"Direct" Synthesis of Unsolvated Aluminum Hydride Involving Lewis and Bronsted Acids

B. M. Bulychev, V. N. Verbetskii, and P. A. Storozhenko

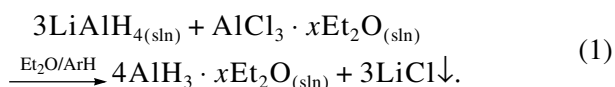*Faculty of Chemistry, Moscow State University, Leninskie gory, Moscow, 119899 Russia*

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Abstract—Unsolvated aluminum hydride has been synthesized by the "direct" reaction of aluminum bromide or sulfuric acid with an alkali metal tetrahydroaluminate at 90–102°C in pure toluene or in toluene containing 5–10 wt % diethyl ether. The reaction involving aluminum bromide yields a mixture of unsolvated aluminum hydride phases of poor quality. The reaction with sulfuric acid affords a single-phase product as α-AlH$_3$ at $\leq$90°C.

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The hydrides of the light nontransition metals belong to the inorganic compounds richest in bound hydrogen. Among these compounds, beryllium and aluminum hydrides have the highest weight contents and space densities of hydrogen atoms. Large-scale use of beryllium hydride is ruled out both because of synthetic difficulties and because of the toxicity of beryllium. Aluminum hydride is free of the latter limitation, and the main obstacles to its application, including as a disposable source of hydrogen, are synthetic difficulties and its high cost.

The only method to synthesize high-quality aluminum hydride known to date is based on the thermochemical cleavage of the Al $\longleftarrow$ O bond in the etherate AlH$_3$ · xEt$_2$O, which is obtained via the Schlesinger reaction [1]:

$$3\text{LiAlH}_{4(\text{sln})} + \text{AlCl}_3 \cdot x\text{Et}_2\text{O}_{(\text{sln})}$$
$$\xrightarrow{\text{Et}_2\text{O/ArH}} 4\text{AlH}_3 \cdot x\text{Et}_2\text{O}_{(\text{sln})} + 3\text{LiCl}\downarrow. \quad (1)$$

The unsolvated product is crystallized from a diethyl ether + aromatic hydrocarbon mixed solvent in the presence of 10–15% LiAlH$_4$ [2]. The quality of aluminum hydride (thermal stability, particle size distribution, and chemical and phase compositions) depends on the concentration of aluminum hydride etherate in its solution (it should not exceed 4–4.5 g/l) and on the purity of all the starting compounds used in reaction (1) [2, 3]. Furthermore, because this technology is extremely fire-hazardous and because all of its products are so sensitive to traces of moisture that the reaction should be conducted in a dry inert atmosphere, it is quite clear why aluminum hydride is very expensive. Obviously, it is a challenging problem to develop a cheaper synthetic method for this product, particularly in the light of its possible application as a disposable source of hydrogen for mobile power supply units.

Here, we present two "direct" methods for the synthesis of unsolvated aluminum hydride, according to which aluminum bromide or 100% sulfuric acid is reacted with lithium (sodium) aluminum hydride in a pure arene medium or in an arene containing a small amount (<10 wt %) of diethyl ether. By "direct" methods, we understand methods that do not include the synthesis of aluminum hydride etherate (reaction (1)) as a separate step.

EXPERIMENTAL

All manipulations involved in the purification, pretreatment, and storage of the starting chemicals, in crystallization, and in the processing of the crystallization products (washing, drying, and prepackaging) were done in a dry-argon glovebox or in vacuo using Schlenk techniques.

Benzene and toluene were purified by standard methods and were distilled from LiAlH$_4$ be fore use. Diethyl ether and tetrahydrofuran, dried and distilled from an alkali, were treated with sodium benzophenone ketyl and were then distilled. Before use, they were refluxed with LiAlH$_4$ or NaAlH$_4$ and were again distilled.

Since the desolvation mechanism and the stability of the unsolvated hydride depend crucially on the quality of the starting chemicals, particularly on the presence of compounds of transition metals, such as titanium, iron, and chromium, even if their concentration is below 10^{-3} mas. %, all the starting crystalline chemicals were carefully purified and the apparatus was thoroughly cleaned.

Commercial LiAlH$_4$ was recrystallized from a diethyl ether + toluene mixture (1 : 1, hydride concentration of about 30 g/l) as is described in [3].

Table 1. Outcomes of the synthesis of unsolvated aluminum hydride from aluminum bromide and lithium (sodium) tetrahydroaluminate

Solvent	Al_2Br_6/$LiAlH_4$	Composition of the precipitate washed with diethyl ether, wt %		Yield, %	Phase composition
		Al	H		
Benzene	1 : 6	74	8.2	10	γ-AlH_3
Toluene	1 : 6	76.3	8.3	15	α,α'-AlH_3
Toluene	1 : 6 ($NaAlH_4$)	75	8.2	13	γ,α'-AlH_3
o-Xylene	1 : 6	80.2	8.3	20	γ,α, α'-AlH_3
Benzene	7 : 6	82.2	9.1	80	α,γ-AlH_3
Toluene	7 : 6	84.6	9.3	84	α,γ-AlH_3
Toluene	7 : 6 ($NaAlH_4$)	85.1	9.3	81	α,γ-AlH_3
o-Xylene	7 : 6	85.0	9.3	85	α,γ-AlH_3
Hexane	7 : 6	52	–	0	–
Heptane	7 : 6	77.8	8.1	15	α,γ, α'-AlH_3
Octane	7 : 6	82.4	8.6	26	α,γ-AlH_3

$NaAlH_4$ was prepared by reacting sodium hydride with aluminum chloride in THF by a standard procedure [4], but using a high-speed stirrer [5].

Al_2Br_6 (pure grade) was sublimed two times from its melt over an aluminum metal powder. To do this, the mixture was placed into a Pyrex tube (no more than 5% by volume) and the tube was evacuated, sealed off, placed into a tubular furnace by 4/5 of its length, and heated to 100°C. The sublimate was condensed in a colder part of the tube, which was then sealed off. To sample the product, this part of the tube was unsealed in a dry inert atmosphere in a glovebox. The product was completely soluble in toluene, yielding a colorless solution.

Anhydrous sulfuric acid (100%) was prepared by dissolving oleum (reagent grade) in 96% sulfuric acid (reagent grade).

Unsolvated aluminum hydride was synthesized by two procedures:

(1) *Isothermal synthesis.* A cold solution of aluminum bromide or sulfuric acid in ArH or in an ArH + diethyl ether (5–10 wt %) mixture was added into a 1-l flask half-filled with a suspension of $LiAlH_4$ (15% excess over the stoichiometry of reaction (1)) in a solvent and preheated on an oil bath to a preset temperature (no higher than 102°C for toluene and xylene). The solution addition rate was adjusted so that the temperature of the reaction mixture differed from the preset temperature by no more than ±1°C.

(2) *Polythermal synthesis.* Appropriate proportions of all inorganic reactants were combined in a one-component solvent in a 1-l flask. The mixture was heated to the boiling point of the solvent (but not above 100°C for

high-boiling solvents) and was then refluxed at this temperature for 30–40 min.

X-ray diffraction patterns were obtained on a Guinier G670 HUBER diffractometer for samples sealed in vacuum-sealed glass capillaries. Differential thermal analyses were carried out on a Q1500D thermoanalytical system at a sample heating rate of 10 K/min. Electron microscopic examinations were done on a JSM 100C microscope.

RESULTS AND DISCUSSION

Although homogeneous and homogeneous–heterogeneous reactions of alkali metal tetrahydroaluminates with various Lewis and Brønsted acids in electron-donor solvents may proceed via different routes, they ultimately yield solutions or precipitates of solvated aluminum hydride [6–8]. It is very difficult or even impossible to convert these products into unsolvated aluminum hydride. Similar reactions in nonsolvating ("inert") solvents have not been carried out as yet, even though it is known that aluminum bromide, unlike aluminum chloride and iodide, is readily soluble in aromatic hydrocarbons [9], yielding weakly bonded molecular π-complexes [10, 11]. In paraffins, Al_2Br_6 is much less soluble [9] and does not form any compounds.

The interaction between Al_2Br_6 and lithium or sodium tetrahydridoaluminate in different arenes above 80°C occurs in the same way and is independent of whether the reaction and crystallization are conducted in the isothermal or polythermal regime, yielding multicomponent mixtures of unsolvated aluminum hydride phases. The most typical results of this interaction are presented in Table 1. It follows from these data that,

under the assumption that reaction (2) occurs, which is similar to the Schlesinger reaction (1), the aluminum hydride yield does not exceed 30%.

$$Al_2Br_{6(sln)} + 6MAlH_{4\,s} \xrightarrow{ArH} 8AlH_3\downarrow + 6MBr\downarrow. \quad (2)$$
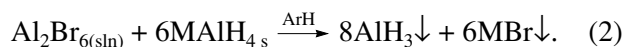
According to X-ray diffraction data, the precipitate resulting from the reaction contains no LiBr or NaBr, although these salts are insoluble in arenes. At the same time, large amounts of free tetrahydroaluminate are identified. The elemental analysis of the substance isolated by evaporating the mother solution indicates the composition $MAl_{2.1-2.3}Br_{7.1-7.4}$. Therefore, the reaction yields, besides aluminum hydride, a mixture of bromoaluminates consisting of the heptabromo complex $MAl_2Br_7^-$ and a minor amount of the decabromo complex MAl_3Br_{10}. These complexes are well known in aluminum halide chemistry [6]. We artificially prepared these two polyaluminates by melting an alkali metal bromide with aluminum bromide and established that, under the above conditions, MAl_2Br_7 does not react with the tetrahydroaluminates at all and MAl_3Br_{10} reacts with them to an extent no larger than 3–5%. This order of reactivities is quite consistent with the stabilities of the complex anions. It is interesting that the same reaction conducted in an electron-donor solvent (e.g., diethyl ether) does not yield an alkali bromide precipitate either, even though it occurs according to chemical equation (2). Because the intrinsic solubility of the alkali metal bromides is somewhat higher than is observed in reaction (2), some authors [12, 13] assume the formation of soluble hydridobromide complexes ($[L \cdot M]^+[AlH_3Br]^-$) stable only in solution.

Thus, it follows from the above data that the stoichiometry of the reaction between Al_2Br_6 and $MAlH_4$ in arenes should be described by the equation

$$7Al_2Br_{6(sln)} + 6MAlH_{4\,s} \xrightarrow{ArH} 8AlH_3\downarrow + 6MAl_2Br_7. \quad (3)$$
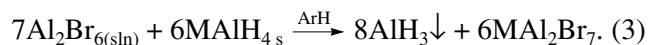
Indeed, it is clear from Table 1 that, in this case, the aluminum hydride yield with respect to the tetrahydroaluminate ranges up to 80%. However, this value was obtained after the by-products were washed out with diethyl ether and, as a consequence, part of the desired product was lost due to solvation and subsequent dissolution in ether. Therefore, the true aluminum hydride yield is nearly quantitative. Nevertheless, reaction (3) as a whole is less efficient than the classical Schlesinger reaction.

Unfortunately, in none of our experiments did we obtain the pure α-phase of aluminum hydride. Its highest percentage in the three-phase mixture of α-, γ-, and α'-AlH₃ (~50 wt %) was attained by performing the reaction at ~100°C in high-boiling arenes, such as toluene and xylene. The reaction carried out in benzene at the lowest temperature examined for arenes (80°C) yielded the pure γ-phase in some cases. The introduction of diethyl ether (up to 5 wt %) into the solvent (toluene) afforded no single-phase aluminum hydride.

As the ionization potential of the arene decreases, the aluminum bromide dimer dissociates increasingly in solution. Even with mesitylene, aluminum bromide forms the π-complex $AlBr_3 \cdot C_6H_2(CH_3)_4$ [9]. However, this does not exert any affect on the general character of the reaction, which was described for other arenes, or on the quality of the product. The latter is much lower than the quality of the hydride obtained by crystallization from diethyl ether–arene media [2, 3]. The AlH_3 samples resulting from reaction (3), in addition to being multiphase, are ultrafine powders with a mean particle size of <1.5 μm, and their purity falls to 90–91% upon two or three washings with diethyl ether. Therefore, the hydride thus obtained readily undergoes solvation, which causes its partial dissolution in diethyl ether and an appreciable decrease in the yield of the unsolvated product. Because of all of these effects, the thermal stability of all aluminum hydride samples obtained by the "direct" method using aluminum bromide is lower than that of the product synthesized via aluminum hydride etherate. The thermal decomposition of these samples, yielding hydrogen, begins at 80–90°C, and their rapid decomposition is observed at 110–120°C (in the polythermal regime at a heating rate of 10 K/min). The samples obtained in ether–arene media under the same conditions begin to decompose at 110–120°C, and their rapid decomposition occurs at 150–170°C [3].

The interaction between Al_2Br_6 and $MAlH_4$ in paraffins is weak. Even for high-boiling alkanes, the aluminum hydride yield does not exceed 26%, irrespective of the reaction stoichiometry (Table 1). Since a similar situation was observed in the synthesis of unsolvated aluminum hydride in diethyl ether + octane mixtures in the polythermal regime [3], it can be assumed that the weak nonvalent interactions of the products of reaction (3), which are Lewis acids, with the π-electron system of the aromatic hydrocarbon somewhat stabilize the coordinatively unsaturated monomer AlH_3 and favor its polymerization into an inorganic polymer.

It was demonstrated in earlier works [2, 3] that unsolvated aluminum hydride can be crystallized from ether–arene mixtures only in the presence of a small amount of $LiAlH_4$. At the same time, aluminum hydride synthesis in aromatic hydrocarbons can be carried out using both pure $LiAlH_4$ and pure $NaAlH_4$. This fact can be viewed as direct evidence that, in all aluminum hydride technologies using diethyl ether, lithium tetrahydroaluminate serves as a desolvating agent favoring the breaking of the Al ⟵ O bond in the etherate. In the absence of ether in the system, there is no agent to play this role and aluminum hydride, though its quality is poor, results directly from the reaction between $NaAlH_4$ and Al_2Br_6.

As was noted above, solvated aluminum hydride as the etherate $AlH_3 \cdot xEt_2O$ can be obtained using both Lewis acids and Brønsted acids, e.g., sulfuric acid [6–8, 14]. For a higher solubility of the starting chemicals, for the sake of safety in conducting the reaction at elevated

Table 2. Outcomes of the synthesis of unsolvated aluminum hydride from sulfuric acid and lithium tetrahydroaluminate

Excess LiAlH$_4$, wt %	LiBH$_4$, added, wt %	c_{eff}, g/l	t_{cryst}, °C	Yield, %	Phase composition
10	–	10	90	73	α-AlH$_3$
10	–	15	89	76	α-AlH$_3$
15	–	18	90	79	α-AlH$_3$
10	–	24	90	82	α-AlH$_3$
10	–	28	90	84	α-AlH$_3$
10	–	39	90	55	α,γ-AlH$_3$
10	–	10	92	64	α,γ-AlH$_3$
20	–	16	92	74	α-AlH$_3$
10	–	16	92	65	α,γ-AlH$_3$
10	–	14	96	72	α,γ-AlH$_3$
15	–	14	101	69	γ,α, α'-AlH$_3$
0 (NaAlH$_4$ as a starting compound)	–	10	90	0	–
15 (NaAlH$_4$ as a starting compound)	–	10	90	0	–
10	10	15	90	54	α,γ-AlH$_3$
10	20	18	96	30	γ,α, α'-AlH$_3$
20	20	14	101	22	γ,α, α'-AlH$_3$
10	50	20	96	51	γ,α, α'-AlH$_3$

temperatures, and considering the data obtained for the synthesis of unsolvated aluminum hydride using aluminum bromide, the aluminum hydride synthesis involving 100% sulfuric acid was performed in the high-boiling solvent toluene in the presence of 5–10 mas % diethyl ether in the isothermal reactant combining regime.

In this case, the "direct" method is so different from "classical" crystallization from ether–arene media [2, 3] and from the above aluminum hydride synthesis using aluminum bromide that we can claim that the formation of the unsolvated product by the reaction

$$2LiAlH_4 + H_2SO_4 \xrightarrow{ArH/Et_2O} 2AlH_3 + Li_2SO_4 + 2H_2 \quad (4)$$
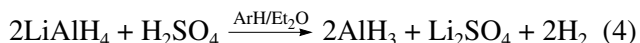
takes place via a different mechanism.

The most illustrative results of our experiments are presented in Table 2. Note that the effective aluminum hydride concentration achieved in this method (amount of the resulting AlH$_3$ (g) per total solvent volume (l)) is higher than that achieved in the syntheses using diethyl ether. While c_{eff} in the classical synthesis is not higher than 5 g/l [3], c_{eff} in this method can be raised up to 30 g/l because it is determined not by the solubility of aluminum hydride etherate, but by the solubility of sulfuric acid and by the safety regulations at the reactant combining stage.

The second distinction of this method is that use of lithium borohydride neither improves the quality of aluminum hydride nor raises its yield, contrary to what was claimed in [2, 3]. Conversely, lithium borohydride

noticeably reduces the aluminum hydride yield and dramatically spoils the quality of the product. The product that forms in the presence of LiBH$_4$ is always a mixture of phases in which the proportion of α-AlH$_3$, the most dense and the most stable aluminum hydride phase, is very small.

The third distinction of this method is that the formation of the pure α-phase with a crystal size of ~6 μm is observed only at synthesis temperatures of ≤ 90°C, while, in the "classical" and bromide methods, the probability of the formation of this phase always increases with an increasing solvent temperature. Furthermore, it was demonstrated by sampling that only the α-modification crystallizes at this temperature (Fig. 1a) and a mixture of the γ-, α-, and α'-phases (Fig. 1b) forms at 93°C and above. Contrary to what was reported in [3], this mixture persists up to 100–102°C. Note also that the quality of the α-phase obtained by this method, primarily its thermal stability, differs only slightly from the quality of the samples resulting from "classical" synthesis and crystallization [3].

Thus, while the first two distinctions of this method from the other known aluminum hydride synthesis methods can be attributed to the formal absence of a distinct step yielding aluminum hydride etherate, whose solubility in ether determines the effective aluminum hydride concentration in the process, and to the occurrence of the side reaction

$$2LiBH_4 + H_2SO_4 \xrightarrow{ArH/Et_2O} B_2H_6 + Li_2SO_4 + 2H_2, \quad (5)$$
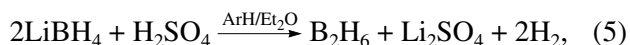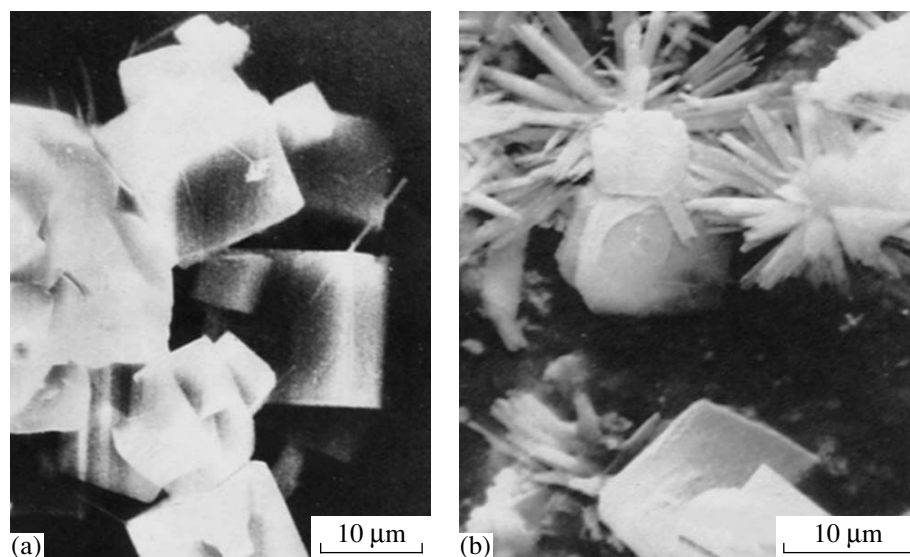
Fig. 1. (a) α-AlH₃ crystals obtained from sulfuric acid and LiAlH₄ at 90°C and (b) α, γ-AlH crystals obtained from sulfuric acid and LiAlH₄ at 95°C.

which yields diborane, a substance capable of reacting with alane to form the rather stable compound Al(BH₄)₃ · Et₂O [15, 16], the last distinction clearly indicates that the AlH₃ formation mechanism in this method is different from that in the "classical" synthesis [2, 3]. We cannot ascertain the cause of the stabilization of the low-density and metastable modifications of aluminum hydride, which were reported to turn readily into α-AlH₃ upon simple heating [2, 3]. The only possible, though rather disputable, cause of this effect is the absence of a lithium halide in the reaction system. Any unsolvated aluminum hydride sample prepared via an aluminum halide (i.e., by the "classical" method) contains ≤0.1 mas % lithium and ≤0.05 mas % chlorine or bromine. The form and location of these elements in the hydride have not been established; however, there is good reason to believe that they are incorporated in the lattice. The hydride samples obtained using sulfuric acid contain ≪0.1% lithium and no chlorine. It is known from aluminum hydride chemistry that some alkali metal halides, particularly lithium chloride, form weakly bonded complexes with aluminum hydrides, thus changing the solubility of both components, and affect the reactivity of the main component [6, 7, 12, 13, 17]. So, we suppose that the lithium chloride resulting from the "classical" Schlesinger reaction (reaction (1)) is not an inert component of the system, but an active participant processes occurring there, including the desolvation of the etherate and the phase transitions of the less dense and thermodynamically less stable modifications of aluminum hydride into α-AlH₃. However, this hypothesis needs experimental verification.

Thus, our experiments demonstrated that the variety of reactants and reactions suitable for the synthesis of unsolvated aluminum hydride is rather wide and is limited by only two factors, namely, economic practicability and the quality of the resulting product. For example, use of the Lewis acid aluminum bromide is inappropriate in terms of both parameters. The technology involving 100% sulfuric acid is simpler than the conventional technology and affords a product of acceptable quality, but it suffers from a greater waste of LiAlH₄ per unit weight of the product.

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