

## IV.A.5h Preparation and Reactions of Complex Hydrides for Hydrogen Storage: Studies of the $\text{Al}(\text{BH}_4)_3$ System

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### Introduction

ORNL is conducting research to develop the chemistry for a hydrogen storage system based on complex hydrides, chosen mostly from the borohydrides, amides/imides, alane or the alanates of the light elements in the periodic table. The focus of our work is the development of synthetic methods based on solution chemistry since these methods offer the most potential for scaling to kg and greater lot size. ORNL is collaborating with Metal Hydride Center of Excellence (MHCoe) partners by developing new materials and synthetic methods for producing materials and by studying chemical reactions. This work could lead to materials that will achieve the DOE/FreedomCAR performance targets for 2010. Synthetic methods are being developed and reactions are being studied for two types of target materials for hydrogen storage: complex anionic materials (MHCoe Project B) and amide/imide (M-N-H) systems (MHCoe Project C). For both types of materials ORNL is seeking (a) methods to scale-up synthesis of known materials or new materials identified by MHCoe partners; and (b) development of new materials. ORNL is also informally collaborating with MHCoe Project D, the alane focus group, with an emphasis on using the methods of organometallic solution chemistry in an effort to make the loss and uptake of hydrogen more reversible.

ORNL is formally participating in two of the MHCoe general projects: Project B – Complex Anionic Materials (borohydrides and alanates) and Project C – Amides/Imides (M-N-H systems). Within MHCoe Project B, the chemistry of liquid and volatile metal borohydrides such as  $\text{Al}(\text{BH}_4)_3$ ,  $\text{Ti}(\text{BH}_4)_3$ , and  $\text{Zr}(\text{BH}_4)_4$

is under investigation. These complexes are covalent molecular compounds with bridging M-H-B bonds. The concept is that volatile (or liquid)  $\text{M}(\text{BH}_4)_n$  can be transported to heated zone containing a catalyst for hydrogen production and deposition of a spent boron containing metal solid. The application of heat and elevated hydrogen pressure in the presence of a catalyst regenerates the hydrogen storage compound, which is transported to a cool zone of the reactor. Borohydride complexes of Al, Ti, and Zr have been shown to be precursors for the chemical vapor deposition of metal borides with the evolution of  $\text{H}_2$  as a by-product – the formation of crystalline ceramic-like metal boride product requires much higher temperature. Our work will focus on making the reaction reversible. Volatile or liquid hydrogen storage materials are anticipated to have some engineering advantages for scale-up including ease of heat and mass transfer. Within MHCoe Project C, the materials we are focusing on in the short run will be the mixtures  $\text{Li}_3\text{AlH}_6$  plus  $\text{LiNH}_2$  and  $\text{Li}_3\text{AlH}_6$  plus  $\text{Mg}(\text{NH}_2)_2$ , which seems to be a promising material, as identified by our collaborators.

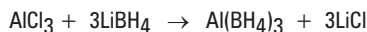
### Approach

This study involves materials from both known synthesis and those from newly designed synthetic procedures. The primary method used to follow the progress of reactions which release hydrogen is temperature programmed pressure measurement in which gaseous reaction products other than hydrogen are analyzed using a mass spectrometer or by infrared spectroscopy. Hydrogen uptake is investigated in a traditional Sieverts apparatus. Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) are available to characterize solid reaction products, and Raman and nuclear magnetic resonance (NMR) are available through collaboration with MHCoe partners. Each material examined will initially be involved in a dehydrogenation study. Those materials found to be suitable hydrogen storage material candidates will then be examined for regenerative (hydrogen absorption) capability. From these results, chemical (and-or procedural) adjustment to the most promising of the materials will be made in order to obtain the optimal hydrogen de/absorption capacity.

### Results

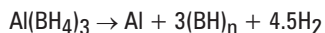
The bulk of the research conducted during this review period was related to MHCoe Project B – Complex Anionic Materials and concentrated on the preparation and dehydrogenation studies of

$\text{Al}(\text{BH}_4)_3$ . This compound is of particular interest because it is a high hydrogen content material (16.8 wt% hydrogen). Although the synthesis of this compound was accomplished by following the method reported by Schlesinger in 1953 [1], we initially obtained a poor yield (~25%). Several trials were performed using the following stepwise displacement reaction,



resulting in the conclusion that the key to a high yield (94% at best) was to use a two-fold excess of “finely ground”  $\text{LiBH}_4$ . Under these conditions, the reaction mixture of aluminum trichloride and lithium borohydride need only be heated to 50–70°C under vacuum with the reaction to ~85% in a period of only 1–2 hours. The product  $\text{Al}(\text{BH}_4)_3$  (found as a colorless volatile liquid with 120 torr vapor pressure at 0°C) was collected in a trap cooled with liquid nitrogen followed by purification by distillation using a -129°C slush bath of methylcyclohexane. All reactions and manipulations were performed on a vacuum line because the reactants, product, and by-products are pyrophoric in moist air. The compound was characterized by its mass spectrum and vapor phase FTIR spectrum. The resulting spectrum confirms the presence and general purity of the  $\text{Al}(\text{BH}_4)_3$  in our product. The spectrum clearly shows the terminal BH stretches at 2,558 and 2,490  $\text{cm}^{-1}$ , bridged BH stretches at 2,039  $\text{cm}^{-1}$ , bridged AlH stretches at 1,508  $\text{cm}^{-1}$ ,  $\text{BH}_2$  bends at 1,113  $\text{cm}^{-1}$ , and a AlB stretch at 607  $\text{cm}^{-1}$ , all of which agree with previously reported data [2].

The thermal decomposition of  $\text{Al}(\text{BH}_4)_3$  (theory 16.8%  $\text{H}_2$ ) was studied by allowing the  $\text{Al}(\text{BH}_4)_3$  vapor to come in contact with a heated tube containing a Ta foil substrate (for future powder XRD studies) and, in select instances, using a  $\text{CaF}_2$  substrate so the transmission FTIR spectrum of the product could be determined. Each pyrolysis study was performed at a fixed temperature for three to six hours, with length of time varied with degree of temperature. The results (shown in Figure 1) indicate that the hydrogen yield approached a value of 4.5 moles of  $\text{H}_2$  per mole of  $\text{Al}(\text{BH}_4)_3$  at 400°C. This was the expected result if the complete thermal decomposition of aluminum borohydride produced elemental aluminum, a polymeric borohydride compound, and hydrogen as shown in the equation:



The quantity of diborane decreases with an increase in temperature to the point that only a trace was evolved from reactions at 300–400°C (Figure 1).

FTIR spectroscopy has confirmed that diborane was produced as one of the gaseous products at lower temperature, with the resulting spectrum agreeing with those found in a previous publication [3]. Although a trace of unreacted  $\text{Al}(\text{BH}_4)_3$  was present in some

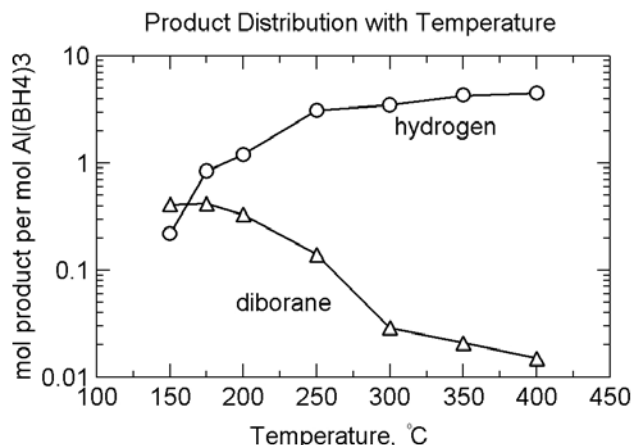
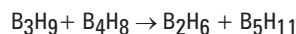
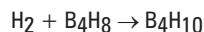
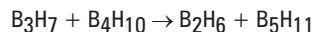
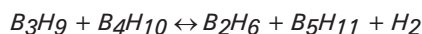
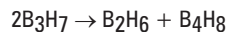
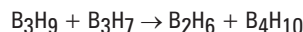
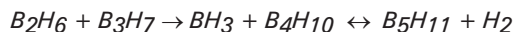
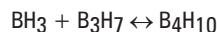
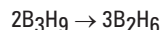
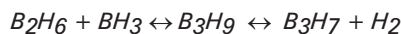


FIGURE 1. Temperature Dependence of the Yield of Hydrogen and Diborane from the Decomposition of  $\text{Al}(\text{BH}_4)_3$

samples, the spectrum obtained in this work is predominately that of diborane with the absorbance peaks observed at around 2,540, 1,600, 1,174, and 973  $\text{cm}^{-1}$ . The results indicate that the distribution of products was observed to be temperature dependent with a greater amount of diborane being collected at the lower temperatures while the hydrogen gas predominates at the higher temperatures.

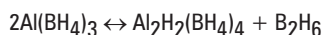
These results also appear to indicate that the release of diborane is first step in the pyrolysis of  $\text{Al}(\text{BH}_4)_3$ . The formation of hydrogen, then, is actually the result of the thermal decomposition of diborane, which has been extensively investigated and is reported to follow a rather complex mechanism as, shown below [4] (reactions involving  $\text{H}_2$  evolution or uptake shown in italics).



Under our experimental conditions and at moderate temperatures (<300°C), much of the diborane produced is able to leave the system. At higher temperatures, however, the diborane undergoes rapid thermolysis,

releasing hydrogen and leaving amorphous boron and/or a  $(\text{BH})_n$  polymer in the reaction tube residue.

At temperatures at or below 200°C, there is a large formation of a colorless, plastic-like solid, believed to be hydridoaluminum tetrahydroborate,  $[\text{AlH}(\text{BH}_4)_2]_n$ , which has been formulated as either a hydrogen-bridged dimer [5,6] or as a complex polymer [7]. This species is formed as the aluminum borohydride material loses diborane, as in the equation:



It was also observed that an equilibrium can be established between the formation of the  $[\text{AlH}(\text{BH}_4)_2]_n$  and the thermal decomposition of  $\text{Al}(\text{BH}_4)_3$ . At this point, it was observed that the formation of both hydrogen and diborane had been reduced to a minimal amount, even with a large amount of  $\text{Al}(\text{BH}_4)_3$  still being available for further pyrolysis. It is believed that as quickly as the  $\text{Al}(\text{BH}_4)_3$  was able to produce the diborane, the  $[\text{AlH}(\text{BH}_4)_2]_n$  present would take it back up and reform the aluminum borohydride. This occurrence, along with the complex mechanism exhibited by the diborane pyrolysis, might indicate one route of reversible hydrogen storage for this type of material. An infrared spectrum of this material shows terminal BH stretches at 2,527 and 2,490  $\text{cm}^{-1}$ , bridged BH stretches at 2,090  $\text{cm}^{-1}$ , bridged AlH stretches at 1,490  $\text{cm}^{-1}$ , and  $\text{BH}_2$  bends at 1108  $\text{cm}^{-1}$  [7]. A very broad peak between 2,000 and 1,600  $\text{cm}^{-1}$  with maximum at 1,838  $\text{cm}^{-1}$  could indicate that this solid contains polymeric Al–H–Al units [7].

At higher temperatures a dark residue remained in the reaction tube. The exact nature of yellow and dark brown residue is yet to be determined and those collected samples are just now being analyzed by inductively coupled plasma atomic emission (ICPAE) spectroscopy and other methods as they become available. While the previous reports have suggested that the yellow residue might actually be as  $\text{AlH}_2(\text{BH}_4)$ , the next step in the material's thermolysis as it evolves even more diborane [7]. Little is known of the exact nature of this species, and the collection of a sufficient amount of this yellow residue for characterization has proven to be difficult. However, methods are currently being devised for the future collection and subsequent characterization of this material.

Early ICPAE results show that the dark brown residue has an Al:B ratio that may be dependant upon the area from which it is collected. Specifically, it was found that, in the higher temperature reactions, residue from the reaction tube wall had a 1:1.5 Al:B ratio while residue from the same reaction but collected from the surface of the Ta foil had a ratio of 1:3.4 Al:B. This may be just another indication of how the diborane is the first product to be formed, resulting in boron being removed

from the initial decomposition product and then being deposited and concentrated onto the Ta foil surface as the diborane further decomposes. Further analysis of this residue will include powder X-ray diffraction, which should assist in establishing the exact nature of this material.

## Conclusions and Future Directions

Studies of the decomposition of  $\text{Al}(\text{BH}_4)_3$  will continue with our study concentrating on the nature of all the residue products being formed. Still slated on the agenda is to prepare a series of samples to be sent to E. Majzoub at Sandia National Laboratories for examination by Raman spectroscopy. We also plan to study the reaction of the residue formed at lower temperatures ( $\leq 300^\circ\text{C}$ ) with hydrogen in a high pressure reactor (2,000 psi) to see if the residue will take up hydrogen. Preparations for this material regeneration experiment are just about complete; the intention is to conduct the experiment in the very near future. Further pyrolysis studies will involve carrying out the reaction so that the diborane product is removed from the heated zone as rapidly as possible (flash vacuum pyrolysis conditions) and couple this with a determination of the ratio  $[\text{B}_2\text{H}_6]:[\text{H}_2]$ . We have the facilities and expertise to determine weight percent hydrogen yield and whether diborane is a product of decomposition of other metal borohydrides ( $\text{Ca}(\text{BH}_4)_2$  and  $\text{Mg}(\text{BH}_4)_2$ ). As time permits, we will begin investigating the chemistry of  $\text{Ti}(\text{BH}_4)_3$  as well. This will allow us to test Ti and Ti-Al catalysis of decomposition reaction of metal borohydrides such as  $\text{Al}(\text{BH}_4)_3$  and to determine whether catalysis helps to make the reaction reversible. The preparation of the known solid compounds  $\text{LiM}(\text{BH}_4)_4$  where  $\text{M} = \text{Al}, \text{Ti}$  will be accomplished by reaction of  $\text{M}(\text{BH}_4)_3$  with  $\text{LiBH}_4$  in solution, and the thermal decomposition reactions to make hydrogen and possible reversibility will be tested. We will attempt the preparation of  $\text{Ca}[\text{M}(\text{BH}_4)_4]_2$  and  $\text{Mg}[\text{M}(\text{BH}_4)_4]_2$  where  $\text{M}$  is Al, Ti by reaction of the alkali earth borohydride with  $\text{Al}(\text{BH}_4)_3$  in a solvent. We will study the thermal decomposition reactions of these compounds and determine reversibility of the hydrogen evolution. In MHCoe Project C, we will investigate the chemistry of  $\text{Li}_3\text{AlH}_6$  with ammonia as a prelude to using this compound in reactions with metal amides.

## FY 2007 Publications/Presentations

1. "Complex Hydrides for Hydrogen Storage: Studies of the  $\text{Al}(\text{BH}_4)_3$  System," Gilbert M. Brown, Douglas A. Knight, Joachim H. Schneibel, Ralph H. Ilgner, and Robert M. Smithwick, III, poster presented at the DOE 2007 Hydrogen Annual Review, Washington D.C., May 15–18, 2007.

2. “Metal borohydrides as Hydrogen Storage Materials: The Study of the Thermal Decomposition of  $\text{Al}(\text{BH}_4)_3$ ,” Douglas A. Knight, Gilbert M. Brown, Ralph H. Ilgner, and Robert M. Smithwick, III, paper presented at the ACS National Meeting, Boston, MA, August 19, 2007.

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