Direct synthesis of dialkoxyaluminum hydrides from aluminum, hydrogen, and alcohols in the presence of trimethylamine and study of their thermal decomposition

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A procedure for the direct synthesis of dialkoxyaluminum hydrides $(RO)_2AlH$ (R = Pr^i, Bu^t, and Et) from aluminum metal and corresponding alcohols in organic solvents (hydrocarbons, ethers) in the presence of catalytic amounts of tertiary amines (NMe_3, NEt_3) at a pressure of H_2 of 80 to 350 atm and at a temperature of 100 to 160 °C has been developed. A possible mechanism for the reaction was proposed. Thermal decomposition of $(RO)_2AlH$ was studied by differential thermogravimetric analysis (DTGA), ^{27}Al NMR spectroscopy, IR spectroscopy, and GLC.

Key words: dialkoxyaluminum hydrides, synthesis.

Hydride compounds of aluminum of the $MAlH_4$, AlH_3, AlH_2Cl, and $AlHCl_2$ type are widely used as efficient reducing agents in the reactions of fine organic and inorganic synthesis.[1] Methods for the preparation of these compounds are based on the interaction between the hydrides of alkaline metals and aluminum chloride in ether media[2] or on the direct synthesis from the elements: Na, K, Al, and H_2.[3–6]

The alkoxy derivatives of lithium[7] and sodium[8] alumohydrides of the $MAl(OR)_3H$ type are also mild selective reducing agents. The alkoxyhydride derivatives of aluminum $HAl(OR)_2$ and H_2AlOR have been less studied as specific reducing agents.[9] Additionally, they could be applied as cocatalysts in the processes of coordination polymerization of olefins and dienes, as well as in microelectronics.

The methods for the synthesis of aluminum alkoxyhydrides known so far are based on the interaction of AlH_3 with alcohols.[10–12]

In this work, we suggest a novel procedure for obtaining dialkylaluminum hydrides, *i.e.*, direct synthesis; it is based on the interaction of 1 g-atom (or more) of Al with 2 moles of alcohol in hydrocarbon or ether medium at a hydrogen pressure of 80—350 atm and at 100—160 °C. Tertiary amines (Me_3N or Et_3N) are catalysts in this reaction. Aluminum powder containing up to 0.3% of Ti is used in the reaction.[13] Other Al powders containing Fe, Cu, and Mn can also be used for this purpose. High purity aluminum reacts reluctantly.

We believe that the process in question proceeds in two stages. First, the known reaction between aluminum and alcohols[14] with the formation of $Al(OR)_3$ proceeds comparatively fast

$$Al + 3\ ROH \longrightarrow Al(OR)_3 + 1.5\ H_2$$

When the whole amount of alcohol is consumed, another, slower reaction begins. It is a reaction of direct synthesis of aluminum hydride from Al and H_2; aluminum hydride is stabilized as fairly stable $AlH_3 \cdot NR_3$ complexes with tertiary amines:

$$Al + 1.5\ H_2 \xrightarrow{NR_3} AlH_3 \cdot NR_3$$

As a result of a continuous alkoxyhydride exchange (disproportionation), thermodynamically stable hydrides $(RO)_2AlH$ are formed; they undergo oligomerization through alkoxide and hydride bridge bonds and, as a consequence, become coordinately saturated, which leads to the exclusion of amine molecules from the coordination sphere of Al:

$$2\ Al(OR)_3 + AlH_3 \cdot NR_3 \longrightarrow 3\ HAl(OR)_2 + NR_3$$

The overall equation of $HAl(OR)_2$ synthesis can be written as follows:

$$Al + 2\ ROH \xrightarrow{NR_3} HAl(OR)_2 + 0.5\ H\ \cdot \qquad (1)$$

Thus, this synthesis is accompanied by hydrogen evolution. Therefore, control of the volumes of the gas

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and liquid phases and of the amounts of Al and alcohol charged into the reactor makes it possible to conduct this reaction without additional pumping of hydrogen into the autoclave provided that the final pressure in the system is not decreased below 80—100 atm. It should be noted that in the first stage of the reaction of Al with alcohols the metal surface is activated for the further reaction with hydrogen. Adding a freshly prepared aluminum isopropoxide in toluene and Me_3N to aluminum and pumping hydrogen into the autoclave to a pressure of 200 atm has almost no effect at 140 °C, and the reaction only begins after the induction period of ~48 h. Among amines, which can be used in this reaction, trimethylamine exhibits the highest activity. Because of its higher volatility, trimethylamine can be easily removed from the reaction medium, freezed out at low temperatures, and repeatedly used in further syntheses of $HAl(OR)_2$.

We synthesized compounds $HAl(OR)_2$ using EtOH, Bu^nOH, Pr^iOH, and Bu^tOH. However, the derivatives of the first two alcohols are almost insoluble in organic media[12] because of their polymeric nature, and therefore it is impossible to separate them from the Al slime and other admixtures. At the same time, $HAl(OPr^i)_2$ and $HAl(OBu^t)_2$ are soluble in hydrocarbon and ether media. They can be easily separated from solid admixtures by filtering under a dry inert atmosphere and isolated as individual compounds by vacuum distillation or crystallization after removing the solvent. It should be noted that we failed to obtain dihydride H_2AlOR complexes using this procedure, because they appeared to be unstable under the temperature conditions of this reaction (see below). The IR spectra of the obtained compounds $HAl(OPr^i)_2$ and $HAl(OBu^t)_2$ corresponded to those reported in Ref. 12.

The possibility of direct synthesis of alkoxyhydride Al derivatives depends first of all on their thermal stability under the conditions used. At present, thermal decomposition of aluminum trialkoxides $Al(OR)_3$ (R = Me, Et, Pr^i, and Bu^t) at different temperatures has been studied in detail by kinetic methods.[15] This thermolysis is followed by the formation of the aluminum oxide and various organic compounds such as alkanes, alkenes, alcohols, aldehydes, and esters. The complete thermal decomposition of $Al(OR)_3$ to Al_2O_3 is temperature and time dependent and occurs in the 200 to 320, 200 to 265, and 166 to 225 °C temperature intervals for R = Et, Pr^i; and Bu^t, respectively (the decomposition begins at the temperature first mentioned and is brought to completion at its second value).[15] Thermolysis of aluminum alkoxyhydrides $HAl(OR)_2$ and H_2AlOR has not been studied up to now, though the investigation of its character is of unquestionable interest for elucidating the peculiarities of the direct synthesis of dialkoxyaluminum hydrides.

According to the following equation, heating H_2AlOR from 20 to 400 °C results in Al_2O_3, Al, RH, and H_2:

$$3\,H_2AlOR \longrightarrow Al_2O_3 + Al + 1.5\,H_2 + 3\,RH \qquad (2)$$

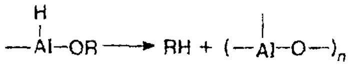
$$R = Pr^i,\ Bu^t$$

Thermal decomposition of $HAl(OR)_2$ is followed by the formation of Al_2O_3 (no Al is formed), RH, H_2, olefins, and gaseous and liquid oxoproducts and is described by the equation

$$\begin{array}{l} 2\,HAl(OR)_2 \longrightarrow Al_2O_3 + 2\,RH + 2\,[R^{\bullet} + {}^{\bullet}OR] \qquad (3) \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad [H_2,\ \mathit{olefins},\ \mathit{oxoproducts}] \end{array}$$

$$R = Pr^i,\ Bu^t$$

Most of the gaseous products correspond to the molecular type of decomposition. For instance, the RH formation can be represented as follows:



$$\overset{H}{\overset{|}{-Al}}-OR \longrightarrow RH + (-\overset{|}{Al}-O-)_n$$

GLC analysis showed that the gaseous products of thermal decomposition of $HAl(OPr^i)_2$ contain propane (85—90%), propylene (1—2%), H_2 (1—2%), methane (3—4%), and ethane (3—4%). Composition of oxoproducts condensed in the trap at −80 °C was not studied in detail.

The study of the character and peculiarities of thermal effects that occur in the course of the thermal decomposition of alkoxyhydride compounds of aluminum was of particular interest. For this purpose, differential thermogravimetric analysis (DTGA) of complexes H_2AlOBu^t, $HAl(OBu^t)_2$, H_2AlOPr^i, and $HAl(OPr^i)_2$ was performed in an inert atmosphere in the 20 to 400 °C temperature interval. The dihydride complexes analyzed were obtained by the procedure reported in Ref. 12.

A small endothermic effect associated with the melt is observed near 70—80 °C when heating H_2AlOBu^t (*cf.* Ref. 12: m.p. 42—50 °C). Then a considerable exothermic effect followed by gas evolution and loss of the main mass is observed at 110—120 °C. The measured mass loss after heating the specimen to 400 °C was 68%, while that calculated using Eq. (2) was 57.8%. Compound $HAl(OBu^t)_2$ exhibits an endothermic effect associated with its melting at 50—55 °C (*cf.* Ref. 12: m.p. 52—57 °C), and a considerable exothermic effect with loss of the main mass is observed at 185—198 °C. The mass loss measured was equal to 73.7%, and that calculated using Eq. (3) was equal to 70.6%. Compound H_2AlOPr^i exhibits a small prolonged endothermic effect at 50—80 °C (which is likely due to elimination of solvated THF, see Ref. 12), a second endothermic effect associated with melting (*cf.* Ref. 12: m.p. 145 °C) at 140—160 °C, and a large exothermic effect at 172—227 °C. The mass loss measured and calculated using Eq. (2) was equal to 59.2% and 51.1%, respectively. Compound $HAl(OPr^i)_2$ exhibits an endothermic effect at 70 °C likely associated with its melting, a small endothermic effect at 115—156 °C (an unknown phase transformation), and a large exothermic effect at 220—230 °C followed by evolution of gaseous products. The measured mass loss was 68.5% (that calculated using Eq. (3) was equal to 65%).

A larger (as compared to the theoretical values) mass loss in these processes is likely due to a partial entrainment of solid species from the reaction vessel as dust.

The ^{27}Al NMR spectra of compounds H_2AlOPr^i, $HAl(OPr^i)_2$, and $Al(OPr^i)_3$ obtained from solutions of AlH_3 in THF under the action of 1, 2, and 3 moles of Pr^iOH, respectively, were recorded in THF. Signals with chemical shifts at δ 108, 56, and 8 are observed in the ^{27}Al NMR spectrum of H_2AlOPr^i. The signal at δ 108 indicates that AlH_3 is present in solution or, in other words, that the following equilibrium can be established for this compound:

$$2\,H_2AlOPr^i \rightleftharpoons AlH_3 + HAl(OPr^i)_2$$

The signals with chemical shifts at δ 108 and 56 correspond to the Al atoms with the coordination number (CN) 4, and that with chemical shift at δ 8 corresponds to the Al atoms with CN 6.

The ^{27}Al NMR spectrum of $HAl(OPr^i)_2$ contains a doublet at δ 52 and 39 and a rather intense signal with chemical shift at δ 4 from the Al atoms with the CNs equal to 4, 5, and 6, respectively. The signal in the region of δ 100—115, characteristic of AlH_3, was not observed. The signal at δ 66 with a shoulder at δ 47 in the spectrum of $Al(OPr^i)_3$ corresponds to the Al atoms with CN 4.

Thus, the Al atoms in the dissolved species of the hydride compound $HAl(OPr^i)_2$ have CNs 4 and 6, whereas the Al atoms in the dissolved species of $Al(OPr^i)_3$ have CN 4. This is likely associated with the additional coordination of the Al atom with traces of THF in the case of $HAl(OPr^i)_2$ or with the spatial coordination with participation of the hydride bridges in the octahedral fragments of the associates of this compound.

The data on thermal stability of compounds $H_nAl(OPr^i)_{3-n}$ obtained by the DTGA method and those of the ^{27}Al NMR spectra of the isopropoxy derivatives of these compounds make it possible to explain the possibility of direct synthesis of $HAl(OPr^i)_2$ and $HAl(OBu^t)_2$ from Al and the corresponding alcohols. Thermal decomposition of these compounds, characterized by exothermic DTGA effects, begins at temperatures above 220 and 185 °C, respectively, whereas their direct synthesis is performed at 100—160 °C. These parameters are critical parameters for $HAl(OBu^t)_2$; for this reason, this compound is synthesized under milder conditions, which causes the duration of the synthesis to increase and the yield of the products to decrease. The dihydride compounds H_2AlOR are not formed at all under conditions of direct synthesis because of their disproportionation to $HAl(OR)_2$ and thermally unstable hydride AlH_3. The H_2AlOR specimens obtained from AlH_3 and Pr^iOH (or Bu^tOH)[12] appeared to have low thermal stability.

Thus, only dialkoxyaluminum hydrides $HAl(OR)_2$ can be obtained under the conditions that we found for the direct synthesis.

Experimental

The ^{27}Al NMR spectra were recorded on a Bruker WP-200 spectrometer operating at 20.80 MHz using a solution of $AlCl_3$ in H_2O as the external standard. The IR spectra were recorded on an UR-20 instrument. Chromatographic analysis was performed on a LKhM-8MD chromatograph using a 4 m × 0.3 cm column and Paropak-Q as the phase. Thermogravimetric measurements were performed on a MOM Q-Derivatograph in the 20 to 400 °C temperature interval and at a rate of heating of 5 deg min^{-1}. Thermal decomposition of $H_nAl(OR)_{3-n}$ (n = 1, 2; R = Pr^i, Bu^t) with trapping liquid and gaseous products was performed using an apparatus consisting of a flask connected to a cooled (−80 °C) trap and a gas burette in the 20—400 °C range. Gaseous products were GLC-analyzed. The Al content was determined trilonometrically. The active hydride hydrogen, H^-, was determined by gas volumetry.

All experiments were carried out under a pure argon or nitrogen atmosphere. The solvents were dried and distilled over CaH_2 or $LiAlH_4$.

Diisopropoxyaluminum hydride. A rotating autoclave of volume 0.5 L was charged with a mixture of the ASD-T aluminum powder (27 g, 1.0 g-atom) containing 0.3% of Ti, isopropyl alcohol (60 g, 1 mol), trimethylamine (11.8 g, 0.2 mol), and toluene (200 mL). Then hydrogen was fed into the autoclave until a pressure of 200 atm was reached. The molar ratio of the components was $Pr^iOH : Al : Me_3N$ = 1 : 1 : 0.2 at a 100% excess of Al. The reaction mixture was heated to 120—140 °C as the autoclave was rotated. The pressure increased to 360 atm and then decreased to 320 atm over a period of 18 h. The autoclave was cooled, the hydrogen pressure was released, and then the autoclave was discharged. The liquid product was filtered under a dry inert atmosphere (Ar). The filtrate (255 mL) was analyzed for the aluminum content (trilonometry) and the active hydrogen (gas volumetry). The concentration of aluminum in the solution was 0.049 g mL^{-1}. A total of 12.5 g of aluminum passed into the solution, and the H : Al ratio was 1 : 1.03 (the theoretical H : Al ratio for $HAl(OPr^i)_2$ is 1 : 1). The yield of the product was 92.5% with respect to $HAl(OPr^i)_2$. The solvent was removed *in vacuo* (water jet pump) at 80 °C, and the residue (67.0 g) was crystallized. After a vacuum distillation (1 Torr, at 110—125 °C), $HAl(OPr^i)_2$ (53.5 g) was obtained as a thick oil crystallizing over a period of 1 month, m.p. 30—35 °C. Found (%): Al, 18.92; H, 0.71. $C_6H_{15}O_2Al$. Calculated (%): Al, 18.47; H, 0.69. IR, ν/cm^{-1}: 1820—1845 (AlH).

Di(*tert*-butoxy)aluminum hydride. A rotating autoclave of volume 0.5 L was charged with a mixture of the ASD-T aluminum powder (14 g), *tert*-butanol (37.0 g, 0.5 mol), and trimethylamine (8.8 g) and with a mixture of toluene with ether (200 mL, 3 : 1). Then steel balls of diameter 5 mm

(100 mL) were added, and hydrogen was fed into the autoclave until a pressure of 120 atm was reached. The reaction mixture was heated to 120—130 °C for 24 h as the autoclave was rotated. The pressure increased to 220 atm over a period of 3 h and then gradually decreased to 200 atm After cooling, the autoclave was discharged. The suspension was filtered, and the solvent and trimethylamine were distilled *in vacuo* (water jet pump) at 60—70 °C. A thick dark mass (360 g) was obtained. According to the analysis for the hydride hydrogen (gas volumetry), the content of the main product was 93%. The subsequent vacuum distillation (1 Torr, at 80—90 °C) gave a white powdered product (31.1 g, 71%), m.p. 55—62 °C. Found (%): Al, 14.98; H, 0.52. $C_8H_{19}O_2Al$. Calculated (%): Al, 15.49; H, 0.57. IR (Vaseline oil), ν/cm^{-1}: 1859 (AlH).

Diethoxyaluminum hydride. A rotating autoclave filled with steel balls (100 mL) was charged with a mixture of the ASD-T aluminum powder (13.5 g), ethanol (23 g), Et_3N (10.4 g), and benzene (200 mL). Then hydrogen was fed into the autoclave until a pressure of 150 atm was reached, and the reaction mixture was heated for 30 h at 160 °C. The autoclave was discharged, and the suspension of the product was separated from the steel balls using a metal sieve and filtered. The residue was washed with hexane (50 mL), dried *in vacuo* at 80 °C, and a gray dry powdered product (34.5 g) was obtained. According to the analysis for the active hydrogen, it contained $HAl(OEt)_2$ (26.8 g) and Al (7.7 g). The filtrate (250 mL) was found to contain the active hydrogen in an amount corresponding to 1.8 g of $HAl(OEt)_2$.

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