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The systems $\text{LiAlH}_4/\text{NH}_4\text{X}$ and $\text{N}_2\text{H}_5\text{Cl}$ as precursor sources for AlN

Jerzy F. Janik¹ and Robert T. Paine

Department of Chemistry, University of New Mexico, Albuquerque, NM 87131 (USA)

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Abstract

The reactions of LiAlH_4 with NH_4X ($\text{X} = \text{Cl}, \text{Br}$), $\text{N}_2\text{H}_4 \cdot \text{HCl}$, and $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ in ethereal solvents have been investigated as potentially simple routes to a processible preceramic polymer. The polymer obtained from NH_4Br is easily converted by pyrolysis at 950°C to crystalline AlN in high ceramic yield. The polymer obtained from $\text{N}_2\text{H}_5\text{Cl}$ provides an ether-soluble fraction that can be used to form AlN coatings.

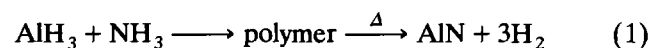
1. Introduction

Aluminum nitride, AlN, is a covalent non-oxide ceramic having a number of technologically significant properties [1]. It has a high thermal conductivity, low coefficient of thermal expansion, high electrical resistivity, good mechanical strength and hardness, and moderately good resistance to chemical attack. The material has most commonly been prepared in powder form by carbothermal reduction and nitridation of Al_2O_3 powders or by direct nitridation of Al or AlCl_3 with N_2 or NH_3 [1]. The powders are obtained with relatively good purity from these classical syntheses; however, removal of small amounts of Al, C, and O impurities that affect physical properties and sintering behavior can be troublesome [1].

In efforts to improve on the classical powder syntheses and obtain alternative forms (*e.g.*, fibers and coatings), several groups have sought to develop polymeric precursors [2–13] and electrochemical syntheses [2,14–16] as sources for AlN. In most instances, these syntheses are straightforward, and the success of the subsequent thermal decompositions depends on facile substituent group elimination chemistry. The ceramic powders obtained are of generally good quality and, in a few cases, the polymers are fusible or soluble, and they

have been processed into coatings or fibers. It is also noteworthy that related precursor chemistry has been used to form several nanodispersed or solid solution ceramic-ceramic composites including AlN/ Si_3N_4 and AlN/ SiC [11,17–21], and this molecular approach to composite syntheses offers considerable future potential.

Among the molecular/polymer systems referenced above, the combination of AlH_3 and NH_3 stands out due to its apparent simplicity. If the reactants can be highly purified and if H_2 elimination chemistry, as idealized in eqn. 1, is facile, this system should serve as a particularly clean source of AlN. Unfortunately, AlH_3 is not stable, and it can be utilized as a stoichiometric synthetic reagent only when coordinated with a donor such as Et_2O , THF, or tertiary amines. The reaction was



first examined by Wiberg and May [22] by using $\text{H}_3\text{Al} \cdot \text{THF}$. They proposed that the 1:1 reaction, as shown in eqn. 1, at -80°C in THF solution produced an adduct $\text{H}_3\text{Al} \cdot \text{NH}_3$ that successively decomposed at -45°C and 20°C with formation of H_2 , H_2AlNH_2 and $(\text{HAlNH})_n$, respectively. In the presence of additional NH_3 (3:1 reactant ratio) at -30°C in THF, it was suggested that $\text{Al}(\text{NH}_2)_3$ formed and decomposed at 20°C with generation of an insoluble polymeric solid represented as $[\text{Al}(\text{NH})\text{NH}_2]_n$. When heated to 400°C or above, the polymeric solid evolved gaseous products, but no description of the formation of AlN was pro-

Correspondence to: Dr. R.T. Paine.

¹ Permanent address: University of Mining and Metallurgy, Cracow, Poland.

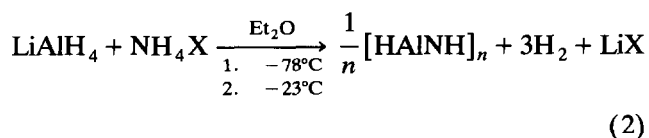
vided. Nonetheless, these observations indicate that the reactions of solvated AlH_3 with NH_3 are more complicated than portrayed in eqn. (1).

Maya [2] reinvestigated this chemistry by using H_3AlOEt_2 and confirmed that, if formed, $\text{H}_3\text{Al} \cdot \text{NH}_3$ and $\text{Al}(\text{NH}_2)_3$ are too unstable to isolate. An insoluble aminoiminoalane polymer, represented as $[\text{Al}(\text{NH}-\text{NH}_2)]_n$, was isolated, and pyrolysis above 1000°C produced AlN with Li and Cl impurities. No information on C and O impurities was provided. Finally, Rhine and coworkers [13] studied this chemistry by utilizing commercially available AlH_3 that contained $1/3$ equivalent of Et_2O , and the reactions with NH_3 were done in THF and toluene solutions. A 1:1 reaction in THF was reported to form a gel that, upon pyrolysis, gave a black solid containing poorly crystallized AlN.

The reactions of LiAlH_4 with monoalkylammonium salts have also been studied by several groups and found to produce structurally interesting molecular N-alkyliminoalane cage compounds and N-alkyliminoalane polymers [23–25]. In addition, Finholt and coworkers [26] have reported on the stoichiometry sensitive reactions of LiAlH_4 and NH_3 that produce complex lithium salts $\text{LiAl}(\text{NH}_2)_4$ and $[\text{LiAlH}(\text{NH}_2)_2]_2\text{NH}$ under selected conditions. Aspects of these studies suggested to us that an organic free polymer might be obtained from the direct combination of LiAlH_4 and NH_4X . In the present paper, we report our study of this reaction in donor solvents and the pyrolysis and processing of the resulting polymeric products that provide AlN.

2. Results and discussion

The 1:1 reactions of LiAlH_4 and NH_4X ($\text{X} = \text{Cl}, \text{Br}$) were studied in Et_2O and DME solutions, and the idealized course of the chemistry is summarized in eqn. (2). The commercially available LiAlH_4 used in



these reactions is gray as received, and it was purified by dissolution in dry Et_2O , filtration and evaporation of the Et_2O from the filtrate. This provides a white, free-flowing powder. Of the two ammonium halide salts utilized, NH_4Br provides the best results since LiBr is soluble in the reaction medium, and only a trace of salt is retained in the insoluble polymeric product. With NH_4Cl , the insoluble LiCl is occluded in the polymer. The LiCl, as it forms, also coats the remaining NH_4Cl , thereby slowing the rate of the elimination reaction.

The reaction with NH_4Br proceeds smoothly in Et_2O , the evolved hydrogen is quantitatively recovered with a Toepler pump, and white, polymeric iminoalane precipitates from the solution. The polymer is washed with fresh solvent and vacuum dried for 12–24 hours at 100°C . Subsequent elemental analyses, TGA, and infrared spectroscopic data indicate that the polymer tenaciously absorbs 5–10wt.% Et_2O and occludes a trace of LiCl. When the reaction is performed in DME, hydrogen evolution is not quantitative (80–90% H_2 collected), and, as indicated by elemental analysis and TGA, a greater percentage of the final polymer weight is made up by solvent ($\sim 25\%$). It is also worth noting that attempts to perform the reaction in THF solution resulted in cleavage of THF and subsequent formation of an oily product. Although this material is soluble in ethers, it produces heavily carbon contaminated AlN upon pyrolysis. As a result, the preferred solvent for the reaction is Et_2O , and further discussion of the characterization and processing of the polymer is limited to the polymer formed from NH_4Br in Et_2O solution, except where comparisons are appropriate.

Thermal gravimetric analysis of $[\text{HAlNH}]_n$ typically shows a three-stage weight loss between 25°C and 1000°C . The first derivative of the TGA trace shows relatively sharp peaks centered at 200°C ($\sim 5\text{wt.}\%$ loss), 500°C ($\sim 5\text{wt.}\%$ loss), and 700°C ($\sim 4\text{wt.}\%$ loss): total mass loss 13–15% or ceramic yield 85–87%. The first two weight losses are dominated by solvent loss; however, IR studies (*vide infra*) show that H_2 is also lost in the early stages. It is interesting to note that TGA data from a series of samples obtained from syntheses accomplished under differing conditions suggest that the amount of absorbed Et_2O can be reduced by allowing the elimination chemistry to proceed at a slower rate. The rate may be reduced by lowering the reaction temperature or by using larger grains of NH_4Br .

The infrared spectrum for the polymer is generally consistent with the proposed iminoalane composition. A medium intensity, broad absorption is observed centered at 3200 cm^{-1} that may be assigned to the N–H stretch and a strong, broad band centered at 1800 cm^{-1} that may be assigned to the Al–H stretch. Weak absorptions at 2979 cm^{-1} are attributed to C–H stretches from residual Et_2O . There are no resolved bands or shoulders in the region expected for NH_2 stretches ($3400\text{--}3200\text{ cm}^{-1}$). The infrared data for products from the reactions accomplished with NH_4Cl or with DME solvent produce polymers with significantly different infrared spectra. In particular, both of these polymers show broad, medium intensity absorptions in the region $3400\text{--}3200\text{ cm}^{-1}$ that are assigned to NH_2 stretches in addition to the broad band cen-

tered at $\sim 3200\text{ cm}^{-1}$. In addition, there is a shoulder on the Al–H stretch at 1650 cm^{-1} . This suggests, as do Toepler pump measurements of evolved H_2 , that the elimination chemistry is not as complete and some aminoalane fragments are present in the polymer structure.

The bulk pyrolysis of samples of $[\text{HAlNH}]_n$ were examined in stages (200, 500, 700, and 950°C) under flowing N_2 or NH_3 as well as under dynamic evaporation conditions. The gross changes in polymer structure were followed by examination of the infrared spectra of samples extracted from these heating stages. After heating the polymer at 200°C for 24 h under the atmospheric conditions described, the infrared bands attributed to the N–H and Al–H stretches are dramatically reduced in intensity. These weak bands continue to decrease in intensity after heating at 500°C and 700°C , and a new band appears at $\sim 2125\text{ cm}^{-1}$. These bands all disappear after heating at 950°C , and a simple spectrum with a single broad band centered at $\sim 700\text{ cm}^{-1}$, typical of AlN [4,12,27], is observed.

In an earlier report [20] on the pyrolysis of $(\text{Me}_3\text{Si})_2\text{AlNH}_2$, a band at 2100 cm^{-1} also appeared after heating the molecular precursor to 300°C . It was proposed that this absorption resulted from the presence of pyrolysis generated Si–H groups. In the present system, silicon is not available; therefore, it is more appropriate to conclude that the absorption results from $\text{C}\equiv\text{N}$ or $\text{C}\equiv\text{C}$ stretches. Such an explanation has been forwarded for a band appearing at $\sim 2100\text{ cm}^{-1}$ in the CVD product from the reaction of Me_3Al and NH_3 [28]. The source of the carbon in the present case must be residual solvent. Under dynamic vacuum evaporation and N_2 flow at 950°C , the product is black or gray, indicating the presence of residual carbon also found in elemental analyses. When NH_3 is used as the pyrolysis atmosphere, the solid residue is white or light gray. This material has been further characterized by elemental analysis and powder X-ray diffraction, and a typical diffraction pattern is similar to that shown in Fig. 1.

In previous studies of poly (borazinyamine) preceramic polymers [29], we noted that these materials are soluble in NH_3 (ℓ) and N_2H_4 (ℓ), and the former makes particularly useful processing solutions for production of BN fibers, coatings, and aerosols. As a result, the solubility of $[\text{HAlNH}]_n$ in NH_3 (ℓ) and N_2H_4 (ℓ) was examined. In NH_3 (ℓ), the polymer appears to be insoluble and unreactive, as indicated by no gas evolution or change in infrared spectrum.

Addition of N_2H_4 (ℓ) to the polymer, on the other hand, results in a *hypergolic* reaction accompanied by strong gas evolution and a blue flame. The light gray product was characterized by infrared spectroscopy,

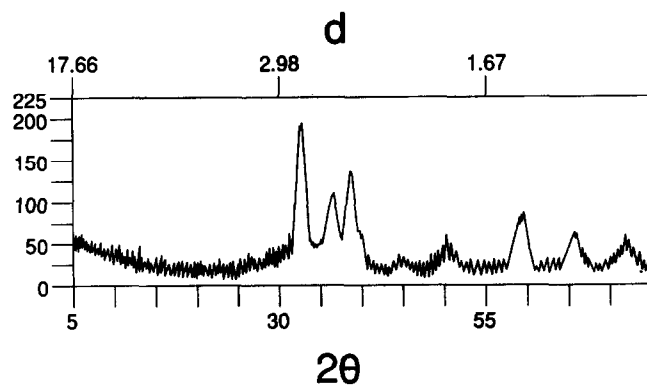


Fig. 1. Powder X-ray diffraction pattern for AlN derived from $[\text{HAlNH}]_n$.

and absorptions in the regions for $\nu(\text{NH}_2)$ and $\nu(\text{NH})$ were found. A powder X-ray pattern was recorded, and it shows the presence of AlN with some degree of crystallinity, although the reflections are relatively broad. Still, the heat of reaction is sufficiently intense to produce some crystalline AlN. In order to control this reaction, the polymer was first slurried with Et_2O and then combined with excess N_2H_4 (ℓ). After stirring for several hours, an oily phase separates from the Et_2O . Measurement of evolved hydrogen indicates that one equivalent of H_2 forms, and the resulting product is proposed to have $[\text{H}_2\text{N}-\text{N}(\text{H})\text{AlNH}]$ units as part of the polymer structure. Infrared spectra are consistent with this proposal since the Al–H stretching frequency is dramatically reduced and new bands at $\sim 3200\text{ cm}^{-1}$ [$\nu(\text{NH}_2)$], $\sim 1600\text{ cm}^{-1}$ [$\nu(\text{NH}_2)$], and 1100 cm^{-1} [$\nu(\text{N}-\text{N})$] are observed. The new polymer is safely pyrolyzed under dynamic vacuum, and AlN with good purity ($\text{C} < 0.5\%$; $\text{Li} < 0.05\%$) and excellent crystallinity is obtained. A typical XRD pattern for this product is shown in Fig. 1. An SEM for a powder sample is shown in Fig. 2. The small crystallites ($\sim 0.5\ \mu$) appear agglomerated or perhaps sintered into larger particles ($1-2\ \mu$).

Since N_2H_4 was found to react with the polymer at the Al–H bond, the reactions of LiAlH_4 with $\text{N}_2\text{H}_4 \cdot \text{HCl}$ and $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ were examined in Et_2O solution. The 1:1 reaction of LiAlH_4 with $\text{N}_2\text{H}_4 \cdot \text{HCl}$ is very slow; however, hydrogen is formed and an insoluble, white solid precipitates from solution. Infrared spectra reveal several bands at 3334, 3314, 3280, 3265, and 3207 cm^{-1} , all in the region for $\nu(\text{NH}_2)$ and $\nu(\text{NH})$. A band at 1133 cm^{-1} is assigned to an N–N stretch. No absorptions in the Al–H stretch region are resolved. Subsequent pyrolysis produces AlN of good quality. More importantly, evaporation of the filtrate from this reaction reveals the formation of an Et_2O soluble fraction. The infrared spectrum of this crys-



Fig. 2. SEM for AlN derived from $[\text{HAlNH}]_n$.

talline solid shows bands in the Al–H region. Subsequent pyrolysis under NH_3 gives AlN. Surprisingly, the reaction of LiAlH_4 with $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ produces elemental aluminium as the primary nonvolatile product. As a result, this reactant system is not useful for formation of AlN.

3. Conclusions

The reaction of LiAlH_4 and NH_4Br in Et_2O produces an insoluble polymer that, upon pyrolysis under NH_3 , gives good quality AlN powder. The reaction is more straightforward than schemes that utilize the complexes $\text{H}_3\text{Al} \cdot \text{base}$; however, it probably does not offer significant practical advantage over other syntheses. Treatment of an Et_2O slurry of the polymer with N_2H_4 (ℓ), followed by pyrolysis, produces particularly high-quality, crystalline AlN. The ether-soluble fraction from the reaction of LiAlH_4 and $\text{N}_2\text{H}_4 \cdot \text{HCl}$ provides a convenient means to form AlN films, and the full characterization of these films is in progress.

4. Experimental section

4.1. General information

Standard inert atmosphere techniques were used for the manipulation of all reagents and products. Infrared spectra were recorded on a Nicolet 6000 FT-IR spectrometer from KBr pellets (solid samples) or with a 10 cm gas cell fitted with KBr windows (gaseous byproducts). Mass spectra were obtained by using the solids

probe on a Finnegan Model 4600 GC/MS spectrometer. A calibrated glass vacuum system, including a Toepler pump, was used to perform volumetric measurements of gaseous reactants and byproducts, and elemental analyses were obtained from the UNM microanalytical services laboratory and Galbraith Laboratories. Powder XRD data were obtained with a Scintag PAD V diffractometer, and TGA/DTA data were measured with a Model 3700 Perkin Elmer instrument.

4.2. Materials

Commercial LiAlH_4 (gray) (Aldrich or Ventron) was dissolved in anhydrous Et_2O (Fischer Scientific), the resulting slurry filtered under dry nitrogen, and the ether removed by vacuum evaporation from the filtrate. The resulting white residue was dried *in vacuo* for 12 h to remove residual ether. The NH_4Cl and NH_4Br (Fischer Scientific) were vacuum dried at 120°C for 12 h, and $\text{N}_2\text{H}_4 \cdot \text{HCl}$ and $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ (Aldrich) were dried with a desiccant under nitrogen. Commercial anhydrous N_2H_4 (Matheson) was further dried by passing a slow gas stream through KOH flakes and CaO. Anhydrous NH_3 (Matheson) was purified by fractional distillation from a Na/ NH_3 mixture. The NH_3 , used as the polymer pyrolysis flow gas, was dried by passing the gas stream through KOH flakes and molecular sieves. All solvents were rigorously dried with appropriate drying agents, vacuum distilled, and stored in glass storage flasks under N_2 .

4.3. Syntheses

4.3.1. Reaction of LiAlH_4 and NH_4Br in Et_2O

A sample of LiAlH_4 (0.15 g, 4.0 mmol) was dissolved in 30 ml of Et_2O , and in a second Schlenk vessel NH_4Br (0.38 g, 3.9 mmol) was combined with 10 ml of Et_2O . The two vessels were frozen at -196°C , evacuated, and then joined through a glass tee. The $\text{LiAlH}_4/\text{Et}_2\text{O}$ solution was added to the rapidly stirred, cold (-78°C) slurry of $\text{NH}_4\text{Br}/\text{Et}_2\text{O}$. Instantaneous gas evolution was noted, and the mixture was stirred at -78° for 10 min, then warmed slowly to 23°C . A large amount of fine, white precipitate formed during stirring overnight. The noncondensable gas (H_2) was quantitatively collected and measured with a Toepler pump, and 11.8 mmol were collected (theoretical yield: 11.7 mmol). The white precipitate was collected by filtration and washed (2X, 10 ml) with fresh Et_2O . The filtrate was vacuum evaporated and LiBr (0.33 g) recovered (theoretical yield: 0.34 g). The ether-insoluble precipitate was vacuum evaporated at 23°C for 70 hours and 0.18 g of product recovered. Mass spectrum (70 eV) [m/e (assignment) rel. int.]: highest mass ~ 800 , 95 (Al_3N) 30, 82 (Al_2N_2) 70, 57 (AlN_2H_2) 100. Infrared

spectrum (cm⁻¹, KBr): 3200m,br, 2974w, 2929w, 2880w, 1806s,br, 1510vw, 1400vw, 1151w,sh, 1093w,sh, 1081w,sh, 900m,sh, 700vs,br. Anal. Calcd for AlNH₂: H, 4.70; N, 32.57. Found: C, 5.48; H, 4.10; N, 21.78; Li, 0.72%.

4.3.2. Reaction of LiAlH₄ and NH₄Cl in Et₂O

The reaction was performed in the same manner described above. The LiCl produced in the reaction is insoluble and can not be readily separated from the product. Infrared spectrum (cm⁻¹, KBr): additional bands at 3420br,m, 3210br,m, 2975w, 2880w, 1800br,m, 1660m, 1400w, 1153w, 910sh,m, 707s. Anal. Calcd for AlNH₂·LiCl: H, 3.00; N, 15.34. Found: C, 4.23; H, 2.54; N, 15.58%.

4.3.3. Reactions of [HAlNH]_n with NH₃ and N₂H₄

(a) A sample of the polymer [HAlNH]_n (0.42 g, 9.8 mmol) was combined with NH₃ (ℓ) (10 ml) at -78°C and stirred for one hour. No noncondensable gas was produced. The NH₃ was evaporated, the remaining solid evacuated for 12 h, and the remaining residue showed a slight weight gain (0.44 g). An infrared spectrum is identical to that of the starting polymer.

(b) A sample of polymer [HAlNH]_n (0.71 g, 16.5 mmol) was combined with 5 ml of N₂H₄ (ℓ) in a 100 ml Schlenk vessel. An immediate hypergolic reaction occurred, accompanied by a light blue flame and massive gas and heat evolution. The resulting hard, white-gray solid was collected and ground to a fine powder. Infrared spectrum (cm⁻¹, KBr): 3300w,br, 3200w,br, 2110w,br, 1700w,br, 1610m, 1060m,sh, 700vs,br. XRD (2θ, deg): 33.5, 36.5, 38.0, 50.8, 60.2.

(c) A sample of polymer [HAlNH]_n (0.34 g, 7.0 mmol) was combined with 30 ml Et₂O and the flask evacuated. A slurry containing 2.6 ml (80 mmol) of N₂H₄ and 30 ml Et₂O was prepared, evacuated, and then combined with the slurry of [HAlNH]_n in Et₂O. The mixture was stirred and a thick oil separated from the Et₂O and gas was evolved. After 48 h stirring, 3.6 mmol H₂ was collected with the Toepler pump. When quantitative gas measurements are not required, the N₂H₄ (ℓ) may be added to the stirred [HAlNH]₂/Et₂O slurry via syringe. The ether was decanted from the oil/hydrazine phase. The hydrazine fraction was evacuated to 4 h, leaving a white solid (0.5 g). Infrared spectrum (cm⁻¹, KBr): 3240m,br, 3160m,br, 2960w, 2870w, 1700w, 1604m, 1383w, 1287w,sh, 1099m, 880s,sh, 700vs,br. Anal. Calcd for AlN₂H₄: H, 5.51; N, 57.35. Found: C, 2.44; H, 4.77; N, 41.24%.

4.3.4. Reaction of LiAlH₄ and N₂H₄·HCl in Et₂O

A sample of LiAlH₄ (0.85 g, 2.2 mmol) was dissolved in 15 ml Et₂O and the flask degassed at -196°C.

In a second flask, N₂H₄·HCl (0.14 g, 2.0 mmol) and 5 ml of Et₂O were combined and the flask vacuum evacuated. The contents of the two flasks were combined at -78°C, warmed to 23°C, and stirred for 7 days. The hydrogen produced in the reaction was collected and measured (2.4 mmol). The fine, white solid obtained was collected by filtration and pumped on for 3 h. Infrared spectrum (cm⁻¹, KBr): 3334s, 3314s, 3280m, 3265m, 3207m, 2960w,br, 1800w,br, 1625m, 1613m, 1592m, 1500w,br, 1360w,sh, 1344w, 1297w, 1272m, 1147m, 1133s, 1116s, 939m, 923m, 720w, 564m, 500s. The filtrate was evaporated, and a crystalline white solid was recovered and recrystallized from cold Et₂O. Mp 130°C. Infrared spectrum (cm⁻¹, KBr): 2995m,sh, 2979m, 2934m, 2901m, 2880m, 1800s,sh, 1610s,br, 1387w, 1149w, 1091w, 1035m, 1000m, 896m, 780s,sh, 700s,br, 610s,br.

4.3.5. Pyrolysis studies

The TGA/DTA of each precursor was first recorded under N₂ or Ar. The results of these scans were used to plan the bulk pyrolysis of each precursor. Bulk pyrolysis samples were contained in quartz or platinum crucibles, and heating was accomplished in a horizontal tube furnace by using continuous evacuation of volatile byproducts or Ar, N₂, or NH₃ flow gases.

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