

PREPARATION OF ALKALI-METAL ALUMINOHYDRIDES
AND GALLOHYDRIDES

S. I. Bakum and S. F. Ershko

UDC 546.623'33'11:546.681'32'11

At present there is no convenient method of preparing MAH_4 or $MGaH_4$ ($M = K, Rb, Cs$). The main disadvantage of direct synthesis of these compounds from their elements [1-4] is that in the case of incompleteness of the reaction, leaching of the end product from the reaction mass is accompanied to some extent by decomposition of the solvent by unreacted alkali metal. Splitting up of the solvent can be avoided either by replacing of the alkali metal by its hydride [5] (but this is realistic only in the preparation of $KAlH_4$), or by preparing the MAH_4 by a more universal method [6]:



However, this method requires an autoclave.

In optimal conditions, exchange reaction in an organic solvent often gives very pure products. Thus, reaction of $LiGaH_4$ with $MA(C_2H_5)_4$, where $M = Rb, Cs$, in ether at $-10^\circ C$ gives $MGaH_4$ [7], reaction of $LiAlH_4$ with metals in ether gives MAH_4 ($M = K, Rb, Cs$) [8], and reaction of $LiAlH_4$ or $LiGaH_4$ with KH in diethylene glycol dimethyl ether [diglyme] [9, 10], ether, or THF [11] gives $KAlH_4$ and $KGaH_4$.

An attempt to obtain $RbAlH_4$ by energetic stirring of a mixture of $RbCl$ and $NaAlH_4$ in diglyme (DG) with heating did not succeed [10], although, in our opinion, this reaction could be a convenient method of preparing MEH_4 . The very low solubility of MCl in the solvents used for MEH_4 might give a fairly high reaction rate while having practically no influence on the purity of the product. The aim of our present work was to study the reactions of $NaAlH_4$ and $NaGaH_4$ with MCl ($M = K, Rb, Cs$) in diglyme and THF.

As seen from Table 1, in THF the reactions of $NaAlH_4$ and $NaGaH_4$ with MCl ($M = Rb, Cs$) (with a 40-50% excess of MCl) occur quantitatively in about 6 h. In diglyme in the same conditions the reactions also occur very smoothly, but the yield of MEH_4 does not exceed 85%, and increasing the reaction time and the excess of MCl does not appreciably increase the yield.

When $NaAlH_4$ or $NaGaH_4$ react with KCl in diglyme or THF, a yield of about 98% is achieved (see Table 1) only in the case of the reaction system KCl - $NaAlH_4$ -THF, apparently owing to the fact that the solubility of $KAlH_4$ in THF is lower than in the systems $KAlH_4$ -diglyme, $KGaH_4$ -diglyme, and $KGaH_4$ -THF.

The use of THF also permits easy separation of the precipitate of MEH_4 from the excess $NaEH_4$ in solution; for this purpose the precipitate was washed after decanting the THF solution and then treated with diglyme. The MEH_4 was then separated from the diglyme solution by evaporation in vacuum. The crystalline aluminohydrides and gallohydrides of potassium, rubidium, and cesium so obtained were 98.5-99.7% pure.

When MEH_4 is obtained directly in diglyme, the solution unavoidably contains a certain amount of unreacted $NaEH_4$; to separate this, MEH_4 must first be precipitated with an inert organic solvent - but this may lead to contamination of the product owing to possible coprecipitation of $NaEH_4$. Direct crystallization of MEH_4 from such solutions by evaporation also leads to contamination of the product with the sodium salt. Similarly, evaporation of $NaGaH_4$ solutions in THF in the presence of small amounts of $LiGaH_4$ gives a product containing an admixture of 0.1-1.0% of Li [11].

On the basis of previously published data [11] and our present work, we can recommend that aluminohydrides and gallohydrides of alkali metals should be prepared by means of the

N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 10, pp. 2183-2185, October, 1981. Original article submitted April 18, 1980.

TABLE 1. Results of Experiments to Obtain MEH₄

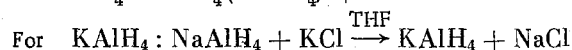
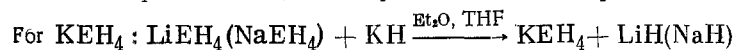
Reagents	Quantity, grams	Excess of MCl, %	Solvent	Volume of solution, ml	Conversion, %, in			Percentage of Na in final product*
					1 h	3 h	6 h	
KCl/NaAlH ₄	25,7/13,8	35	THF	200	79,2	87,0	98,2	None
KCl/NaAlH ₄	27,1/4,9	42	DG	100	34,6	40,8	52,6	3,5
RbCl/NaAlH ₄	62,8/18,7	50	THF	200	69,4	90,6	100	None
RbCl/NaAlH ₄	26,6/8,7	36,5	DG	150	54,6	71,3	83,5	1,00
CsCl/NaAlH ₄	88,0/20,4	38	THF	200	41,7	74,0	100	None
CsCl/NaAlH ₄	22,0/5,0	41	DG	170	83	85	85	0,51
KCl/NaGaH ₄	6,0/5,4	44,5	THF	100	22	41	58	None
KCl/NaGaH ₄	5,85/5,4	40,7	DG	100	66	66	68	ND
RbCl/NaGaH ₄	57,6/30,5	51,0	THF	350	62,6	87,1	100 †	None
RbCl/NaGaH ₄	46,4/27,0	37,5	DG	300	67,0	72,0	72,8	ND
CsCl/NaGaH ₄	73,4/28,4	48	THF	400	51,7	91,4	100 ‡	None
CsCl/NaGaH ₄	11,7/4,9	37	DG	150	54,0	79,0	79,5	ND

* ND = not determined.

† Reaction time 3.5 h.

‡ Reaction time 4.5 h.

following reactions:



EXPERIMENTAL

The experiments were performed at about 20°C; we used a solution of NaAlH₄ or NaGaH₄ in THF or diglyme and a slight superstoichiometric excess of finely powdered (≤0.2 mm) pre-melted MCl of analytical reagent grade. The degree of conversion of NaEH₄ to MEH₄ was estimated by means of the Na content of periodically withdrawn samples of the solution. The experimental results are listed in Table 1.

CONCLUSIONS

Pure aluminohydrides and gallohydrides of potassium, rubidium, and cesium can be obtained with high yields by means of the reactions of NaEH₄ (E = Al, Ga) with the appropriate alkali-metal chloride in THF.

LITERATURE CITED

1. H. Clasen, *Angew. Chem.*, **73**, 322 (1961).
2. T. N. Dymova, M. S. Selivokhina, N. G. Eliseeva, and N. T. Osipenko, *Inventor's Certificate No. 259,060* (1963); *Byull. Izobr.*, No. 3, 208 (1974).
3. V. V. Gavrilenko, Yu. N. Karaksin, and L. I. Zakharkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1838 (1971).
4. T. N. Dymova and Yu. M. Dergachev, *Inventor's Certificate No. 364,562* (1971); *Byull. Izobr.*, No. 5, 66 (1973).
5. L. I. Zakharkin and V. V. Gavrilenko, *Dokl. Akad. Nauk SSSR*, **145**, 793 (1962).
6. S. I. Bakum, U. Mirsaidov, S. F. Ereshko, and T. N. Dymova, *Inventor's Certificate No. 521,221* (1973); *Byull. Izobr.* No. 26, 68 (1976).
7. L. I. Zakharkin, V. V. Gavrilenko, and Yu. N. Karaksin, *Inorg. Metal.-Org. Chem.*, **1** (1), 37 (1971).
8. L. I. Zakharkin and V. V. Gavrilenko, *Zh. Neorg. Khim.*, **11**, 977 (1966).
9. L. I. Zakharkin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1146 (1962).
10. L. I. Zakharkin, V. V. Gavrilenko, and Yu. N. Karaksin, *Zh. Obshch. Khim.*, **41**, 2689 (1971).
11. S. I. Bakum and S. F. Ereshko, *Zh. Neorg. Khim.*, **22**, 655 (1977).