Complex Hydrides for Hydrogen Storage: Studies of the $Al(BH_4)_3$ System

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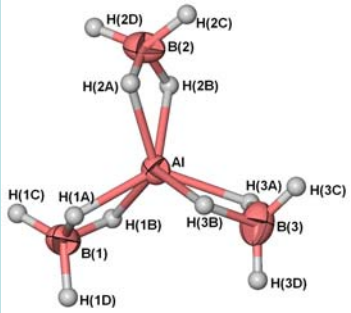
Project Outline

In collaboration with the Department of Energy's Metal Hydride Center of Excellence (MHCoE) team, this project focuses on the development of the chemistry for a hydrogen storage system based on complex metal hydrides.

- ORNL is looking at new materials and methods for synthesis of borohydrides, amides/imides, alane, and the alanates of the light elements in the periodic table.
- This presentation focuses on a preliminary study of the dehydrogenation chemistry exhibited by aluminum tris(tetrahydroborane), $Al(BH_4)_3$.

Chemistry of Liquid and/or Volatile Metal Borohydrides

The thermal decomposition of $Al(BH_4)_3$, $Ti(BH_4)_3$, and $Zr(BH_4)_4$ are under investigation for H_2 storage.



These covalent molecular compounds have double bridge M-H-B bonding as illustrated for $Al(BH_4)_3$.*

* Aldridge, S; Blake, A. J.; Downs, A. J.; Gould, R. O.; Parsons, S.; Pulham, C. R.; *Dalton Trans.*, 1007, **1997**.

Advantages for Using Metal Borohydrides

- **The high hydrogen content of these materials more then meets the DOE requirements.**
- **Laboratory synthesis is fairly easy while many metal borohydrides are already commercially available.**
- **The liquid and volatile nature of some of these type of materials may aid mass-transfer in complicated on-board fuel systems.**
- **Although these materials tend to be pyrophoric and reactive in air, they can be easily handled using established methods developed for the manipulation of air-sensitive materials.**

Preparation of $Al(BH_4)_3$

$$AlCl_3 + 3\ LiBH_3 \rightarrow Al(BH_4)_3 + 3LiCl$$

A 50 - 130 °C, stepwise replacement reaction.*

The product is a volatile, pyrophoric liquid (120 torr at 0 °C, ρ = 0.55 g/mL) that can be isolated and purified on a high vacuum line.

Final product can be characterized by MS, IR, and NMR analysis.

The key component in this reaction is to use a two fold excess of finely ground $LiBH_4$, which is necessary in order to achieve a 94 % yield.

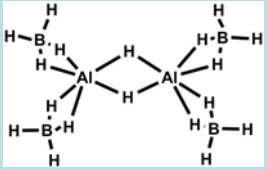
* Schlesinger, H. I.; Brown, H. C.; Hyde, E. K.; *J. Am. Chem. Soc.*; *75*, *209*, **1953**.

Dehydrogenation Reaction Conditions

- **~1.5 to 3.0 mmol of $Al(BH_4)_3$ material was collected in a liquid N_2 cold trap adjacent to the reaction tube.**
- **$Al(BH_4)_3$ vapor (vapor pressure = 359 torr at 25 °C) was allowed to flow into the reaction tube which was constantly heated at selected temperatures.**
- **H_2 and B_2H_6 levels were examined and removed from the reaction tube at regular (15 – 60 min.) intervals.**

The Reversible Loss of Diborane is the First Step in the Dehydrogenation Process

The $Al_2H_2(BH_4)_4$ Dimer is One Possible Result From the Loss of Diborane



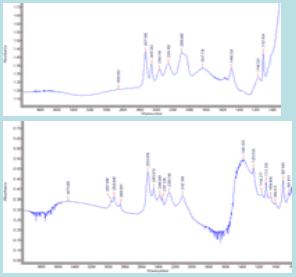
At the lower temperatures (<200° C), an equilibrium was established between $Al(BH_4)_3$ and $Al_2H_2(BH_4)_4$ as shown in:

$$2Al(BH_4)_3 \leftrightarrow Al_2H_2(BH_4)_4 + B_2H_6^*$$

* (a) Maybury, P. C.; Larrobu, J. C.; *Inorg. Chem.*, 2, *885*, **1963**. (b) Noth, H.; Rurlander, R.; *Inorg. Chem.*, 20, *1063*, **1981**. (c) Demachy, I.; Volatron, F.; *Inorg. Chem.*, 33, *3985*, **1994**.

The IR Spectra of the Colorless Solid Formed at 175° C

- **Top – The sample was deposited on the CaF_2 plate *in situ*.**
- **Bottom – The colorless residue was dissolved in toluene, applied drop-wise to the CaF_2 plate, and then vacuum dried.**
- **Both are typical results as were previously reported found for the $[AlH(BH_4)_2]_n$ polymer.***



* Oddy, P. R.; Wallbridge, M. G. H.; *Dalton Trans.*, 572, **1978**.

Dehydrogenation of $Al(BH_4)_3$

theory 16.8 wt % H_2

(Product distribution is temperature dependent – 3 to 6 hr reaction time)

Temperature ° C	H_2 per $Al(BH_4)_3$ (wt % H_2)	B_2H_6 per $Al(BH_4)_3$	Residue
175	1.4 (3.9 wt %)	0.68	Colorless, sublimable residue, likely composition $[AlH(BH_4)_2]_2$
200	1.3 (3.8 wt %)	0.36	Both light brown and colorless residue
250	3.5 (10.0 wt %)	0.16	Dark brown residue with a trace of colorless residue
300	5.0 (13.8 wt %)	0.041	Dark brown residue
350	5.4 (15.3 wt %)	0.026	Dark brown residue
400	5.9 (16.5 wt %)	0.021	Dark brown residue

Clues to the $Al(BH_4)_3$ Dehydrogenation Mechanism

- **The Al and B elemental analysis of the residue formed at the higher temperature indicates that boron is more concentrated on surfaces facing the reaction gasses.**
- **The colorless residue found at low temperatures is suspected to be an $[AlH(BH_4)_2]_2$ dimer or a complex hydrogen-bridged polymer.**
- **The first step in the $Al(BH_4)_3$ pyrolysis appears to be the release of diborane, followed by its own thermal decomposition to form H_2.**

Diborane Thermal Decomposition

A Complex Mechanism Forming H_2 in Several Steps:*

$$2B_2H_6 \leftrightarrow BH_3 + B_3H_9$$
$$B_2H_6 + BH_3 \leftrightarrow B_3H_9 \leftrightarrow B_3H_7 + H_2$$
$$2B_3H_9 \leftrightarrow 3B_2H_6$$
$$BH_3 + B_3H_7 \leftrightarrow B_4H_{10}$$
$$B_2H_6 + B_3H_7 \leftrightarrow BH_3 + B_4H_{10} \leftrightarrow B_5H_{11} + H_2$$
$$B_3H_9 + B_3H_7 \leftrightarrow B_2H_6 + B_4H_{10}$$
$$2B_3H_7 \leftrightarrow B_2H_6 + B_4H_8$$
$$B_3H_9 + B_4H_{10} \leftrightarrow B_2H_6 + B_5H_{11} + H_2$$
$$B_3H_7 + B_4H_{10} \leftrightarrow B_2H_6 + B_5H_{11}$$
$$H_2 + B_4H_8 \leftrightarrow B_4H_{10}$$
$$BH_3 + B_4H_8 \leftrightarrow B_5H_{11}$$
$$B_3H_9 + B_4H_8 \leftrightarrow B_2H_6 + B_5H_{11}$$

* L. H. Long, *J Inorg Nucl Chem*, 32, *1097*, **1970**, and references therein.

The Potential for Reversible Hydrogen Storage

- The equilibrium observed between $Al(BH_4)_3$ and $Al_2H_2(BH_4)_4$ suggests one route of hydrogen storage reversibility.
- The complex diborane thermal decomposition mechanism also indicates several points of reversibility.
- These two anomalies combined may be key factors leading to the viable regeneration of metal borohydride hydrogen storage materials.

Project Summary

- Pyrolysis of aluminum borohydride demonstrates how a substantial amount of hydrogen can be obtained from these complex borohydride materials.
- The equilibrium observed between $Al(BH_4)_3$ and $Al_2H_2(BH_4)_4$, in conjunction with the complex mechanism of the pyrolysis of diborane, suggests a route for reversible hydrogen storage.
- Further studies of metal borohydrides (including those with Mg, Ca, and Ti) are planned to identify those materials having the most favorable hydrogen evolution and regenerative capabilities.

(This presentation does not contain any proprietary information)