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A Study of the Thermal Decomposition of Complex Metal Hydrides

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The thermal decomposition of $LiAlH_4$, $NaAlH_4$, $KAlH_4$, $MAlH_4 \cdot L$ (L = tertiary amine; M = Li or Na), $Mg(AlH_4)_2 \cdot 4THF$, Li_3AlH_6, Na_3AlH_6, MgH_2, and $Ca(AlH_4)_2$ has been investigated using differential thermal analysis and thermogravimetric analysis. Evidence is presented that $MAlH_4$ compounds decompose through the corresponding M_3AlH_6 species. The amine complexes of $LiAlH_4$ have been demonstrated to have a higher thermal stability than the parent complex hydride. With $NaAlH_4 \cdot L$ (L = amine) complexes, desolvation precedes decomposition. However both $Mg(AlH_4)_2 \cdot 4THF$ and $ClMgAlH_4 \cdot 4THF$ undergo complex thermal decomposition involving loss of THF and hydrogen as well as THF cleavage. Decomposition of $Ca(AlH_4)_2$ is directly to CaH_2, aluminum metal, and hydrogen. The solid-state reaction between MH and $MAlH_4$ is discussed.

Introduction

Few systematic studies on the manner of thermal decomposition of complex metal hydrides have been reported. Garner and Haycock[1] analyzed time–decomposition curves (isothermal) for $LiAlH_4$ and concluded that decomposition occurred in three stages. The first of these was an initial surface reaction which was followed by loss of half of the hydridic hydrogen according to eq 1. This in turn was followed by loss of

$$LiAlH_4 \longrightarrow LiAlH_2 + H_2 \quad (1)$$

the third hydrogen at a much slower rate (eq 2).

$$LiAlH_2 \longrightarrow LiH + Al + {}^1/_2H_2 \quad (2)$$

Wiberg and coworkers have represented the thermal decomposition of $LiAlH_4$ in solution as occurring to give LiH directly (eq 3). This mode of decomposition has

$$LiAlH_4 \longrightarrow LiH + {}^3/_2H_2 + Al \quad (3)$$

been suggested by these investigators for a number of complex metal hydrides.[2]

Mikheeva and coworkers[3] examined the thermal decomposition of $LiAlH_4$ using combined differential thermal analysis (dta) and effluent gas analysis (ega). They found an endothermic effect at 154–161° accompanied by evolution of 1 mol of hydrogen; a second endothermic effect at 197–227° resulted in another 0.5 mol of hydrogen, with the final hydrogen evolution occurring at 580–586°.

Employing the technique of differential scanning calorimetry, Block and Gray[4] verified the three endothermic effects reported by Mikheeva in addition to finding two exothermic effects. One of these was associated with decomposition resulting from a surface contamination as noted by Garner and Haycock earlier, and the second with the decomposition reaction shown in eq 1. They did not insist that $LiAlH_2$ was a real compound, but the exothermic effect they observed was consistent with an ega peak showing loss of 1 mol of hydrogen per mole of $LiAlH_4$. The endothermic effect that Mikheeva had associated with this decomposition was clearly demonstrated to be a reversible phase change by these workers.

The study of Maycock and coworkers[5] verified the results of Block and Gray without adding anything to the understanding of the nature of $LiAlH_2$ which they also proposed as the product of the initial decomposition.

In a further study of the thermal decomposition by Mikheeva and Arkhipov,[6] substantiation of the results of Block and Gray was made in addition to studying the effects of impurities on the decomposition reactions. These workers suggested that the stoichiometry of eq 1 might represent the formation of Li_3AlH_6, a complex metal hydride reported by Ehrlich.[7] They confirmed this conclusion by X-ray powder diffraction studies of partially decomposed $LiAlH_4$. Additional studies by French workers[8,9] have noted the effects of impurities and atmospheric contamination on the thermal decomposition of $LiAlH_4$. Although the latter workers concurred basically with earlier reports and demonstrated that the decomposition proceeds through Li_3AlH_6, the samples used appear to be impure, and their interpretation of the highest temperature endotherm, assigned by previous investigators to the decomposition of LiH, is interpreted as a reaction between LiH and LiOH.

Ashby and Kobetz[10] reported that the controlled pyrolysis of $NaAlH_4$ leads to the formation of Na_3AlH_6 which they had been able to prepare independently from sodium, aluminum, and hydrogen under high pressure

$$3Na + Al + 3H_2 \longrightarrow Na_3AlH_6 \quad (4)$$

$$3NaAlH_4 \longrightarrow Na_3AlH_6 + 2Al + 3H_2 \quad (5)$$

Russian workers[11] have recently reported that the thermal decomposition of $NaAlH_4$ proceeds in three stages. They attributed the formation of Na_3AlH_6 to an exothermic effect at 220° and in addition claimed to have observed the fusion of $NaAlH_4$.

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[1] W. E. Garner and E. W. Haycock, *Proc. Roy. Soc., Ser. A*, **211**, 235 (1952).

[2] E. Wiberg, *Angew. Chem.*, **65**, 16 (1953), and references therein.

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[11] T. M. Dymova and S. I. Bakum, *Russ. J. Inorg. Chem.*, **14**, 1683 (1969).

We report here an initial account of a study covering several complex metal hydrides in an attempt to arrive at a systematic understanding of the thermal decomposition of complex aluminum hydrides.

Experimental Section

Preparation of Compounds.—Lithium hydride was obtained from Alfa Inorganics as a 50% dispersion in mineral oil and used as obtained after washing several times with diethyl ether. A pyrophoric LiH was prepared by treating *tert*-butyllithium with hydrogen (3000 psi, ambient temperature) overnight. This material was stored under hexane and isolated dry only as needed to preserve its activity. Sodium hydride was also obtained commercially as a mineral oil dispersion and similarly treated. KH was prepared from potassium metal and hydrogen in an autoclave. $LiAlH_4$ and $NaAlH_4$ were obtained commercially and recrystallized from ether and tetrahydrofuran–toluene, respectively. $KAlH_4$ was prepared by the interaction of AlH_3 in diglyme with an excess of KH or the interaction of KH with $LiAlH_4$ in diglyme. The product was isolated by toluene precipitation. Magnesium aluminum hydride compounds were prepared as reported in the literature[12] as were amine adducts of $LiAlH_4$ and $NaAlH_4$.[13] Li_3AlH_6 and Na_3AlH_6 were prepared by literature methods.[7,14]

Simultaneous dta–tga measurements were performed on a Mettler Thermoanalyzer II. Samples were contained in either alumina or platinum crucibles using 60-mesh alumina in the reference crucible. The weights of samples used are given in the appropriate tables. The weight of Al_2O_3 in the reference crucible was approximately 100 mg. Heating rates are listed in the tables. Samples were loaded onto the thermoanalyzer under an atmosphere of argon and an argon atmosphere was maintained during the run. Sample weight was monitored on two sensitivities (usually 10 and 1 mg/in.) so that gross weight losses, *e.g.*, solvent, as well as fine losses, hydrogen for example, could be observed. Data in the tables were obtained as follows. The range of transition refers to the initial and final points of the recorded endotherm or exotherm as determined by the initial deviation or return to the base line, respectively. The temperatues at which an endotherm or exotherm was at a maximum was taken as the peak maximum. Samples for differential scanning calorimetry (Perkin-Elmer DSC-1b) were loaded into hermetically sealed aluminum sample pans in an inert-atmosphere enclosure. Once an atmosphere of argon was established over the sample (on the instrument), the pans were punctured to allow hydrogen resulting from decomposition to escape. In the case of simple metal hydrides, the presence of hydrogen was detected by a thermal conductivity cell operating at 100°.

Results

Our observations on the thermal decomposition of $LiAlH_4$ are in agreement with those of Mikheeva and Arkhipov. Figure 1 shows the clearly resolved endothermic phase transition and exothermic effect, the latter being associated with a loss of weight. The second endothermic effect can be easily associated with the decomposition of Li_3AlH_6 as shown by the superimposition of the dta curve for this compound. The last endothermic effect is due to the decomposition of LiH in both cases.

It is interesting to note that the decomposition of LiH formed from $LiAlH_4$ and Li_3AlH_6 appears to decompose at somewhat different temperatures. This clearly indicates the possibility of a solid-state reaction between LiH and aluminum as has been suggested by Aronson and Salzano.[15] In the case of Li_3AlH_6, less aluminum would be present for a given amount of LiH and therefore one might expect that the decomposition of LiH would occur at a higher temperature than the relatively aluminum-rich mixture obtained from the decomposition of $LiAlH_4$.

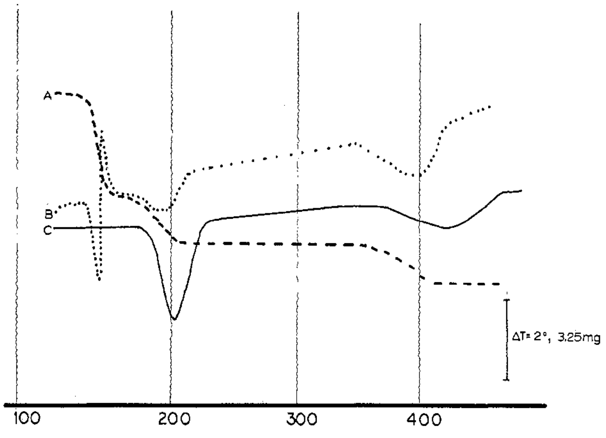

Figure 1.—Tga trace for $LiAlH_4$ (A); dta traces for $LiAlH_4$ (B) and Li_3AlH_6 (C).

The exothermic effect leading to the formation of Li_3AlH_6 presumably involves the reaction of LiH generated by the partial decomposition of $LiAlH_4$ with remaining $LiAlH_4$. This reaction has been previously reported[16] using a hydrocarbon medium in which neither LiH nor $LiAlH_4$ is soluble. We have verified the solid-state reaction in the absence of hydrocarbon between LiH and $LiAlH_4$ (Figure 2) and by X-ray powder pattern we have identified the product as Li_3AlH_6. Unfortunately the solid-state reaction does not appear to be a good means of preparing pure Li_3AlH_6 in that the reaction occurs at a temperature where the Li_3AlH_6 being formed is already decomposing. This is a probable explanation as to why the ratio of weight losses in the case of $LiAlH_4$ decomposition does not correspond exactly to 2:1:1.

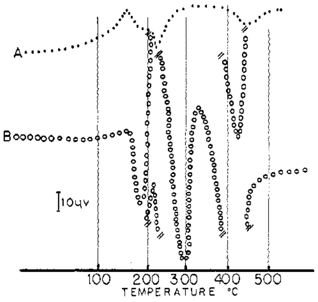

Figure 2.—Dta traces: (A) $2LiH + LiAlH_4$; (B) $2NaH + NaAlH_4$.

It is also noteworthy that while the appearances of the dta and dsc[4] traces are different, they are reproducible. The dsc trace might suggest there is a good separation between the endothermic phase transition and the formation of Li_3AlH_6, but the dta and ega traces (Figures 1 and 2) show more accurately that this is not the case. Differences in sample configuration as well as use of aluminum sample pans in the case of dsc measurements are the probable explanations for this—the latter especially in light of the apparent reaction between LiH and possibly $LiAlH_4$ and aluminum metal.

In the case of $NaAlH_4$, the stepwise decomposition

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[12] E. C. Ashby, R. Schwartz, and B. D. James, *Inorg. Chem.*, **9**, 325 (1970).

[13] J. A. Dilts and E. C. Ashby, *ibid.*, **9**, 855 (1970).

[14] E. C. Ashby and B. D. James, *ibid.*, **8**, 2468 (1969).

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[16] P. Chini, A. Baradel, and C. Vacca, *Chim. Ind.* (*Milan*), **48**, 596 (1966).

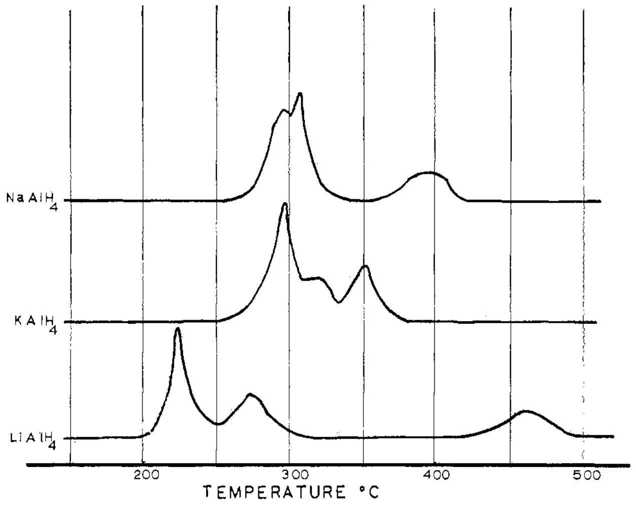

Figure 3.—Ega traces for $LiAlH_4$, $NaAlH_4$, and $KAlH_4$.

is not as well resolved as with $LiAlH_4$. Figure 3 shows the ega trace for the decomposition of $NaAlH_4$ and Figure 4 shows the dta–tga plots for $NaAlH_4$. A strong endothermic effect (165–205°) proved to be reversible and is associated with a phase change. This endotherm is accompanied by a small weight loss if the hydride is not of a high degree of purity. Two subsequent endotherms are accompanied by weight losses corresponding to 75% of the hydrogen evolved. The tga curve does not have a uniform slope and shows an inflection point consistent with the formation of Na_3AlH_6 according to eq 5. Comparison of the dta curves for $NaAlH_4$ and Na_3AlH_6 suggests that the second of these endothermic effects is associated with the decomposition of Na_3AlH_6. The last endothermic effect (250–300°) results from the decomposition of NaH. Again the maximum of the NaH peak seems to show a dependence on the presence of aluminum. The effect is less pronounced than was observed in the decomposition of LiH.

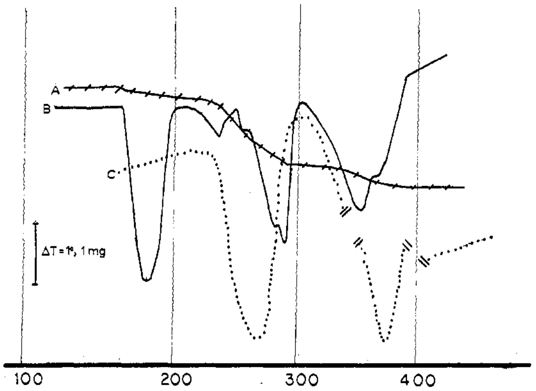

Figure 4.—Tga trace for $NaAlH_4$ (A); dta traces for $NaAlH_4$ (B) and Na_3AlH_6 (C).

The thermal decomposition of $KAlH_4$ is quite similar to that observed for $NaAlH_4$. The weight loss is not clearly resolved although an inflection point in the tga curve is evident. Two endothermic effects correspond to a loss of 75% of the hydrogen and the third endotherm results from the final decomposition of KH as is shown by a superimposition of the dta trace of KH (Figure 5). The three-step loss of hydrogen for $KAlH_4$ is demonstrated clearly in the ega trace shown in Figure 3. Table I summarizes these data.

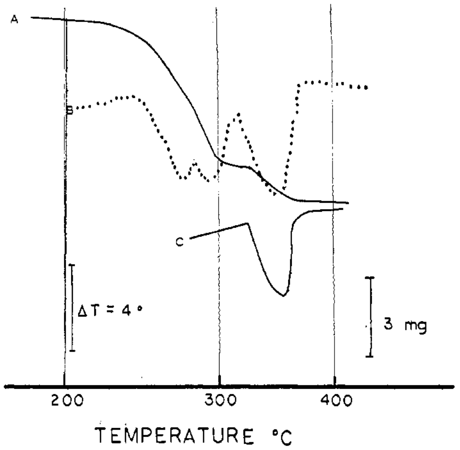

Figure 5.—Tga trace for $KAlH_4$ (A); dta traces for $KAlH_4$ (B) and KH (C).

Table I

Thermal Decomposition of Alkali Metal Complex Hydrides

Compd (sample wt, mg)	Thermicity	Range of transition, (peak max), °C	% wt loss
$LiAlH_4$ [a] (96.53)	Endo	150–175 (162)	(Phase change)
	Exo	150–175 (165)	4.25
	Endo	180–224 (201)	1.97
	Endo	362–425 (409)	1.76
$NaAlH_4$ [a] (49.0)	Endo	165–205 (183)	(Phase change)
	Endo	212–250 (229)	3.37
	Endo	250–300 (285)	2.06
	Endo	300–402 (335)	1.63
$KAlH_4$ [a] (168.6)	Endo	235–280 (270)	3.63
	Endo	280–320 (290)	
	Endo	320–400 (384)	0.77
Li_3AlH_6 [a] (58.52)	Endo	182–227 (220)	
	Endo	370–455 (430)	
Na_3AlH_6 [b] (155.4)	Endo	223–305 (262)	(Ratio of wt loss 0.97:1)
	Endo	305–405 (378)	

[a] Heating rate 2°/min. [b] Heating rate 4°/min.

It is not possible totally to desolvate $Mg(AlH_4)_2 \cdot 4THF$. The dta–tga trace for partially desolvated $Mg(AlH_4)_2$ is shown in Figure 6. The few per cent THF remaining is lost in an exothermic reaction together with some hydrogen. The weight losses are not reproducible suggesting that decomposition as well as desolvation is occurring. The last endothermic effect agrees well with that found for MgH_2 prepared by the action of $LiAlH_4$ with diethylmagnesium in THF.

The preparation of $Ca(AlH_4)_2$ in THF results in a

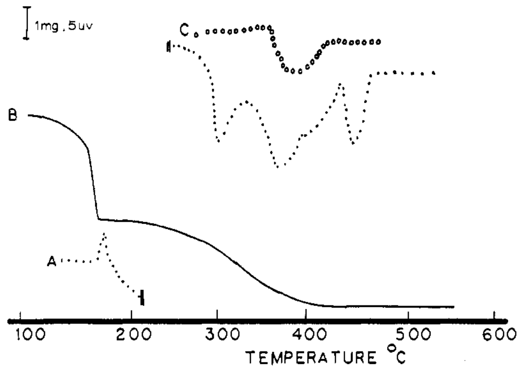

Figure 6.—(A) Dta trace for $Mg(AlH_4)_2 \cdot x THF$; (B) tga trace for $Mg(AlH_4)_2 \cdot x THF$; (C) dta trace for MgH_2 (from THF).

monosolvate species which can be desolvated without decomposition. The remaining endothermic effect is accompanied by weight loss which corresponds to the formation of CaH_2 (Figure 7).

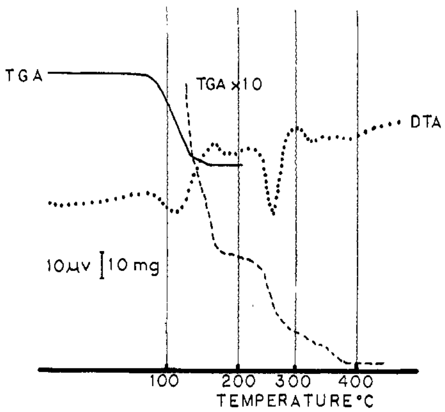

Figure 7.—Dta–tga traces for $Ca(AlH_4)_2 \cdot THF$.

$LiAlH_4 \cdot L$.—The TEDA (triethylenediamine) complex of $LiAlH_4$ shows two endothermic effects (Figure 8). The second of these is similar to the effect observed in the case of $LiAlH_4$; this was shown to be due to the decomposition of LiH in the presence of aluminum. The first effect which is associated with a major weight loss (196°, 76.2% weight loss, 75% calculated for amine loss) corresponds to the decomposition shown in (6). The net effect of amine coordination is the stabilization of the complex metal hydride. Since decomposition begins at a temperature above the decomposition temperature of Li_3AlH_6, it is not surprising that Li_3AlH_6 is not an intermediate in the decomposition although it is an intermediate in the decomposition of unsolvated $LiAlH_4$. It is also interesting to note that $TEDA \cdot AlH_3$ has an appreciably higher decomposition temperature than AlH_3 although disproportionation as shown in eq 7 does not occur.

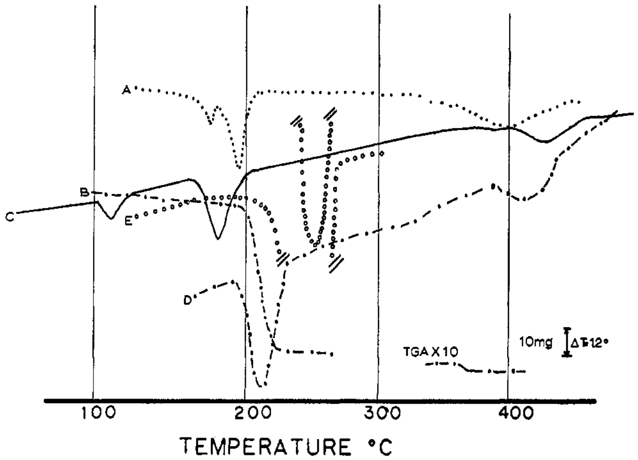

Figure 8.—Dta trace for $LiAlH_4 \cdot TMED$ (A); tga trace for $LiAlH_4 \cdot TEDA$ (B); dta traces for $(LiAlH_4)_2 \cdot TMED$ (C), $LiAlH_4 \cdot TEDA$ (D), and $AlH_3 \cdot TEDA$ (E).

$$LiAlH_4 \cdot TEDA \xrightarrow{195°} LiH + TEDA + {}^3/_2H_2 + Al \qquad (6)$$

$$LiAlH_4 \cdot TEDA \longrightarrow LiH + AlH_3 \cdot TEDA \qquad (7)$$

$(LiAlH_4)_2 \cdot TMED$ (TMED = *N,N′,N″,N‴*-tetramethylethylenediamine) has, in addition to the two endothermic decomposition effects, an endothermic peak associated with a reversible phase change (Figure 8). $LiAlH_4 \cdot TMED$ shows two endothermic effects accompanied with the major (loss of ligand) weight loss. It was not possible to determine if one of these was due to a phase change because their transition temperatures occurred so closely together. For clarity of presentation, tga data were not plotted on Figure 8 but have been summarized with the temperature data in Table II.

$NaAlH_4 \cdot$amine Complexes.—The *N,N′,N″,N‴*-

TABLE II

THERMAL DECOMPOSITION OF COMPLEX METAL HYDRIDE–AMINE ADDUCTS

Compd (sample wt, mg)	Thermicity	Range of transition (peak max), °C	% wt loss
$LiAlH_4 \cdot TEDA$ (90.43)	Endo	196–238 (208)	76.2
	Endo	340–425 (391)	0.35
$LiAlH_4 \cdot TMED^a$ (111.42)	Endo	175–180 (177)	
	Endo	182–205 (193)	73.1
	Endo	360–430 (399)	0.36
$(LiAlH_4)_2 \cdot TMED^c$ (141.62)	Endo	100–132 (112)	(Phase change)
	Endo	167–207 (180)	56.1
	Endo	395–420 (405)	0.77
$AlH_3 \cdot TEDA^a$ (120.1)	Endo	200–238 (235)	. . .
$NaAlH_4 \cdot TEDA^a$ (112.4)	Endo	195–290 (240)	59.6
	Endo	Max 260 sh	. . .
	Endo	290–370 (340)	0.56
$NaAlH_4 \cdot TMED^b$ (71.12)	Endo	35–50 (45)	(Phase change)
	Endo	80–154 (111)	60.42
	Endo	163–200 (171)	(Phase change)
	Endo	235–250 (246)	1.26
	Endo	250–290 (259)	
	Endo	290–365 (336)	0.42

[a] Heating rate 2°/min. [b] Heating rate 4°/min. [c] Heating rate 6°/min.

tetramethylethylenediamine complex of ($NaAlH_4 \cdot TMED$) decomposes thermally as expected for a simple solvate (Figure 9). The first endothermic effect is the result of a phase change and no weight loss was noted. The second endothermic effect is accompanied by loss of 69.6% of the weight of the sample (calculated for loss of TMED from $NaAlH_4 \cdot TMED$, 68.3%). The remaining three endothermic effects are consistent with the decomposition of $NaAlH_4$ which is shown superimposed on the $NaAlH_4 \cdot TMED$ trace. Differences in the location of the peaks are not surprising in light of the different heating rates used (Table II).

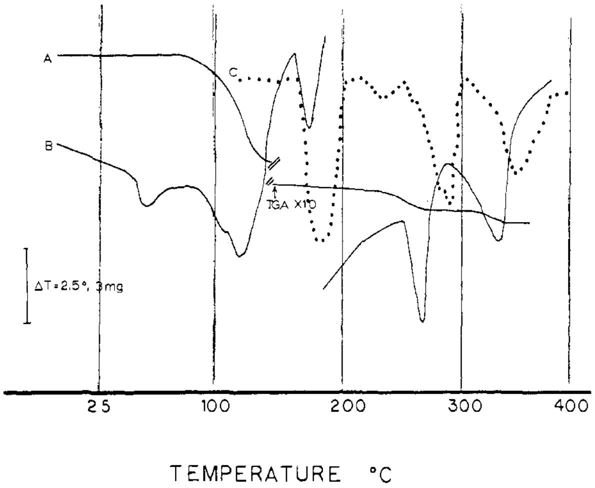

Figure 9.—Tga trace for $NaAlH_4 \cdot TMED$ (A); dta traces for $NaAlH_4 \cdot TMED$ (B) and $NaAlH_4$ (C).

The interpretation of the data for decomposition of $NaAlH_4 \cdot TEDA$ is not so clear-cut (Figure 10). While the last endothermic effect corresponds to the decomposition of NaH, the exact nature of the decomposition leading to this product is not clear. For example, the weight loss for the first exothermic effect corresponds to the loss of all the TEDA. The hydrogen loss however cannot be resolved in the massive weight loss of the amine. The dta peak corresponding to this weight loss is in the same region as the decomposition of $NaAlH_4$ and may be a composite of the three processes

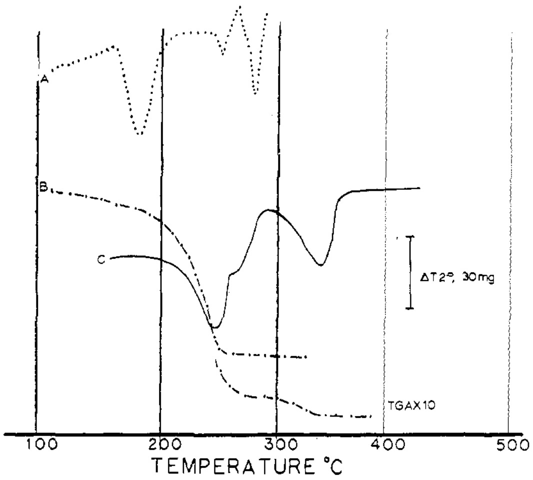

Figure 10.—(A) Dta trace for $NaAlH_4$ (not showing NaH decomposition); (B) tga trace for $NaAlH_4 \cdot TEDA$; (C) dta trace for $NaAlH_4 \cdot TEDA$.

$$NaAlH_4 \cdot TEDA \longrightarrow NaAlH_4 + TEDA \quad (8)$$

$$3NaAlH_4 \longrightarrow Na_3AlH_6 + 2Al + 3H_2 \quad (9)$$

$$Na_3AlH_6 \longrightarrow Al + 3NaH + {}^3/_2H_2 \quad (10)$$

or

$$3NaAlH_4 \cdot TEDA \longrightarrow Na_3AlH_6 + 3TEDA + 3H_2 \quad (11)$$

followed by eq 10, or

$$NaAlH_4 \cdot TEDA \longrightarrow NaH + Al + {}^3/_2H_2 + TEDA \quad (12)$$

In light of the behavior of $NaAlH_4 \cdot TMED$, the first sequence of reactions seems most plausible. Further there appears to be a good correlation between the shoulder on the first endothermic effect and the endothermic effect of the $NaAlH_4$ decomposition which is attributed to the decomposition of Na_3AlH_6. This is only indirect evidence however.

Discussion

The first generalization concerning the thermal decomposition of complex metal hydrides is that the same order of stability (with respect to the nature of M) of $MAlH_4$ compounds as compared to MBH_4 compounds has been found.[17] The increase in stability follows the increase in cation size ($Li < Na < K$) and the simple interpretation of this order is based on increasing stabilizing power of the larger cation. Although it is difficult to put this argument on a sound quantitative basis, the suggestion that the degree of distortion of the BH_4^- tetrahedron strongly affects chemical behavior of BH_4 compounds has been made.[18]

While our results with $LiAlH_4$ substantiate in general the reports of Block and Gray,[4] as well as McCarty, Maycock, and Verneker,[5] there are several points of difference in interpretation of the dta–tga data.

The work reported here was performed on a $LiAlH_4$ sample that had been twice recrystallized (once from ether and once from ether–benzene); we failed to observe the first exothermic transition that Block and Gray attributed to a surface reaction and McCarty, *et al.*, attributed to a melting of $LiAlH_4$. The presence of ether may account for this exotherm and/or the darkening of $LiAlH_4$ at this point. Our samples were essentially ether free and no darkening of the sample was noted through the first endothermic effect. In further contrast to the work of McCarty, *et al.*, even slow scan rates (2°/min) still showed the distinct endothermic effect associated with the phase change.

While nothing definite was concluded about the nature of the impurity giving rise to the exothermic effect observed by these two groups, the work of Dymova, *et al.*,[19] on the thermal decomposition of $LiAlH_4 \cdot nAlH_3$ species is quite similar to the behavior observed in the impure $LiAlH_4$ samples. The compound claimed to be Li_2AlH_7 decomposed with a strong exothermic effect from 160 to 220°.

The exothermic effect following the endothermic phase transition (only exotherm of Figure 1) has widely been interpreted as indicating the formation of $LiAlH_2$.

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[17] D. S. Stasinevich and G. A. Egorenko, *Russ. J. Inorg. Chem.*, **13**, 341 (1968).

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Recent work[5] has shown that this compound is most probably $\mathrm{Li_3AlH_6}$. Comparison of the thermograms of an authentic sample of $\mathrm{Li_3AlH_6}$ support this conclusion (Figure 1).

The mechanism of the formation of $\mathrm{Li_3AlH_6}$ is of considerable interest. The reactions of LiH and NaH with $\mathrm{LiAlH_4}$ and $\mathrm{NaAlH_4}$, respectively, are well known; however the conditions under which these reactions are carried out involve ball-milling the reactants under a hydrocarbon medium at elevated temperatures. The finding that these reactions occur in the solid state under the influence of heat alone suggests that the mechanism of $\mathrm{M_3AlH_6}$ formation involves the partial decomposition of $\mathrm{MAlH_4}$ to the metal hydride (MH), Al, and hydrogen followed by the reaction of the highly reactive MH with undecomposed $\mathrm{MAlH_4}$ to yield $\mathrm{M_3AlH_6}$ (eq 13–16). Alternatively the first of these reac-

$$\mathrm{MAlH_4} \longrightarrow \mathrm{MH} + \mathrm{Al} + {}^3/_2\mathrm{H_2} \qquad (13)$$

$$2\mathrm{MH} + \mathrm{MAlH_4} \longrightarrow \mathrm{M_3AlH_6} \qquad (14)$$

tions could be followed by the formation of an unstable $\mathrm{M_2AlH_5}$ species which disproportionates into $\mathrm{M_3AlH_6}$ and $\mathrm{MAlH_4}$ (eq 15 and 16). Unfortunately the iso-

$$\mathrm{MH} + \mathrm{MAlH_4} = \mathrm{M_2AlH_5} \qquad (15)$$

$$2\mathrm{M_2AlH_5} = \mathrm{MAlH_4} + \mathrm{M_3AlH_6} \qquad (16)$$

thermal kinetic data in the literature are not of sufficient quality to distinguish between these possibilities. Attempts to synthesize[4] $\mathrm{M_2AlH_5}$ by allowing 2 g-atoms of the alkali metal, 1 g-atom of aluminum, and 1 mol of hydrogen to react at temperatures and pressures known to give $\mathrm{MAlH_4}$ and $\mathrm{M_3AlH_6}$ yield an equimolar mixture of these two suggesting that if $\mathrm{M_2AlH_5}$ is an intermediate in the course of the reaction, it is unstable with respect to disproportionation.

The last reaction is of interest in that pure LiH melts with little decomposition at 680° while LiH in the presence of Al metal has been shown to decompose at much lower temperatures (presumably involving a solid-state reaction between LiH and Al[15]). A thorough study of this reaction has not been made, but it would appear that there is some dependence of the temperature of decomposition on the ratio of LiH to Al metal. At any rate, there is little to indicate the necessity for invoking[8,9] the reaction of LiH with LiOH for the explanation for this effect.

The thermal decomposition of $\mathrm{LiAlH_4}$ is then summarized by

$$3\mathrm{LiAlH_4} \longrightarrow \mathrm{Li_3AlH_6} + 3\mathrm{H_2} + 2\mathrm{Al} \qquad (17)$$

$$\mathrm{Li_3AlH_6} \longrightarrow 3\mathrm{LiH} + {}^3/_2\mathrm{H_2} + \mathrm{Al} \qquad (18)$$

$$\mathrm{LiH} + \mathrm{Al} \longrightarrow \text{“LiAl”} + {}^1/_2\mathrm{H_2} \qquad (19)$$

Results from the dta–tga study of $\mathrm{NaAlH_4}$ and $\mathrm{KAlH_4}$ suggest that these complex metal hydrides decompose by a mechanism similar to that found for $\mathrm{LiAlH_4}$. Figure 4 illustrates a typical result for the thermal decomposition of $\mathrm{NaAlH_4}$. Following a strong endothermic effect which is reversible and associated with a phase change, two endothermic effects (212–250 and 250–300°) occur concurrently with the loss of 75% of the hydridic hydrogen. Although a clear break in the tga curve is not evident, there is an inflection point suggesting that the loss of hydrogen is occurring in two steps (eq 20, 21). The presence of a total of two un-

$$3\mathrm{NaAlH_4} \longrightarrow \mathrm{Na_3AlH_6} + 3\mathrm{H_2} + 2\mathrm{Al} \qquad (20)$$

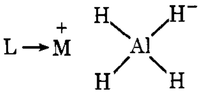
$$\mathrm{Na_3AlH_6} \longrightarrow 3\mathrm{NaH} + \mathrm{Al} + {}^3/_2\mathrm{H_2} \qquad (21)$$

resolved losses of hydrogen in the 200–300° region is demonstrated by the ega trace shown in Figure 3. The high-temperature endotherm (300–402°) is most reasonably assigned to the decomposition of NaH. The conclusion that $\mathrm{NaAlH_4}$ decomposes through $\mathrm{Na_3AlH_6}$ is supported by the thermal decomposition of an authentic sample of the latter which undergoes decomposition in the same region as the third endothermic effect found for $\mathrm{NaAlH_4}$.

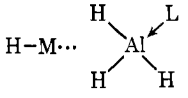
While the dta results for $\mathrm{NAlH_4}$ agree well with the Russian report, no evidence was found for the exothermic effect attributed to the formation of $\mathrm{Na_3AlH_6}$.[11] Two overlapping endothermic effects from 212 to 300° account first for the formation of $\mathrm{Na_3AlH_6}$ and second for its decomposition. Again the mechanism suggested here is an *in situ* generation of alkali metal hydride which then reacts with $\mathrm{MAlH_4}$ to give the corresponding $\mathrm{M_3AlH_6}$. This solid-state reaction does occur as judged by dta (Figure 2) and X-ray powder data.

The dta–tga trace for $\mathrm{KAlH_4}$ shows three endothermic effects which are accompanied by weight loss. Again the formation of $\mathrm{K_3AlH_6}$ is not clearly resolved in the tga curve but is strongly suggested by an inflection in this curve and the ega trace (Figure 3).

Complexes of the type $\mathrm{MAlH_4 \cdot L}$ (M = Li or Na; L = tertiary amine) have been assigned two structures on the basis of infrared data (I[13] and II[20]). The ther-



I



II

mal decomposition of a species such as I might be expected to be similar to that of the parent complex metal hydride, especially if coordination is weak. Decomposition of II might be expected to be more complicated in light of the amine–alane character this compound would be expected to show. A prediction regarding the relative thermal stabilities of these two alternatives is also possible. The net effect of structure I would be a reduction in the distortion of the $\mathrm{AlH_4}$ tetrahedron through covalent interaction with the alkali metal as well as effectively increasing the size of the cation. In light of the increasing thermal stability of the $\mathrm{MAlH_4}$ series, it is anticipated that such a structure would result in an enhanced thermal stability. Increasing the $\mathrm{AlH_3}$ character, as is the case in structure II, might be anticipated to reduce the thermal stability.

The $\mathrm{NaAlH_4 \cdot}$TMED thermal decomposition involves the initial loss of amine (80–154°) followed by decomposition of the remaining $\mathrm{NaAlH_4}$ (Figure 9). Interpretation of the thermal decomposition of $\mathrm{NaAlH_4 \cdot}$TEDA is more complex. The endothermic effect occurring from 195 to 295° reflects a weight loss corresponding to loss of all the amine (Table II). A shoulder on this endotherm suggests that concurrent with the loss of amine, $\mathrm{NaAlH_4}$ may be decomposing to give $\mathrm{Na_3AlH_6}$ whose decomposition is reflected by the shoulder at 260°. NaH is produced as a result of this decomposition as evidenced by an endothermic effect at 340–425°.

No clear desolvation steps were found with the amine

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[20] R. Ehrlich and G. Rice, *Inorg. Chem.*, **5**, 1281 (1966).

complexes of $LiAlH_4$. Enhanced thermal stability of the amine complexes over $LiAlH_4$ itself (and Li_3AlH_6) result in the ambiguous nature of the dta–tga curves. It is not possible to resolve the question of the possible formation of Li_3AlH_6 in the course of the decomposition. In all cases investigated, LiH is the end product as evidenced by its characteristic endothermic decomposition. It is not possible to say if this LiH is produced directly from the decomposition of $LiAlH_4 \cdot L$ (eq 22) or from an Li_3AlH_6 intermediate (eq 23).

$$LiAlH_4 \cdot L = LiH + Al + {}^3/_2H_2 + L \qquad (22)$$

$$3LiAlH_4 \cdot L = Li_3AlH_6 + 2Al + 6H_2 + 3L \qquad (23)$$

The thermal decomposition of species involving the AlH_4 group attached to magnesium is not straightforward. (See Table III.) Several workers have observed that borohydride analogs as THF solvates cannot be desolvated by heating under vacuum without loss of boron from the compound as volatile *n*-butoxyboranes.[13,21] The same problem of THF cleavage appears to be occurring in the case of $ClMgAlH_4 \cdot 4THF$ and $Mg(AlH_4)_2 \cdot 4THF$. As has been shown[22] to be the case with AlH_3, such compounds are unstable with respect to formation of alkoxy species as a result of opening of the THF ring. In the case of AlH_3, this occurs slowly even at room temperature. When "$THF \cdot AlH_3$" is heated, the reaction occurs with explosive violence at about 60°. Similar strong exothermic effects are noted in attempts to desolvate $Mg(AlH_4)_2$ and related species on the thermobalance. $Ca(AlH_4)_2 \cdot THF$ can be isolated according to a published procedure[23] and desolvation of this species proceeds smoothly (Figure 7). The resulting unsolvated material decomposes to CaH_2, Al, and H_2. Carefully desolvated $Mg(AlH_4)_2$ which contains only 7% THF shows an exothermic effect which we assign to ring opening of the THF (Figure 6). The final endothermic effect is most probably the decomposition of MgH_2 formed by the decomposition of $Mg(AlH_4)_2$. The assignment of the first endothermic effect is not clear because the exothermic effect apparently causes local heating which results in partial decomposition of unsolvated $Mg(AlH_4)_2$ and consequently irratic and irreproducible weight losses for subsequent endotherms. The most probable products of the first endotherm are MgH_2, Al, and H_2 by analogy to $Ca(AlH_4)_2$.

TABLE III

THERMAL DECOMPOSITION OF GROUP II HYDRIDE SPECIES

Compd (sample wt, mg)	Thermicity	Range of transition (peak max), °C	% wt loss
$MgH_2 \cdot THF$[b,d] (81.5)	Endo	345–425 (391)	5.3
$MgH_2 \cdot$ ether[a,d] (121.54)	Endo	320–360 (335)	2.4
$(AlH_4)_4 \cdot THF$[a] (69.76)	Exo	35–90 (65)	34.4
	Endo	120–172 (159)	5.4
	Endo	172–192 (177)	
	Endo	205–230 (213)	
	Exo	360–495 (373)	16.4
	Exo	495–510 (505)	
$Mg(AlH_4)_2 \cdot 0.04THF$[c] (47.82)	Exo	170–195 (177)	7.15
	Endo	282–330 (300)	5.45
	Endo	330–402 (370)	
	Endo	432–460 (445)	(Alloy formation)
$Ca(AlH_4)_2 \cdot THF$[c] (105.45)	Endo	85–175 (119)	33.35
	Endo	225–300 (261)	2.85
	Endo	300–355 (350)	1.14
	Endo	335–430 (399)	

[a] Heating rate 2°/min. [b] Heating rate 4°/min. [c] Heating rate 6°/min. [d] Sample weight of solvated species (see Experimental Section).

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