Study of the Reaction of $MAlH_4$ (M = 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):

$$LiAlH_4 + KH \longrightarrow KAlH_4 + LiH$$

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 $AlEt_3/LiAlH_4$ in the range 0.3 to 1. Yield is quantitative.

Pure $KAlH_4$ is obtained by washing with diethylether 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 $NaAlH_4$ + 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:

$$MAlH_4 + 2\,MH \longrightarrow M_3AlH_6$$

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 $MAlH_4/MH = 2$ is used.

(iii) Reaction $MAlH_4$ and $M'H$ either give the exchange hydride $M'AlH_4$ or the addition hydride MM'_2AlH_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	$NaAlH_4$, KH + $AlEt_3$	$KAlH_4$
2	1	1	0.3	$AlEt_3$ + KH + $NaAlH_4$	K_2NaAlH_6
3	1	1	1	$AlEt_3$ + $NaAlH_4$ + KH	$KAlH_4$ + X
4	1	2	0.3	$AlEt_3$ + $NaAlH_4$ + KH	$KAlH_4$ + KH
5	2	1	0.3	$AlEt_3$ + $NaAlH_4$ + KH	$KAlH_4$ + Na_3AlH_6

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$MAlH_4 + AlEt_3 \longrightarrow MAlEtH_3 + AlEt_2H$

$MH + AlEt_3 \longrightarrow MalEt_3H$

$MH + AlEt_2H \longrightarrow MAlEt_2H_2$

$3\ MAlH_2Et_2 \longrightarrow M_3AlH_6 + 2\ AlEt_3$

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.

References

1 L. I. Zakharkin and V. V. Gavrilenko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1146 (1962).
2 J. A. Dilts and E. C. Ashby, *Inorg. Chem., 11*, 6, 1230 (1972).
3 J. El Hajri, *These*, IDTC 1.86-02, I.N.S.A. Lyon, France, 1986.
4 J. P. Bastide, P. Claudy, J. M.Létoffé and J. El Hajri, *Rev. Chim. Miner., 2*, (1987), in press.
5 P. Claudy, B. Bonnetot, J. P. Bastide and J. M. Létoffé, *Mater. Res. Bull., 17*, 1499 (1982).
6 G. E. Coates, M. L. H. Green and K. Wade, 'Organometallic Compounds', Vol. 1, Methuen, London, 1967, p. 313.
7 L. I. Zakharkin and V. V. Gavrilenko, *Zh. Obsch. Khim., 32*, 3, 689 (1962).
8 A. N. Nesmeyanov and R. A. Sokolik, 'The Organic Compounds of Boron, Aluminum, Gallium, Indium and Thallium', North Holland, Amsterdam, 1967, p. 437.
9 K. Ziegler, in H. Zeiss (ed.), 'Organo-aluminum Compounds in Organometallic Chemistry', A.C.S. Monograph Series, New York, 1960, p. 194.