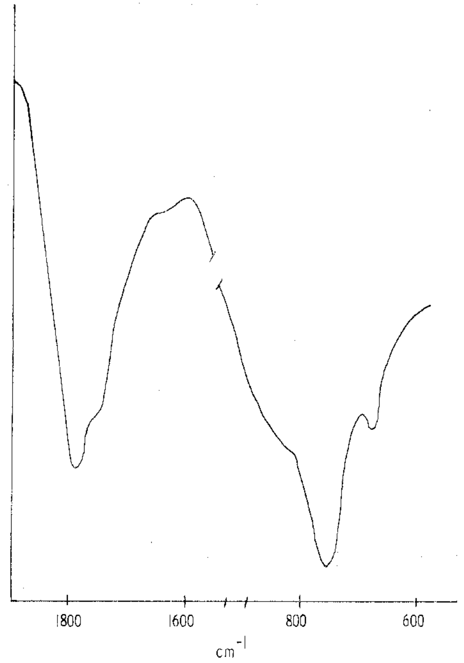

Figure 7. Infrared spectrum of the solution resulting on admixture of LiH and AlH_3 in 1:4 molar ratio in diethyl ether.

Results and Discussion

The infrared spectra of $LiAlH_4$ and AlH_3 in diethyl ether and tetrahydrofuran as well as mixtures of these compounds in 1:1, 1:2, 1:3, and 1:4 ratios are shown in Figures 1 and 6. In each case the infrared spectrum of a mixture of $LiAlH_4$

Table II. X-Ray Powder Diffraction Patterns of the Solid Products Obtained in the Reactions of $LiAlH_4$ with AlH_3 in Diethyl Ether

"$LiAl_2H_7$"[a]		"$LiAl_3H_{10}$"[b]		"$LiAl_4H_{13}$"[c]		"$LiAl_5H_{16}$"[d]		$LiAlH_4$[e]		AlH_3[f]		$LiAl_2H_7$[h]		$LiAl_4H_{13}$[i]		$LiAl_4H_{13}$[j]	
d, Å	I/I_0[g]	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0
11.4	m	11.6	m	11.6	s	11.6	s	5.36	w	11.6	vs	4.43	ms	9.450	ms	11.6	s
5.31	w	5.30	w	5.33	w	4.61	ms	4.48	m	4.59	s	4.20	w	5.586	w	6.7	w
4.61	mw	4.65	m	4.62	m	4.47	vw	4.00	vw	3.24	ms	3.89	s	5.265	vw	4.55	s
4.45	m	4.41	m	4.44	w	3.87	ms	3.89	s	2.89	ms	3.68	vw	4.548	s	4.30	s
3.85	s	3.85	s	3.85	s	3.65	vw	3.68	m			3.55	mw	4.439	vs	3.85	s
3.67	m	3.63	m	3.66	w	3.31	w	3.53	vw			3.30	mw	3.045	ms	3.66	m
3.41	m	3.47	m	3.45	w	3.25	s	3.43	w			2.90	vww	3.888	s	3.45	m
3.31	m	3.30	m	3.33	m	3.00	vw	3.32	m			2.65	mw	3.666	vs	3.33	w
3.22	mw	3.24	m	3.24	s	2.87	ms	3.24	m			2.588	w	3.527	w	3.02	w
3.00	w	3.01	w	3.01	w	2.66	vw	3.03	m			2.504	m	3.456	m	2.95	m
2.92	w	2.96	w	2.95	w	2.40	vw	3.00	w			2.376	w	3.324	w	2.85	s
2.85	mw	2.85	m	2.85	m			2.95	m			2.337	vw	3.229	vs	2.65	vw
2.67	w	2.65	w	2.65	w			2.68	m			2.295	vw	3.035	ms	2.54	m
2.45	w	2.45	vw	2.45	vw			2.54	vw			2.093	mw	2.952	vw	2.39	w
2.16	w	2.40	w	2.39	vw			2.45	w			1.992	mw	2.882	vs	2.29	m
2.01	w	2.02	vw	2.12	vw			2.42	m			1.949	mw	2.799	vw	2.25	w
1.78	w							2.24	w			1.929	vvw	2.680	w	2.075	w
								2.15	w			1.883	vvw	2.566	vw	1.98	vvw
								2.05	w			1.782	vvw	2.506	vvw	1.80	w
								2.01	vw			1.765	w	2.424	w	1.69	vw
								1.98	w			1.655	w	2.405	w	1.65	vvw
								1.92	vw			1.604	vvw	2.342	s	1.54	vw
								1.89	vw			1.572	vw	2.316	s	1.52	vw
								1.80	vw			1.558	vvw	2.271	ms	1.34	vvw
								1.78	w			1.517	w	2.220	ms		
								1.76	w			1.480	w	2.038	ms		
								1.74	w			1.375	vvw	1.530	ms		
												1.352	vvw	1.473	w		
												1.301	vvw	1.442	w		
												1.281	vvw	1.415	w		
												1.194	vvw	1.344	w		

[a] Solid from $LiAlH_4 + AlH_3$ in 1:1 molar ratio. [b] Solid from $LiAlH_4 + AlH_3$ in 1:2 molar ratio. [c] Solid from $LiAlH_4 + AlH_3$ in 1:3 molar ratio. [d] Solid from $LiAlH_4 + AlH_3$ in 1:4 molar ratio. [e] Solid from evaporating ethereal $LiAlH_4$. [f] Solid from evaporating ethereal AlH_3· AlH_3 prepared from 2:1 $BeCl_2 + LiAlH_4$. [g] Key: s, strong; m, moderate; w, weak; v, very. [h] See ref 5. [i] See ref 6.

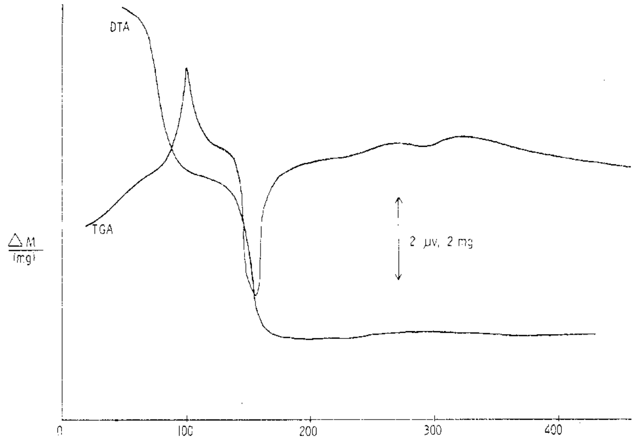

Figure 8. Dta–tga of $LiAl_4H_{13}$ ($LiAlH_4 + 3AlH_3$) under static argon atmosphere.

and AlH_3 corresponds to a superposition of the same bands for $LiAlH_4$ and AlH_3 in the same solvent. If an actual complex between $LiAlH_4$ and AlH_3 were formed in any of the four cases studied, the infrared spectrum of the resulting solution would be expected to be different from the individual components. For example, a complex between $LiAlH_4$ and AlH_3 in solution would be expected to exhibit an Al–H–Al bridge bond. The asymmetric Al–H stretching vibration for such a bond in diethyl ether or tetrahydrofuran would be expected to occur between 1600 and 1400 cm^{-1}.[9] No such band was observed for any of the mixtures mentioned above; therefore, in diethyl ether or THF solution there is no evidence that $LiAlH_4$ and AlH_3 form complexes of the type $LiAlH_4 \cdot n(AlH_3)$ where n = 1, 2, 3 or 4.

Other workers[4–6] have reported that complexes of the type $LiAlH_4 \cdot n(AlH_3)$ are not stable in diethyl ether or tetrahydrofuran but are stable in the solid state. In order to investigate this possibility, the same 1:1, 1:2, 1:3, and 1:4 mixtures of $LiAlH_4$ and AlH_3 in diethyl ether, on which the infrared

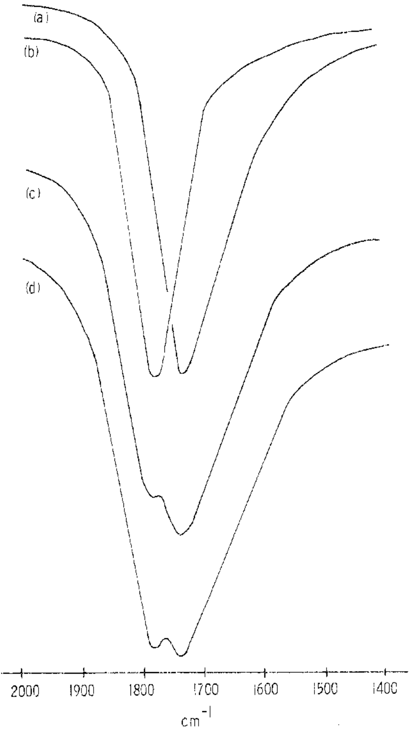

Figure 9. Infrared spectra in the 2000–1400-cm^{-1} region for diethyl ether solutions of (a) $LiAlH_4$, (b) AlH_3, (c) the supernatant remaining after the reaction of $LiAlH_4$ with $BeCl_2$ in 4:1 molar ratio, "$LiAl_2H_7$," and (d) the supernatant remaining after the reaction of $LiAlH_4$ with $BeCl_2$ in 3:1 molar ratio, "$LiAl_3H_{10}$."

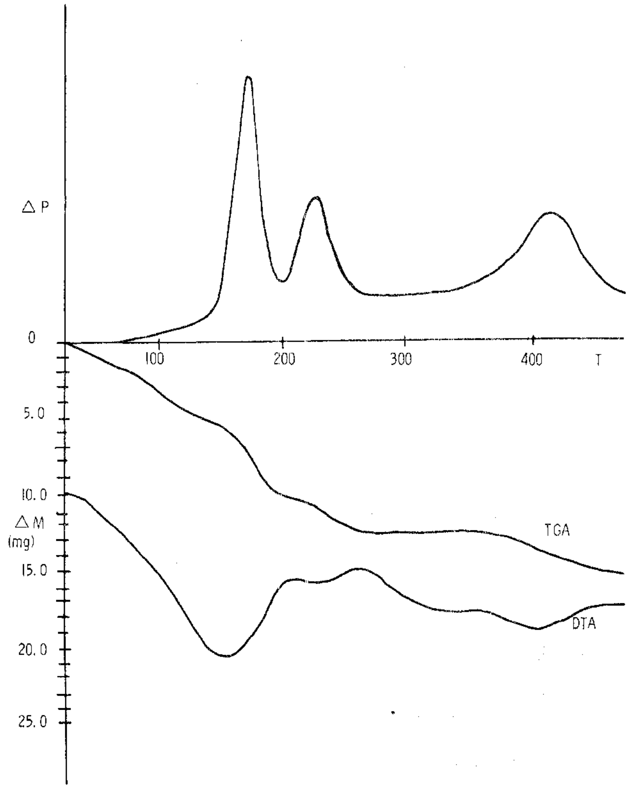

Figure 10. Vacuum dta–tga of $LiAlH_4$.

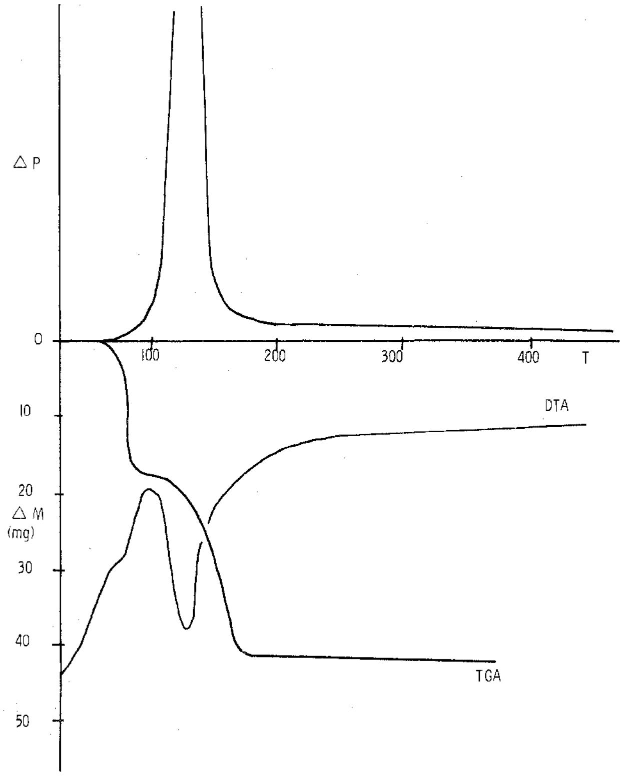

Figure 11. Vacuum dta–tga of AlH_3.

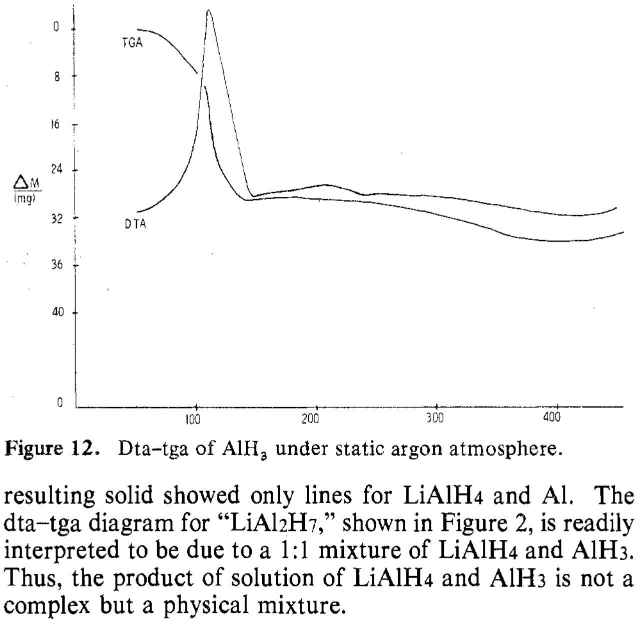

Figure 12. Dta–tga of AlH_3 under static argon atmosphere.

spectra were taken, were evaporated to dryness. Analysis of the resulting white solids indicated the appropriate empirical formula (Table I) ($LiAl_2H_7$, $LiAl_3H_{10}$, $LiAl_4H_{13}$, and $LiAl_5H_{16}$) which indicated the proper stoichiometric ratios and the absence of hydrolysis or ether cleavage. In each case these white solids were subjected to dta–tga and X-ray powder diffraction analysis.

The X-ray powder diffraction pattern for "$LiAl_2H_7$" is shown in Table II. It is readily seen that the so-called complex corresponds to a mixture of $LiAlH_4$ and AlH_3. The vacuum dta–tga of "$LiAl_2H_7$" is shown in Figure 2. The thermogram shows gas evolution at 110, 163, 221, and 355° with simultaneous weight losses of 14.75, 1.00, 0.50, and 0.50 mg. The vacuum dta–tga diagrams of separate samples of $LiAlH_4$ and AlH_3 are shown in Figures 10 and 11. (The dta–tga diagram of AlH_3 under static argon pressure is shown in Figure 12.) Aluminum hydride (Figure 11) is seen to decompose at 110° with almost simultaneous loss of both solvent and hydrogen. (See eq 4.) The first gas evolution in Figure 2 for "$LiAl_2H_7$"

$$AlH_3 \rightarrow Al + {}^3/_2H_2 \quad (4)$$

also occurs at 110° and its corresponding large weight loss is undoubtedly due to loss of both solvent and hydrogen. Due to large amounts of solvent loss, only the lower portions of the tga curves are shown in Figures 2–5 so that the weight losses for the last three gas evolutions could be seen more easily. $LiAlH_4$ (Figure 10) is seen to decompose with gas evolution at 165, 224, and 410° with simultaneous weight loss in the ratio of 2:1:1. (See eq 5–7.) The last three gas evolutions

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2 \quad (165°) \quad (5)$$

$$Li_3AlH_6 \rightarrow 3LiH + Al + {}^3/_2H_2 \quad (224°) \quad (6)$$

$$2LiH \rightarrow 3Li + {}^3/_2H_2 \quad (410°) \quad (7)$$

in Figure 2 correspond exactly with the gas evolutions in Figure 10, except for the last one; however, the ratio of the weight loss for the last three gas evolutions in Figure 2 is 2:1:1, the same as for $LiAlH_4$. When "$LiAl_2H_7$" was heated to 130° under vacuum and stopped, the X-ray powder pattern of the resulting solid showed only lines for $LiAlH_4$ and Al. The dta–tga diagram for "$LiAl_2H_7$," shown in Figure 2, is readily interpreted to be due to a 1:1 mixture of $LiAlH_4$ and AlH_3. Thus, the product of solution of $LiAlH_4$ and AlH_3 is not a complex but a physical mixture.

The data indicating the composition of "$LiAl_2H_7$" as a physical mixture of AlH_3 and $LiAlH_4$ could be explained by assuming the existence of the complex $LiAl_2H_7$ which then dissociates at 110° to $LiAlH_4$ and AlH_3. However, the powder diffraction data were obtained at room temperature which shows the product "$LiAl_2H_7$" to be actually a physical mixture of $LiAlH_4$ and AlH_3. Although the preparations of $LiAl_2H_7$ and $LiAl_3H_{10}$ have been reported[4] by the reaction of $LiAlH_4$ and $BeCl_2$, the infrared spectra (Figure 9) of the solutions obtained by allowing $LiAlH_4$ and $BeCl_2$ to react in diethyl ether in 4:1 and 3:1 mole ratios clearly show the presence of $LiAlH_4$ and AlH_3 in the solution. (See eq 8–10.) The infrared

$$2LiAlH_4 + BeCl_2 \rightarrow BeH_2\downarrow + 2LiCl\downarrow + 2AlH_3 \quad (8)$$

$$3LiAlH_4 + BeCl_2 \rightarrow BeH_2\downarrow + 2LiCl + 2AlH_3 + LiAlH_4 \quad (9)$$

$$4LiAlH_4 + BeCl_2 \rightarrow BeH_2\downarrow + 2LiCl + 2AlH_3 + 2LiAlH_4 \quad (10)$$

spectrum of the solution obtained by the reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether at −5° in 2:1 mole ratio indicates the presence of only AlH_3 in solution.

The X-ray powder diffraction patterns for the proposed compounds "$LiAl_3H_{10}$," "$LiAl_4H_{13}$," and "$LiAl_5H_{16}$" are shown in Table II. The dta–tga thermograms for these compounds are shown in Figures 3–5. Analogous to the reasoning used for "$LiAl_2H_7$," these compounds are also shown to be mixtures of $LiAlH_4$ and AlH_3.

We have repeated the work of Bousquet and coworkers[6] in an attempt to prepare $LiAl_4H_{13}$ by the method used in their laboratory. The infrared spectrum of the solution obtained by reaction of an ether solution of $LiAlH_4$ with an ether solution of AlH_3 (eq 11) is shown in Figure 7. The infrared

$$LiH + AlH_3 \xrightarrow{Et_2O} LiAl_4H_{13} \qquad (11)$$

spectrum of the solution clearly shows the presence of $LiAlH_4$ and AlH_3 in the solution. The X-ray powder pattern of the solid obtained on complete removal of solvent is shown in Table II. It is readily seen that the proposed complex closely corresponds to a mixture of $LiAlH_4$ and AlH_3. The dta–tga thermograms for the solids obtained by ether evaporation of the solutions formed on mixing $LiAlH_4$ and AlH_3 in diethyl ether in 1:3 mole ratio and by reaction 11 are shown in Figures 8 and 13. The dta–tga diagrams of both solids are identical. Also there is a striking similarity between these thermograms and the dta–tga of a physical mixture of 1 mol of $LiAlH_4$ and 3 mol of $LiAlH_4$.

The X-ray powder pattern for "$LiAl_2H_7$" reported by Mayet and coworkers[5] is shown in Table I. This powder pattern resembles that of $LiAlH_4$, although no lines for AlH_3 can be detected. The "$LiAl_2H_7$" was prepared by the reaction shown in eq 12. Unfortunately, these workers did not report any

$$7LiH + 2AlCl_3 \rightarrow LiAl_2H_7 + 6LiCl \qquad (12)$$

dta–tga data or infrared spectra in their studies.

In this study, evidence has been presented to show that $LiAlH_4$ and AlH_3 do not react, under the conditions studied, to form complexes of the type $LiAlH_4 \cdot n(AlH_3)$ in either diethyl ether or THF solution. Also, evidence has been presented showing that the solids left after evaporation of the solvent from 1:1, 1:2, 1:3, and 1:4 mixtures of $LiAlH_4$ and AlH_3 in diethyl ether failed to produce complexes of the type $LiAlH_4 \cdot n(AlH_3)$. The equivalence of solutions formed by (1) addition of $LiAlH_4$ and AlH_3 in diethyl ether, (2) reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether, and (3) reaction of LiH and AlH_3 has been demonstrated and the solids resulting from these solutions have been shown by X-ray powder diffraction and dta–tga to be physical mixtures of $LiAlH_4$ and AlH_3.[15]

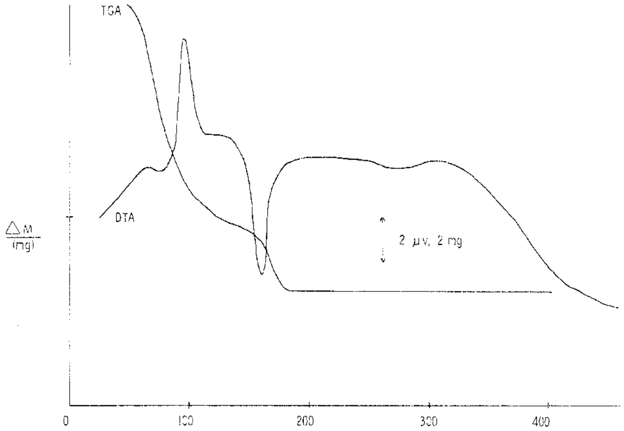

Figure 13. Dta–tga of $LiAl_4H_{13}$ (LiH + $4AlH_3$) under static argon atmosphere.

Registry No. $LiAlH_4$, 16853-85-3; AlH_3, 7784-21-6; LiH, 7580-67-8; $BeCl_2$, 7787-47-5.

References and Notes

(1) E. C. Ashby, J. P. Sanders, P. Claudy, and R. D. Schwartz, *Inorg. Chem.*, **12**, 2860 (1973).
(2) E. C. Ashby, J. R. Sanders, P. Claudy, and R. D. Schwartz, *J. Amer. Chem. Soc.*, **95**, 6485 (1973).
(3) H. C. Brown and H. M. Yoon, *J. Amer. Chem. Soc.*, **88**, 1464, (1966).
(4) J. N. Dymova, *et al.*, *Dokl. Akad. Nauk SSSR*, **184**, 1338 (1969).
(5) J. Mayet, S. Kovacevic, and J. Tranchant, *Bull. Soc. Chim. Fr.*, 506 (1973).
(6) J. Bousquet, J. Choury, and P. Claudy, *Bull. Soc. Chim. Fr.*, 3852 (1967).
(7) Yu M. Kessler, N. M. Alpatova, and O. R. Osipov, *Usp. Khim.*, **33**, 261 (1964).
(8) H. Noth, British Patent 820,513 (1959).
(9) P. Kobetz, W. E. Becker, R. Pinkerton, and J. B. Honeycutt, *Inorg. Chem.*, **2**, 859 (1963).
(10) N. M. Alpatova, T. N. Dymova, Yu M. Kessler, and O. R. Osipov, *Russ. Chem. Rev.*, **37**, 99 (1968).
(11) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N.Y., 1969.
(12) E. C. Ashby and R. D. Schwartz, *J. Chem. Educ.*, **51**, 65 (1974).
(13) E. C. Ashby and John J. Watkins, *Inorg. Chem.*, **12**, 2493 (1973).
(14) E. C. Ashby and P. Claudy, *J. Chem. Educ.*, in press.
(15) **Note Added in Proof.** We have recently repeated the work of Dymova[4] ($LiAlH_4$ + $AlCl_3$) and Mayet[5] (LiH + $AlCl_3$) and have found evidence for $LiAl_2H_7$ as reported. We shall report in detail on our findings in a separate paper.