

Hydrolysis and Alcoholysis of Alkali Metal Aluminium Hydrides

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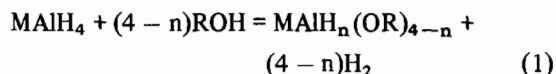
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Received June 19, 1976

The alcoholysis and hydrolysis of $MAIH_4$ ($M = Li, Na, K, Cs$) has been studied in solutions in ether, tetrahydrofuran, and diglyme at 20 °C. All the compounds studied react with primary and secondary alcohols in the stoichiometric ratio of 1:4 to yield $MAI(OR)_4$. Likewise goes the reaction of compounds $MAIH_4$ ($M = Na, K, Cs$) with water. In the case of tert-butyl alcohol, the reaction terminates after the addition of 3 mol of the alcohol to 1 mol of a complex hydride to give $MAIH(OBu-tert)_3$. Completion of the hydrolysis of $LiAlH_4$ occurs at the H_2O to $LiAlH_4$ ratio of 2.6 in solutions in tetrahydrofuran and of 7:1 in solutions in ether. Smooth gas evolution curves indicate a one-step course of both hydrolysis and alcoholysis with the formation of metal hydroxo- and alkoxoaluminates. The IR spectra and X-ray powder photographs show the products of partial solvolysis to be mixtures of metal aluminium hydrides and the final alcoholysis (hydrolysis) products. Evidence is presented against the existence of solid metal alkoxoaluminium hydrides as individual compounds, except in the case of $MAIH(OBu-tert)_3$.

Introduction

The alcoholysis of complex lithium and sodium hydrides is known to be a preparative route to metal alkoxoaluminium hydrides $MAIH_n(OR)_{4-n}$ ($n = 0-3$, $R = Me, Et, iso-Pr, tert-Bu$):



The latter are milder reducing agents than $LiAlH_4$ and have found application to reduction of carbonyl, nitrile, and nitro derivatives [1–3]. According to Brown [1] and Zakharkin [3], the action of 4 mol of an alcohol on 1 mol of $MAIH_4$ results in the substitution of all four hydrogen atoms with the alkoxy groups thus yielding metal tetraalkoxoaluminates, $MAI(OR)_4$.

The reaction of complex hydrides with alcohols (or water) is known as a technique for the determination of “active” hydrogen in analytical chemistry.

The data available, however, concern almost exclusively the higher alcohols [4–8]. Attempts to apply $LiAlH_4$ to water determination have proved a failure: in diglyme or N-ethylmorpholine solutions, the reaction goes with higher yields of hydrogen than can be expected from actual water content [8–10], whereas precipitates from THF solutions contain greater amounts of water than that corresponding to the formula $LiAl(OH)_4$ (Lepin [11]).

In spite of the fact that the reaction is widely practiced its quantitative characteristics have been unknown so far; in particular, the dependence of the hydrogen yield on the ROH to $MAIH_4$ ratio ($R = H, alkyl$) has not been studied. Metal alkoxoaluminium hydrides made from $LiAlH_4$ according to (I) or by reacting MH with $Al(OEt)_3$ in ether or THF solutions are very common in current organic synthesis. Nevertheless, they have scarcely ever been isolated or characterized as individual compounds [1, 3, 12–14].

In this work we have studied hydrogen evolution in reactions of $MAIH_4$ ($M = Li, Na, K, Cs$) with alcohols and water as depending on the reagent ratio, ROH: $MAIH_4$. The intermediate alcoholysis products have been characterized by elemental analysis, X-ray powder photographs and IR spectra. The alcoholysis and hydrolysis of $MAIH_4$ has been studied in ether and tetrahydrofuran solutions ($M = Li$), in tetrahydrofuran ($M = Na$), and in diglyme ($M = K, Cs$).

Experimental

Solutions of $MAIH_4$ (ca. 0.5 M) were prepared in a centrifuge tube, evacuated and filled with argon prior to use. Slurries of $MAIH_4$ in freshly distilled solvents were stirred with a magnet stirrer at 20 °C for 1.5 hours and then centrifugalized. Cleared solutions were pressure transferred under argon into the reaction vessel or ground-glass stopper flasks which were stored under argon in dessicators containing $LiAlH_4$ and P_2O_5 . Aluminium was determined by EDTA titration (with xylenol orange), alkali metals by flame photometry in air-acetylene flame on a Hilger “Atom Spek” instrument, C and H by elemental microanalysis in the presence of quartz sand added to avoid the formation of metal

carbonates. Hydride hydrogen was determined by volume and tensimeter measurements. Alcohols were dehydrated by refluxing with zeolite and then with calcium or magnesium alkoxides, diethyl ether was repeatedly distilled from LiAlH_4 , tetrahydrofuran was refluxed over Na for several hours and then over NaAlH_4 until no gas evolution was observed on addition of LiAlH_4 , and diglyme was repeatedly redistilled from Na.

Gas evolution during the decomposition of MAIH_4 with alcohols and water was monitored by gas volume and tensimeter measurements. The volumetric technique was described in detail elsewhere [15]. The reaction vessel fitted with a dropping funnel was attached to Hüttig's tensiometer for tensimeter measurements. The system was evacuated. When handling solutions, the operating volume of the system was filled with solvent vapour saturated at room temperature. Then, solutions of alcohols or water were added dropwise to a solution or a solid sample in the vessel. Pressure measurements were taken with a Hg manometer.

Table I exemplifies a typical tensimeter experiment (see Fig. 1).

Preparation of metal alkoxoaluminates and alkoxoaluminium hydrides was run under dry argon

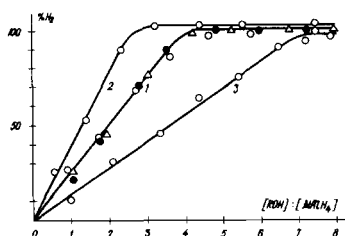


Figure 1. Hydrogen evolution curves: 1, alcoholysis of LiAlH_4 (in Et_2O), NaAlH_4 (in THF), CsAlH_4 (in diglyme), and hydrolysis of NaAlH_4 and CsAlH_4 ; 2, hydrolysis of LiAlH_4 in THF; 3, hydrolysis of LiAlH_4 in ether.

TABLE I. Methanolysis of LiAlH_4 (5.5×10^{-3} mol) in THF Solution (ca. 0.5 M).^a

No.	Amount of MeOH Added		MeOH: LiAlH_4	H_2			Yield, %
	V_1 , ml	mol $\times 10^3$		P_1 , mm Hg	P_2 , mm Hg	Mol $\times 10^3$	
1	0	0	0	245	0	0	0
2	1	4.7	0.855	315	70	5.73	25.8
3	2	9.6	1.75	365	120	9.84	44.2
4	3	1.44.10	2.62	435	190	1.56.10	70.3
5	4	1.92.10	3.47	484	239	1.96.10	88.3
6	5	2.4.10	4.36	518	273	2.23.10	100
7	6	2.88.10	5.23	518	273	2.23.10	100

^a V_1 is the volume of MeOH solution in THF added; P_1 is manometer readings; P_2 is P_1 less the starting pressure of 245 mm Hg; mol of H_2 are calculated as $[\text{H}_2] = P_2 \cdot V_3 / RT$, where $V_3 = V_0 - V_2$ (V_0 is the system volume and V_2 is the volume of solutions present in the dropping funnel and in the reaction vessel); the ratio of the current P_2 value to the final one (273 mm Hg) gives the hydrogen yield.

in flasks equipped with a reflux condenser and a dropping funnel. A calculated quantity of an alcohol was added dropwise to a continuously stirred solution of MAIH_4 in ether ($M = \text{Li}$), THF ($M = \text{Na}$) or diglyme ($M = \text{K}, \text{Cs}$) (0.5 M, 150 ml). Precipitates of $\text{MAI}(\text{OR})_4$ were isolated by centrifugation after the addition of 4 mol of ROH. Residual solvent was removed from the solids under vacuum. $\text{MAI}(\text{OBU-tert})_4$ were prepared by refluxing solutions of $\text{MAIH}(\text{OBU-tert})_3$ in THF or diglyme with excess tert-BuOH for several hours, until gas evolution ceased.

The analytical data for the compounds isolated are given in Table II.

The isolation of the products of partial alcoholysis (Table III) was performed by removal of the solvent *in vacuo* after addition of 2 mol of alcohol.

The IR spectra (mulls in nujol and hexachlorobutadiene) were registered on UR-20 (4000–400 cm^{-1}) and IKS-22 (400–200 cm^{-1}) instruments.

X-ray powder photographs of $\text{MAI}(\text{OR})_4$, $\text{MAIH}(\text{OBU-tert})_3$, and " $\text{MAIH}_n(\text{OR})_{4-n}$ " were taken with a Guinier focussing camera using $\text{Cu-K}\alpha$ radiation. The samples were prepared as mulls in water-free nujol in a dry box into which a beaker with liquid nitrogen was placed.

Results and Discussion

Gas evolution profiles characterizing alcoholysis of metal aluminium hydrides (Fig. 1) show that primary and secondary alcohols react according to the stoichiometry (eq. 1). The reaction continues until 4 mol of ROH per 1 mol of MAIH_4 are consumed to give 4 mol of hydrogen and metal alkoxoaluminates as end products. The latter may precipitate in the form of solvates of varying composition, $\text{LiAl}(\text{OR})_4 \cdot n\text{ROH}$ (with n up to 1 in the case of methyl and up to 0.5 in the case of isopropyl alcohols). $\text{LiAl}(\text{OEt})_4$ and other $\text{MAI}(\text{OR})_4$ do not form solvates.

TABLE II. Analytical Data for the Products of Alcoholysis of MAIH₄.

Compound	Al(%)		Li(%)		C(%)		H(%)	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
LiAl(OMe) ₄	16.89	17.10	4.38	4.34	30.69	30.40	7.82	7.60
LiAl(OEt) ₄	12.32	12.61	3.16	3.27	44.36	44.80	9.33	9.35
LiAl(OPr-iso) ₄	9.85	10.00	2.57	2.59	53.21	53.40	10.36	10.38
LiAlH(OBu-tert) ₃	10.30	10.61	2.46	2.76	56.85	56.70	10.53	11.02
LiAl(OBu-tert) ₄	7.90	8.30	2.06	2.15	59.16	58.80	11.05	11.05
NaAl(OMe) ₄	15.51	15.51			27.48	27.61	6.64	6.90
NaAl(OEt) ₄	11.26	11.74			41.59	41.70	8.74	8.70
NaAl(OPr-iso) ₄	9.16	9.45			49.87	50.30	9.45	9.80
NaAlH(OBu-tert) ₃	9.60	10.00			52.60	53.30	10.88	10.37
NaAl(OBu-tert) ₄	7.90	7.90			56.96	56.20	10.96	10.51
KAlH(OBu-tert) ₃	9.50	9.44			49.77	50.40	10.30	9.79
KAl(OBu-tert) ₄	7.22	7.55			52.92	53.60	10.16	10.05
CsAl(OMe) ₄	10.09	9.50			16.29	16.90	4.46	4.23
CsAl(OEt) ₄	7.69	7.96			28.18	28.20	6.44	5.89
CsAl(OPr-iso) ₄	7.30	6.83			34.44	36.40	7.46	7.07
CsAlH(OBu-tert) ₃	6.83	7.12			37.84	37.90	7.78	7.36
CsAl(OBu-tert) ₄	6.04	5.98			42.46	42.50	8.01	7.99

TABLE III. Analytical Data for the Products of Partial Alcoholysis of Solutions of MAIH₄ in Ether and Tetrahydrofuran.

Composition	Solvent	Al(%)		Hydride H(%)	
		Found	Calc.	Found	Calc.
LiAlH _{1.75} (OMe) _{2.25}	Ether	25.25	25.60	1.75	1.66
LiAlH _{2.25} (OEt) _{1.75}	Ether	23.39	23.50	1.95	1.96
LiAlH _{0.72} (OPr-iso) _{3.28}	Ether	12.15	12.00	0.325	0.320
NaAlH ₂ (OMe) ₂	THF	23.67	23.70	1.75	1.83
NaAlH ₂ (OEt) ₂	THF	18.72	19.05	1.33	1.39

According to Brown [1] and Zakharkin [3], tert-butyl alcohol reacts with lithium and sodium aluminium hydrides at room temperature to release only three mol of hydrogen:



Fully substituted species are only formed in THF or diglyme solutions at reflux temperatures. KAlH₄ reacts likewise.

CsAlH₄ reacts at 20 °C with as little as 2.5 mol of tert-BuOH. The substitution of further 0.5 hydrogen atoms occurs at 140 °C, the product attaining the composition CsAlH(OBu-tert)₃. The decomposition of the complex hydride is only completed under very stringent conditions, after refluxing diglyme solutions of the reactants at 160 °C for many hours.

The smooth gas evolution curves in the case of the reactions of MAIH₄ (M = Li, Na, K, Cs) with primary and secondary alcohols and water indicate that the solvolysis follows a one-step scheme, in contrast with what has been suggested in the earlier papers [1, 3] claiming the formation of intermediates of the composition $\text{MalH}_n(\text{OR})_{4-n}$. X-ray powder photographs

of the products of partial alcoholysis (isolated after the addition of 2 mol of alcohol to 1 mol of MAIH₄) show them to be mixtures of MAIH₄ and MAI(OR)₄ (Fig. 2)*. The IR spectra of all solid "metal alkoxo-aluminium hydrides" in the region of vibrations of the alkoxy groups closely approximate those of MAI(OR)₄ (Fig. 3). The band at 1780 to 1760 cm⁻¹ observed in the spectrum of "LiAlH₂(OR)₂" is positioned very near to ν Al-H in the spectrum of LiAlH₄ (1780 cm⁻¹).

On the other hand, both X-ray and IR data evidence individuality of MAIH(OBu-tert)₃ (M = Li, Na) (Fig. 4). In particular, ν Al-H is observed at 1719 cm⁻¹ in the Li and Na derivatives**. It is worth mentioning that other branched or bulky ligands also give exceptionally stable mixed metal aluminium hydrides of the same 3:1 composition. Thus,

*Some weak reflections with no equivalent ones in NaAl(OMe)₄ or NaAlH₄ were registered only in case of "NaAlH₂(OMe)₂".

**Compounds MAIH(OBu-tert)₃ and MAI(OR)₄ will be discussed in detail in a separate communication.

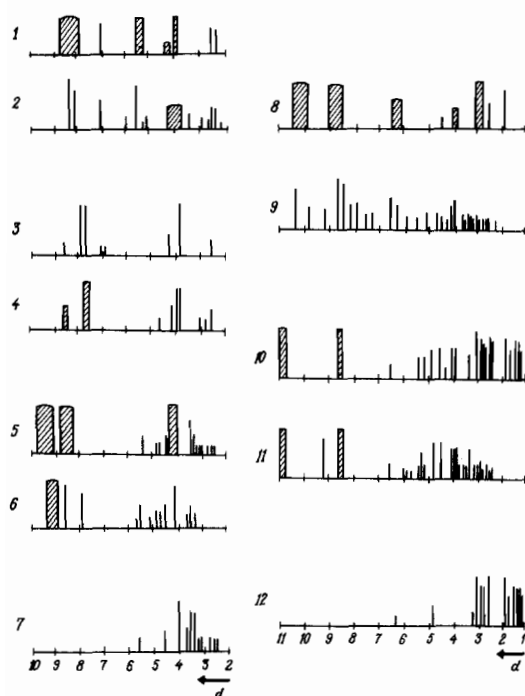


Figure 2. X-ray powder patterns for the products of partial alcoholysis of MAIH_4 : 1, " $\text{LiAlH}_2(\text{OMe})_2$ "; 2, $\text{LiAl}(\text{OME})_4$; 3, " $\text{LiAlH}_2(\text{OEt})_2$ "; 4, $\text{LiAl}(\text{OEt})_4$; 5, " $\text{LiAlH}_2(\text{OPr-iso})_2$ "; 6, $\text{LiAl}(\text{OPr-iso})_4$; 7, LiAlH_4 ; 8, " $\text{NaAlH}_2(\text{OMe})_2$ "; 9, $\text{NaAl}(\text{OMe})_4$; 10, " $\text{NaAlH}_2(\text{OEt})_2$ "; 11, $\text{NaAl}(\text{OEt})_4$; 12, NaAlH_4 .

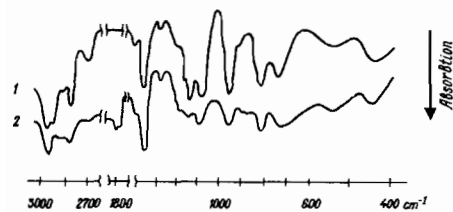


Figure 3. Comparison of the IR spectra of $\text{LiAl}(\text{OEt})_4$ (1) and " $\text{LiAlH}_2(\text{OEt})_2$ " (2).

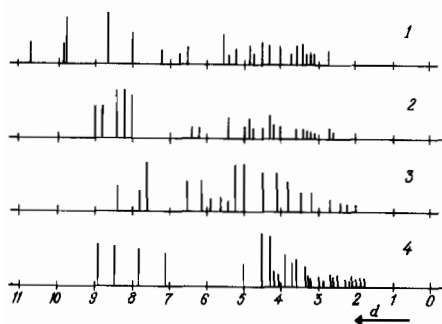


Figure 4. Comparison of the X-ray powder patterns from $\text{MAIH}(\text{OBu-tert})_3$ (1, $M = \text{Li}$ and 3, $M = \text{Na}$) and $\text{MAI}(\text{OBu-tert})_4$ (2, $M = \text{Li}$ and 4, $M = \text{Na}$).

MAIHPh_3 are the only known metal arylaluminum hydrides. Dialkylphosphine reacts with LiAlH_4 to give $\text{LiAlH}(\text{PMe}_2)_3$ as the only product [16].

NaAlH_4 and CsAlH_4 react with water in THF solutions in the stoichiometric ratio (Fig. 1, curve 1). In the case of LiAlH_4 , the hydrolysis goes to conversions depending on the solvent: in THF, hydrogen evolution ceases after 2.6 mol of H_2O per 1 mol of LiAlH_4 are added, while in ether completion of the reaction requires the addition of 7 mol of H_2O . It thus appears that an appreciable amount of dehydration of lithium hydroxoaluminates, which are known to be less stable than the corresponding sodium derivatives, occurs while the hydrolysis of LiAlH_4 is still in progress. Released water reacts with more LiAlH_4 to the effect that the ratio of H_2O to LiAlH_4 remains below 4:1 when gas evolution ceases. This agrees well with what has been observed earlier for diglyme and N-ethylmorpholine solutions [8–10].

The composition of *in situ* metal aluminates as derived from the final H_2O to MAIH_4 ratio shows that the degree of dehydration of metal tetrahydroxoaluminates under the conditions studied is only very little below that observed for aqueous solutions at high values: cf. $\text{LiAlO}_2 \cdot 0.6\text{H}_2\text{O}$ and $\text{LiAlO}_2 \cdot 0.25\text{H}_2\text{O}$ [17], $\text{NaAlO}_2 \cdot 2\text{H}_2\text{O} = \text{Na}[\text{Al}(\text{OH})_4]$ and $\text{NaAlO}_2 \cdot 1.25\text{H}_2\text{O}$ [17], respectively.

The first formed lithium aluminates can add appreciable amounts of excess water. In this work, precipitates of the composition $\text{LiAlO}_2 \cdot n\text{H}_2\text{O}$ ($n = 2, 8$ etc.) have been isolated*. Consumption of water above the stoichiometric quantity in the hydrolysis of LiAlH_4 in ether solutions may be attributed to hydration of lithium aluminate before the completion of the hydrolysis, in contrast to what occurs in THF solutions. Earlier, we have observed similar phenomena in studying hydrolysis and alcoholysis of Grignard reagents in ether solutions [15]. A sufficiently increased strength of binding water by lithium aluminates in ether compared with THF solutions depends on the heterogeneous nature of the reaction in the former solvent.

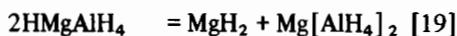
We conclude that the alcoholysis and hydrolysis of MAIH_4 gives no solid metal alkoxo(hydroxo) aluminum hydrides, with the only exception of $\text{MAIH}(\text{OBu-tert})_3$ ($M = \text{Li}, \text{Na}, \text{K}, \text{Cs}$) which undoubtedly exist as individual compounds. The fact that no precipitates are formed in the partial decomposition of complex hydrides has been claimed [1, 3] to substantiate the formation of metal alkoxohydrides, since $\text{MAI}(\text{OR})_4$ are known to be insoluble in ether and THF. We found that solubilities of freshly formed metal alkoxoaluminate precipitates

*It is clear from the gas evolution curve (Fig. 1, curve 2) that these products cannot be regarded as metal tetrahydroxoaluminates, according to Lepin' *et al.* [11].

obtained by reaction (I) may greatly exceed the equilibrium values characteristic of isolated solid compounds. In fact, precipitates formed in the methanolysis of MAIH_4 are readily soluble in THF or diglyme on addition of a negligible amount of excess methanol immediately after the completion of the reaction.

We do not, however, mean to assert that complexes of the type $\text{MAIH}_4 \cdot n\text{MAI}(\text{OR})_4$ cannot occur in solutions. The fact that NaH and LiH are soluble in solutions of $\text{Al}(\text{OEt})_3$ in ether or THF [12, 13] as well as the residual solubility of $\text{MAI}(\text{OR})_4$ or $\text{MAIO}_2 \cdot n\text{H}_2\text{O}$ in solutions of MAIH_4 argue for this possibility*. The formation of chelate complexes $\text{NaAlH}_n(\text{OR})_{4-n}$ (OR = an alkoxy radical having ethero- or amino- substituents) in solutions in aromatic hydrocarbons or ethers deserves special interest [18].

Quite a number of complexes with mixed ligands are known which, though stable in solutions, undergo partial or complete symmetrization after the removal of the solvent or decomposition of the solvates:



The role of ether solvents, we believe, is to act as electron donor species binding cations to solvates and thus enhancing the stability of the complexes.

Metal alkoxoaluminium hydrides known as reducing agents represent either solutions of the composition $\text{MAIH}_n(\text{OR})_{4-n}$ or heterogeneous mixtures [2, 13]. Their mild action may be attributed to a lower reactivity of the complexes $\text{MAIH}_4 \cdot n\text{MAI}(\text{OR})_4$ compared with pure MAIH_4 . On the other hand, it may well be that free LiAlH_4 is the only compound reactive in Brown's reduction. In fact, the same products occur in the reduction of quinones, carboxylic acids, esters, epoxides, nitro-

compounds with both LiAlH_4 and metal "alkoxoaluminium hydrides". With nitriles and amides, a deeper reduction by LiAlH_4 compared with mixed complexes may be attributed to the higher concentration of this compound in pure solutions than when in equilibrium with the complexes $\text{LiAlH}_4 \cdot n\text{LiAl}(\text{OR})_4$. $\text{LiAlH}(\text{O}i\text{Bu-tert})_3$ alone behaves specifically toward the above mentioned classes of organic compounds [2].

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*Quite recently, Ashby and co-workers [21] have reported conductance and ebullioscopic molecular weight measurements that confirm the formation of complex species in THF solutions containing LiAlH_4 and $\text{LiAl}(\text{OR})_4$, although the composition of the complexes has not been determined. It should, however, be noted that $\nu_{\text{Al-H}}$ has been found by the authors to shift from its value in LiAlH_4 in the case of $\text{LiAlH}(\text{O}i\text{Bu-tert})_3$ and $\text{LiAlH}(\text{O}i\text{CPh}_2)_3$ only, that is when the complexes exist in the solid state as well.