

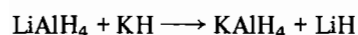
Study of the Reaction of MAlH_4 ($\text{M} = \text{Li, Na}$) and KH in an Organic Non-solvent

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Potassium tetrahydridoaluminate, KAlH_4 can be prepared [1, 2] by an exchange reaction in diglyme (diethylene glycol dimethylether):



However, our results have shown that total elimination of the solvent is impossible, and pure KAlH_4 was not obtained. In a recent work [3], pure solvent-free KAlH_4 was prepared using the above reaction, performed in a non-solvent medium such as toluene. Experimental conditions are: atmospheric pressure, temperature 100 °C, during 2 h. Some triethylaluminum is added, with a molar ratio $\text{AlEt}_3/\text{LiAlH}_4$ in the range 0.3 to 1. Yield is quantitative.

Pure KAlH_4 is obtained by washing with diethyl-ether Et_2O . This reaction is reproducible and the nature of the products does not depend on the amount of AlEt_3 nor on the adding sequence [4].

In contrast, a similar reaction between NaAlH_4 and KH leads to different products when experimental conditions are changed. The nature of the products depends on the amount of AlEt_3 and on the sequence of addition of the reactives. Experimental conditions were the same for each test discussed below: toluene medium, atmospheric pressure, temperature 110 °C during 2 h. Tests 1, 2, 3 were done using various amounts of AlEt_3 and changing the order of addition of the reactives. In tests 4 and 5 an excess of KH or NaAlH_4 was used. After reaction the product was washed with THF, which dissolves NaAlH_4 and AlEt_3 . Analysis of the insoluble part are given in Table I.

Products were characterized by chemical analysis,

X-ray spectra and D.S.C. as described elsewhere [3, 4].

Several facts have to be pointed out:

(i) Only KAlH_4 was formed when AlEt_3 was added to the $\text{NaAlH}_4 + \text{KH}$ mixture.

(ii) Only the addition compound K_2NaAlH_6 was formed when KH was added first to AlEt_3 dissolved in toluene.

(iii) An excess of AlEt_3 gave one or several non-identified compounds labelled X. They showed a diffuse X-ray pattern in addition to the lines of KAlH_4 .

(iv) An initial excess of KH did not react.

(v) An initial excess of NaAlH_4 transformed to Na_3AlH_6 , found mixed with KAlH_4 .

Discussion

The reactions reported are usually used to obtain hexahydridoaluminates as addition products:



In fact, this reaction is complex, as indicated by Table I and previous results [5]. The following seems to be clear:

(i) No reaction occurs if AlEt_3 is not used.

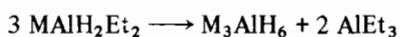
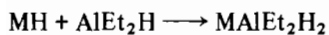
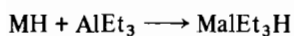
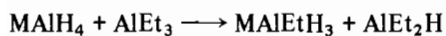
(ii) Reaction between an alkaline tetrahydridoaluminate MAlH_4 and the corresponding hydride always gives the addition compound M_3AlH_6 . However an excess of MAlH_4 is found in the product even if the molar ratio $\text{MAlH}_4/\text{MH} = 2$ is used.

(iii) Reaction MAlH_4 and $\text{M}'\text{H}$ either give the exchange hydride $\text{M}'\text{AlH}_4$ or the addition hydride $\text{MM}'_2\text{AlH}_6$. Exchange is the only reaction observed when M and M' cations are very different, such as Li and K . Moreover this reaction does not depend on the initial molar ratio. On the contrary, if M and M' are closely related, such as Na and K , a slight modification of the experimental conditions greatly affects the resulting products.

The role of AlEt_3 in these reactions is not clearly understood. However it accounts for the dissolution of the MH hydride, with reactions of the type:

TABLE I. Analysis of the Insoluble Part

Test no.	Molar ratio			Reactives	Products
	NaAlH_4	KH	AlEt_3		
1	1	1	0.3	$\text{NaAlH}_4, \text{KH} + \text{AlEt}_3$	KAlH_4
2	1	1	0.3	$\text{AlEt}_3 + \text{KH} + \text{NaAlH}_4$	K_2NaAlH_6
3	1	1	1	$\text{AlEt}_3 + \text{NaAlH}_4 + \text{KH}$	$\text{KAlH}_4 + \text{X}$
4	1	2	0.3	$\text{AlEt}_3 + \text{NaAlH}_4 + \text{KH}$	$\text{KAlH}_4 + \text{KH}$
5	2	1	0.3	$\text{AlEt}_3 + \text{NaAlH}_4 + \text{KH}$	$\text{KAlH}_4 + \text{Na}_3\text{AlH}_6$



The formation of these Ziegler or Wittig complexes [6-9] may also be dependent on the alkaline cation. Thus a preferential path to the final product may exist.

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