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L. I. Zakharkin and V. V. Gavrilenko

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Abstract

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L. I. Zakharkin and V. V. Gavrilenko

ON THE DIRECT SYNTHESIS OF SODIUM AND POTASSIUM ALUMINUM HYDRIDES FROM THE ELEMENTS

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Alkali-metal aluminum hydrides, among which lithium aluminum hydride has been the most widely studied, are effective reducing agents in organic and inorganic chemistry. The usual method for their preparation consists in treating an aluminum halide with the hydride of the corresponding metal according to the scheme:

$$4\mathrm{MeH} + \mathrm{AlX_3} \rightarrow \mathrm{MeAlH_4} + 3\mathrm{MeX_3} \quad (\mathrm{Me} = \mathrm{Li},\ \mathrm{Na},\ \mathrm{K};\ \mathrm{X} = \mathrm{Cl},\ \mathrm{Br}).$$

At present this method is used in the manufacture of lithium aluminum hydride. Recently we developed, according to this scheme, a simple method for obtaining sodium and potassium aluminum hydrides from aluminum chloride ([1]). Despite the high yields of aluminum hydrides and the simplicity of the process, this method has a drawback, namely the need to work with a large amount of metal hydride (4 moles per 1 mole of aluminum hydride).

Clasen recently reported ([2]) on the direct synthesis of alkali-metal aluminum hydrides from aluminum, metal hydride, and hydrogen in a tetrahydrofuran medium:

$$\mathrm{Al} + \mathrm{MeH} + 1.5\mathrm{H_2} \rightarrow \mathrm{MeAlH_4} \quad (\mathrm{Me} = \mathrm{Li},\ \mathrm{Na},\ \mathrm{K}).$$

As Clasen indicates, metals may be taken instead of the metal hydrides. This new method of synthesizing lithium, sodium, and potassium aluminum hydrides opens up great possibilities for the industrial production of these important compounds, and especially of the cheapest of them—sodium aluminum hydride.

A drawback of the process developed by Clasen is the use of tetrahydrofuran as the reaction medium, since under the conditions of direct synthesis (temperature 150°) tetrahydrofuran is to a considerable extent cleaved by the aluminum hydride; this lowers the yield of aluminum hydride and creates considerable difficulties in isolating it in pure form. With an increase in temperature, the process of tetrahydrofuran cleavage intensifies and may assume an explosive character.

In the present work we report our studies on the direct synthesis of sodium and potassium aluminum hydrides. We found that sodium and potassium aluminum hydrides are readily formed from the elements when the process is carried out in hydrocarbon media (aliphatic hydrocarbons: heptane, isooctane, purified benzine; aromatic hydrocarbons: benzene, toluene, xylenes):

$$\mathrm{Al} + \mathrm{Na} + 2\mathrm{H_2} \rightarrow \mathrm{NaAlH_4};$$

$$\mathrm{Al} + \mathrm{K} + 2\mathrm{H_2} \rightarrow \mathrm{KAlH_4}.$$

The synthesis proceeds equally readily both with the use of sodium and potassium and with ready-made sodium and potassium hydrides; however, it is more convenient to work with the metals. When the reaction is carried out in hydrocarbon media, the drawbacks of the method of direct synthesis of sodium and potassium aluminum hydrides in tetrahydrofuran medium are eliminated. In the case of using the metal, the reaction proceeds in two stages: first the metal hydride is formed, which then enters into reaction. It should be assumed that, under the synthesis conditions, from aluminum there is formed—

aluminum hydride, $\mathrm{AlH_3}$, is formed, which is then stabilized by combining with the hydride of an alkali metal. It is not excluded, of course, that aluminum with hydrogen gives some other intermediate aluminum hydride, which is stabilized by combination with the alkali-metal hydride and, upon further hydrogenation, forms the alkali-metal alumohydride. The preparation of sodium alumohydride from the elements may be represented as follows:

$$\mathrm{Na} + 0.5\mathrm{H_2} \rightarrow \mathrm{NaH};$$

$$\mathrm{Al} + 1.5\mathrm{H_2} \rightarrow \mathrm{AlH_3};$$

$$\mathrm{NaH} + \mathrm{AlH_3} \rightarrow \mathrm{NaAlH_4}.$$

The reaction proceeds at a temperature of 120–200° and a hydrogen pressure above 30 atm; usually we worked at 140–160° and a pressure of 100–150 atm. The aluminum for the synthesis must be taken in a finely dispersed state and preliminarily activated (mechanically in vibratory or ball mills, or chemically—

with the aid of alkyl halides, organometallic compounds, etc.). It turned out that aluminum containing about 0.1% titanium also possesses high activity.

In studying the process of direct synthesis, we found that organoaluminum compounds—aluminum trialkyls and dialkylaluminum hydrides—greatly increase the rate of this reaction. It was established that in the presence of triethylaluminum (taken in an amount of 5%) the reaction proceeds practically to completion within 5-6 hr, whereas in the absence of triethylaluminum the reaction in 10 hr proceeds only approximately 60%. The catalytic role of organoaluminum compounds in the direct synthesis of sodium alumohydride apparently consists in converting sodium hydride into a soluble state in the form of a complex with the organoaluminum compound, for example, $NaAl(C_2H_5)_3H$ or $NaAl(C_2H_5)_2H_2$, thereby facilitating the interaction of sodium hydride with the intermediately formed aluminum hydride. Indeed, it was found that the reaction between aluminum hydride and sodium diethylaluminum dihydride proceeds very rapidly with formation of sodium alumohydride:

$$AlH_3 + NaAl(C_2H_5)_2H_2 \rightarrow NaAlH_4 + (C_2H_5)_2AlH.$$

The interaction of aluminum hydride with potassium dimethylaluminum dihydride proceeds analogously:

$$AlH_3 + KAl(CH_3)_2H_2 \rightarrow KAlH_4 + (CH_3)_2AlH.$$

It was found that the yield of sodium alumohydride depends on the ratio of aluminum and sodium taken into the reaction. It turned out that, at an aluminum-to-sodium ratio of 1:1, the yield of alumohydride did not exceed 60-65%, although the amount of hydrogen absorbed was greater than would follow from the amount of sodium alumohydride obtained. It was suggested that part of the sodium alumohydride formed is bound in the course of synthesis with sodium hydride, giving a more complex hydride, for example Na_3AlH_6. Indeed, we found that after heating 1 mole of sodium alumohydride with 2 moles of sodium hydride at 160° in heptane and under hydrogen pressure, sodium alumohydride cannot be extracted from the reaction mass with tetrahydrofuran; it is somehow bound with sodium hydride. Because of the insolubility of the reaction product in any suitable solvents, we were unable to isolate it in pure form and determine its composition. It may be assumed that sodium hydride reacts with sodium alumohydride according to the scheme:

$$NaAlH_4 + 2NaH \rightarrow Na_3AlH_6.$$

After treatment of the product of this reaction with 2 moles of diisobutylaluminum hydride in ether, a solid residue was obtained that readily dissolved in in tetrahydrofuran and proved to be sodium aluminum hydride. From the ether solution sodium diisobutylaluminum dihydride was isolated. This result indicates that, on treatment with diisobutylaluminum hydride, the reaction proceeds according to the scheme:

$$Na_3AlH_6 + 2\ (\text{iso-}C_4H_9)_2AlH \rightarrow NaAlH_4 + 2NaAl(\text{iso-}C_4H_9)_2H_2.$$

In a similar way, the presence of sodium aluminum hydride bound to sodium hydride was demonstrated in an experiment on direct synthesis. The reaction product from the direct synthesis of sodium aluminum hydride was extracted with tetrahydrofuran until the sodium aluminum hydride had been completely removed, and the residue was treated with diisobutylaluminum hydride. After this, extraction with tetrahydrofuran gave an additional quantity of sodium aluminum hydride.

An increase, relative to stoichiometry, in the amount of aluminum in the direct synthesis promotes an increase in the yield of sodium aluminum hydride. In the presence of an excess of aluminum the formation of a by-product is suppressed. Thus, at a sodium-to-aluminum ratio of 1 : 1.5, sodium aluminum hydride was obtained in 86% yield, and at a ratio of 1 : 2—in 93% yield.

Sodium aluminum hydride from aluminum, sodium, and hydrogen. a) 40.5 g of aluminum, ground in a vibratory mill for 10 hours in heptane medium (80 ml), 23 g of sodium, 5 g of triethylaluminum, and 400 ml of heptane were charged into a rotating autoclave (2 l). Metal balls (1.5 kg) of 10 mm diameter were also charged into the autoclave. The hydrogen pressure was 120 atm; the autoclave was heated while rotating to 150°. At this temperature, absorption of hydrogen was completed within 6 hours. The reaction product—a gray, readily settling suspension—was filtered under nitrogen, and the solid precipitate was washed with a small amount of ether. Solvent residues were removed in vacuo. The pyrophoric precipitate was transferred under nitrogen to a liter flask and treated with tetrahydrofuran (500 ml). After centrifugation and removal of the solvent by distillation, 46.5 g (86% of theory) of sodium aluminum hydride was obtained.

Found, %: Al 49.89; 49.90

$NaAlH_4$. Calculated, %: Al 49.96

b) Analogously, from 27 g of aluminum and 23 g of sodium, 33.5 g (62% of theory) of sodium aluminum hydride was obtained. c) Analogously, from 54 g of aluminum and 23 g of sodium in benzene medium, 50.2 g (93% of theory) of sodium aluminum hydride was obtained.

Sodium aluminum hydride from aluminum, sodium hydride, and hydrogen. 27 g of aluminum and 24 g of sodium hydride, ground together in a vibratory mill in hexane medium (80 l), were charged into an autoclave; 5 g of triethylaluminum, 400 ml of hexane, and 130 atm of dry and pure hydrogen were added there. The autoclave was heated to 150–160°. Absorption of hydrogen continued for 5 hours. After the usual work-up, 34 g (63% of theory) of sodium aluminum hydride was obtained. Analogously, but without triethylaluminum, over a reaction time of 10 hours, 27 g (50% of theory) of sodium aluminum hydride was obtained.

Potassium aluminum hydride from aluminum, potassium hydride, and hydrogen. 27 g of aluminum and 40 g of potassium hydride, ground together in a vibratory mill in heptane medium, were charged into an autoclave together with 8 g of diisobutylaluminum hydride and 300 ml of heptane. Hydrogen pressure was 120 atm. The autoclave was heated to 140–150° for 6 hours, until hydrogen absorption ceased. From the filtered and dried reaction product, 52.6 g (75% of theory) of potassium aluminum hydride was extracted with diglyme (500 ml). The diglyme was removed by distillation in vacuo.

Found, %: Al 38.38; 38.40
$KAlH_4$. Calculated, %: Al 38.48

Sodium aluminum hydride from aluminum containing 0.1% titanium, sodium, and hydrogen. 40 g of ground

···aluminum containing 0.1% titanium, 23 g of sodium, 6 g of triethylaluminum, and 300 ml of heptane were charged into an autoclave with balls. The hydrogen pressure was 130 atm. The autoclave was heated at 140–160° for 8 h. After the usual work-up, 43.3 g (80% of theory) of sodium alumohydride were obtained. Similarly, but without triethylaluminum, 35 g (65% of theory) of sodium alumohydride were obtained.

Reaction of sodium diethylaluminum dihydride with aluminum hydride. In a nitrogen atmosphere, to an ether solution (25 ml) containing 1.5 g of aluminum hydride was added an ether solution of sodium diethylaluminum dihydride (5.5 g). A precipitate of sodium alumohydride immediately formed. After filtration and drying, 2.5 g of sodium alumohydride were obtained.

Reaction of potassium dimethylaluminum dihydride with aluminum hydride. Similarly, from 1.5 g of aluminum hydride and 5 g of potassium dimethylaluminum dihydride in tetrahydrofuran, 3.3 g of potassium alumohydride were obtained.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.