

IV.B.5j Safety Analysis and Applied Research on the Use of Borane-Amines for Hydrogen Storage

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* Deceased, May 19, 2007
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Contract Number: DE-FC36-05GO15060

Project Start Date: March 1, 2005
Project End Date: October 31, 2009

Accomplishments

- Various processes were evaluated for the laboratory preparation of ammonia-borane (AB). Borane-tetrahydrofuran (THF) plus ammonia gave the best yield and purity.
- Various processes were evaluated for the laboratory preparation of methylamine-borane (MeAB). Borane-THF plus methylamine gave the best yield and purity.
- As a first attempt to produce a "liquid fuel," melting points were measured for nine AB/MeAB mixtures over the range: (90-10%)AB/(10-90%)MeAB. The 30-40% AB mixtures had the lowest melting point of 35-37°C.
- Co-synthesis of a 35% AB/65% MeAB mixture gave an oil product at 30°C, a near "liquid fuel," which crystallized at 25°C.
- AB and MeAB samples were provided to the University of Washington and Pacific Northwest National Laboratory (PNNL) partners in the CHSCoE. Additional studies on the thermal and catalytic release of hydrogen from these compounds or their mixtures were performed at PNNL.



Objectives

- Provide guidance for safe handling of amine-borane compounds throughout the Chemical Hydrogen Storage Center of Excellence (CHSCoE).
- Evaluate hydrogen on-board generation and off-board regeneration capability and capacity of N-substituted amine-borane compounds to determine if a laboratory scale system can be developed that safely meets the DOE 2010 target of 6 wt% hydrogen.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Weight and Volume
- (C) Efficiency
- (R) Regeneration Processes

Technical Targets

- Safety Analysis of Storage Materials
- DOE 2010 target of 6 wt% Hydrogen Release

Introduction

To enable chemical hydrogen storage using amine-boranes, their safety, cost, synthesis efficiency, and ability of to meet DOE technical targets must be evaluated. Specifically, improved processes for low cost and high yield preparation of ammonia borane and N-substituted amine borane compounds are required, as are the parameters for the safe handling and transportation of these compounds and mixtures. Liquid fuel formulations are also desired to enable simplified hydrogen release and off-board regeneration processes.

Approach

Chemical synthesis techniques and our knowledge of amine-borane chemistry were applied to evaluate the most efficient syntheses of ammonia borane and N-substituted amine boranes. Reaction byproducts and their influence on fuel properties were determined. Using kinetics analysis of the thermal decomposition of the products at various times and temperatures, an evaluation of the safe handling parameters of this class of compounds was performed. Materials prepared in-house were compared with those available from

commercial vendors. Blending of liquid N-substituted amine boranes with solid ammonia borane was performed to search for low-melting mixtures that may be suitable as liquid fuel formulations. In addition, co-synthesis of promising compositions was carried out to evaluate co-synthesis strategies and the physical properties of blended vs. co-synthesized materials. Promising materials were supplied to partners within the CHSCoE for further evaluation of thermal, chemical, or catalytic activation of hydrogen release from these compounds.

Results

Synthesis of Ammonia Borane (AB): Several synthetic routes were surveyed to assess the chemical yield and purity of the resulting AB. Salt displacement reactions and borane-donor exchange reactions with ammonia were carried out and the products analyzed.

Salt displacement reactions to prepare ammonia borane (AB):



Table 1 outlines the results of salt displacement reactions, where X = carbonate, bicarbonate, formate, acetate, and the halides chloride, bromide, and fluoride. The most efficient salt displacement reactions that also yielded the most pure product as determined by melting point and B-11 nuclear magnetic resonance (NMR)

TABLE 1. Survey of Salt Displacement Reactions for the Preparation of Ammonia Borane (AB)

Ammonium Salt	Solvent & conditions	Results
(NH ₄) ₂ CO ₃	<ul style="list-style-type: none"> THF Room temp then heat 	<ul style="list-style-type: none"> 70% yield mp¹ 115 -120°C clean NMR
(NH ₄)HCO ₃	<ul style="list-style-type: none"> THF Room temp then heat Difficult to stir 	<ul style="list-style-type: none"> 64% yield mp 120 -125°C clean NMR
NH ₄ OCHO	<ul style="list-style-type: none"> THF Room temp then heat 	<ul style="list-style-type: none"> 60% yield mp 100 -105°C impurities in NMR
NH ₄ OAc	<ul style="list-style-type: none"> THF Room temp then heat Difficult filtration 	<ul style="list-style-type: none"> 70% crude yield very impure
NH ₄ Br	<ul style="list-style-type: none"> THF Room temp then heat 	<ul style="list-style-type: none"> 31% yield clean NMR
NH ₄ Br	<ul style="list-style-type: none"> THF plus additive Room temp then heat 	<ul style="list-style-type: none"> 45% yield clean NMR
NH ₄ Cl	<ul style="list-style-type: none"> THF plus additive Room temp then heat 	<ul style="list-style-type: none"> 4% yield
NH ₄ F	<ul style="list-style-type: none"> THF plus additive Room temp then heat 	<ul style="list-style-type: none"> low yield very impure by NMR

¹ mp - melting point

resulted from the reaction of sodium borohydride with ammonium carbonate or bicarbonate. Other salts provided for poor yield and/or low purity.

Borane donor exchange syntheses provided better purity and yields as compared to the salt displacement reactions.



Table 2 summarizes the results of the borane donor exchange synthesis. It was found that ammonia displacement of the borane-THF complex gave the best yields and purities, and that this approach was superior to the salt displacement reaction.

TABLE 2. Survey of Donor Exchange with Ammonia for the Preparation of AB

Borane complex	Solvent & conditions	Results
BH ₃ -THF	<ul style="list-style-type: none"> THF BH₃-THF added to NH₃ -78°C then room temp 	<ul style="list-style-type: none"> 68% yield mp 120 -125°C clean NMR
BH ₃ -SMe ₂	<ul style="list-style-type: none"> THF -20°C then room temp 	<ul style="list-style-type: none"> 62% crude yield strong sulfur odor

Synthesis of methylamine borane (MeAB):

Methylamine borane syntheses were also surveyed, and, similarly to the AB synthesis, donor exchange reactions gave higher yields with better purities.

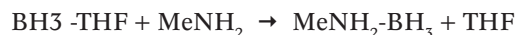


Table 3 summarizes the results of MeAB synthesis. Reaction of the THF adduct of borane with methylamine at low temperatures gave high yields of product MeAB. The melting point varied considerably with the temperature at which the methylamine was added to the borane-THF adduct. Addition at lower temperature resulted in a higher melting point of MeAB. This may be an important variable to control for the preparation of liquid fuel compositions.

TABLE 3. Survey of Donor Exchange with Methylamine for the Preparation of MeAB

Reaction Route to MeAB	Solvent & conditions	Results
Salt Elimination: MeNH ₃ Cl + NaBH ₄	<ul style="list-style-type: none"> THF solvent plus additive Room temp then heat 	<ul style="list-style-type: none"> 51% yield
Donor Exchange: BH ₃ -THF + MeNH ₂	<ul style="list-style-type: none"> THF solvent CH₃NH₂ added to BH₃-THF -20°C then room temp 	<ul style="list-style-type: none"> 91% yield mp 55 - 56°C clean NMR
BH ₃ -THF + MeNH ₂	<ul style="list-style-type: none"> THF solvent (CH₃)₂NH added to BH₃-THF -5°C then room temp 	<ul style="list-style-type: none"> 88% yield mp 36 - 38°C clean NMR

Preparation of liquid MeAB/AB mixtures: Because MeAB is a low melting solid, it was felt that making mixtures of MeAB with high melting AB could result in low melting mixtures leading to potential liquid fuel compositions. To search for such low melting compositions, an array of nine compositions of MeAB in AB ranging from 90% MeAB: 10% AB to 10% MeAB:90% AB were prepared. Compositions in the 70-60% MeAB:30-40% AB mixtures were found to have low melting points of around 36-37°C. Assuming that MeAB can release 2 equivalents of hydrogen, and AB releases 2 to 2.5 equivalents of hydrogen, the low melting MeAB/AB compositions can potentially release 10-11 wt% hydrogen, exceeding the 2010 targets and potentially meeting 2015 hydrogen capacity targets.

Co-synthesis of MeAB/AB mixtures: In the large scale synthesis of a fuel mixture such as MeAB/AB, it may be possible to co-synthesize the mixture rather than independently preparing the two pure components and blending them. This is particularly appropriate given that both MeAB and AB are efficiently prepared using the ammonia-donor exchange reactions described above. Scoping reactions were performed to examine the feasibility of this approach. Using a similar procedure to that developed for the donor exchange reactions of the pure components, methylamine and ammonia (mole ratio 65:35) were added to a THF solution of the THF-borane adduct at low temperature. Warming the mixture to room temperature followed by isolation of the products resulted in a mixture of MeAB/AB that had a few minor impurities as determined by NMR, took the form of an oil at 30°C, and solidified at 25°C. Because handling safety of these materials has yet to be determined, shipment to CHSCoE partners was not completed.

Conclusions and Future Directions

Professor Clint Lane passed away suddenly, shortly after returning from the annual Hydrogen Program Merit Review Meeting. The work that Dr. Lane and his student, Sharon Baker, were performing is crucial to the CHSCoE; therefore, the CHSCoE is currently working through this loss. While there is no way to replace Dr. Lane's expertise or his valuable contributions to the CHSCoE and to the fields of boron and process chemistry, his important work must be carried on as part

of the CHSCoE's activities. Dr. Lane's work has laid the groundwork for large scale processes for the preparation of amine borane fuels, including the potential for liquid fuel formulations. While the CHSCoE does not yet have a definite plan as to how to carry on his work, his recent results point the direction that must be followed:

- Optimize the yields and characterize any impurities in the AB and MeAB syntheses.
- Examine the *in situ* generation of THF-borane as a means to lower the cost of fuel synthesis.
- Continue the search for low melting liquid fuel compositions and evaluate the role of minor impurities on the lowering of the melting point, as well as their influence on hydrogen release and spent fuel regeneration.
- Determine safe handling parameters of these materials, particularly the new liquid fuels compositions, to enable sharing of samples with CHSCoE partners.

FY 2007 Publications/Presentations

Reports

Four Quarterly Reports to DOE.

Presentations

1. Clint Lane and Sharon Baker, poster, "Applied Research on the Use of Amine-Borane Materials for Hydrogen Storage," DOE Hydrogen Annual Merit Review Meeting, Washington, D.C., May, 2007.