

Safety Analysis and Applied Research on the Use of Borane-Amines for Hydrogen Storage

Clint Lane

May 2005

A project that is part of
**DOE Chemical Hydrogen Storage
Center of Excellence**

This presentation does not contain any proprietary or confidential information



Project ID # STP14

General Project Overview

Timeline

- Project start date - FY2005
- Project end date - FY2009
- Percent complete - New Start

Budget

- Total project funding - \$420K (requested)
 - DOE share - \$332K
 - Contractor share - \$88K
- Funding for FY2005 - \$76K

Project Partner

Sigma-Aldrich Corporation

In addition to the internal partners that are part of the Chemical Hydrogen Storage Center of Excellence, Sigma-Aldrich is an external partner for the project efforts at Northern Arizona University.

Numerous borane-amines are manufactured by Sigma-Aldrich and this partner will supply safety, reactivity and preparative methods to enable the design and discovery of new borane-amines as potential chemical hydrogen storage materials.

The contractor cost sharing mainly comes from Sigma-Aldrich in the form of contributions of all required chemicals, reagents, solvents and all common laboratory equipment and supplies that are needed for the project work at NAU.

Weight and Volume Technical Barrier

Borane-amine complexes have great potential for use as a chemical hydrogen storage fuel due to their stability and the high gravimetric content of hydrogen. For example, the simplest complex, borane-ammonia (H_3NBH_3), contains 19.5 wt% H, which is higher than the wt% H in LiBH_4 . The development of new borane-amine based materials appears to have a very high potential to meet the 2010 goal of 6 wt% system-level capacity and perhaps even the 2015 goal of 9 wt%.

The goal is to develop a process to release significant hydrogen to provide a viable fuel, and to give a stable dehydrogenated intermediate that can be conveniently and safely pumped out of the spent fuel tank for off-board hydrogenation back to a stable borane-amine based fuel.

Regeneration Process Technical Barrier

Realistically, all the hydrogen in borane-ammonia will not be available for use as a fuel because the product of such a direct thermolysis is boron nitride, $(\text{BN})_x$, which is a solid with near diamond like physical properties and insoluble in any convenient solvent. Controlled partial dehydrogenation of borane-ammonia is known to give borazine which is the boron-nitrogen analog of benzene.

Based on the known processes for catalytic hydrogenation of benzene, it appears that catalytic hydrogenation of a substituted borazine could potentially be developed into an energy efficient process for the off-board regeneration of a borane-amine based chemical hydrogen storage fuel.

Overall Project Objectives

- Provide guidance for safe handling of borane-amine compounds throughout the Chemical Hydrogen Storage Center.
- Evaluate the hydrogen on-board generation and off-board regeneration capability and capacity of N-substituted borane-amines.

Project Collaborations

- Safety analysis and the development of safety protocols will involve working closely with LANL and PNNL.
- Guidance for safe handling of boron hydride compounds is being offered to those partners in the Chemical Hydrogen Storage Center of Excellence that lack experience with these reactive materials. Intematix is one example of a partner where safety assistance is being provided.
- All work involving the on-board hydrogen generation capability and capacity of borane-amines and the off-board hydrogenation of substituted borazines will be done in close cooperation with the following partners:
 - LANL and PNNL
 - University of Pennsylvania
 - University of Alabama

Approach for FY2005 Tasks

Safe Handling of Borane-Amine Compounds and Safety Guidance for Chemical Hydrogen Storage Center.

- Technical articles and patents dealing with the preparation, physical properties, chemical properties, safety aspects of borane-amines and borazines will be collected and a report and electronic database will be shared with the Center team members.
- Anecdotal observations will be collected from organizations and research groups currently or formerly active in borane-amine chemistry and reports will be shared with Center team members.
- Active consultation and review of the Chemical Hygiene Plans of team members regarding methods and apparatus for safe handling of borane-amine and related compounds.

FY2005 Project Task Summary

Task 1 Evaluation of safe handling for Borane-amines.

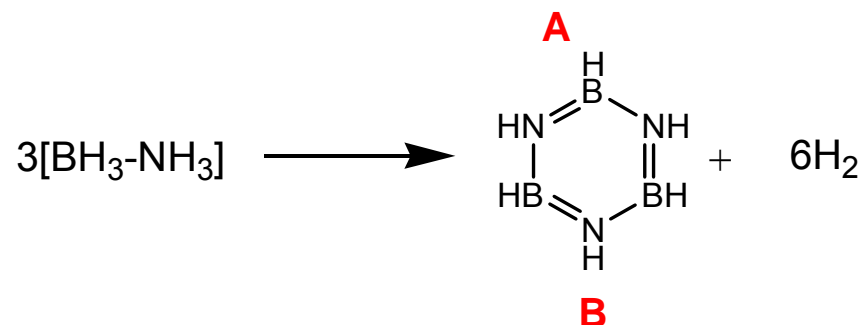
Milestone - Deliverable report on or before 08/31/05 to Center team members on hazards associated with the preparation and handling of borane-amines and means to mitigate these hazards.

Task 2 Safety guidance for CHS Center of Excellence.

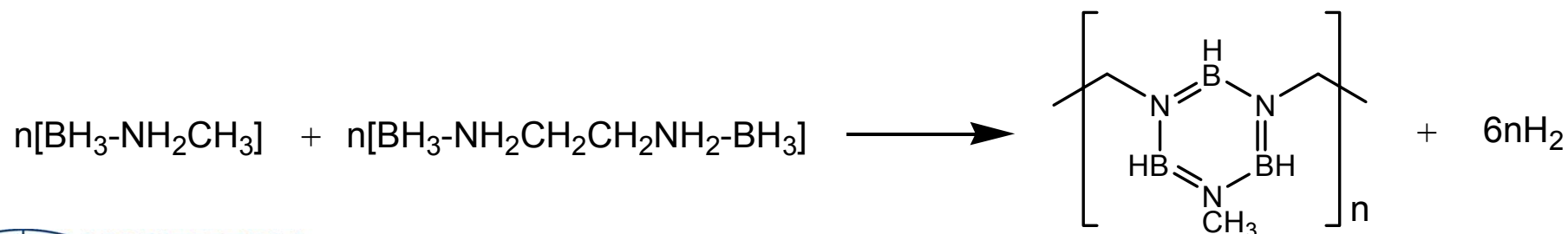
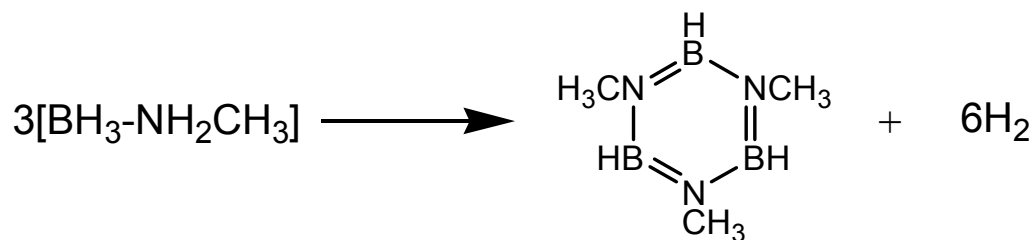
Milestones - Three or four safety related site visits during second and third quarters of 2005 with a deliverable trip report for each site visit that is shared with LANL and PNNL and team member visited.

Technical Concept Summary - Future Work

Thermolysis of borane-ammonia is known:



However, boron nitride (**A**) and borazine (**B**) have unattractive properties. Can N-substituted compounds provide a solution?



Future Work - Project Task Summary

Task 3 Prepare $\text{CH}_3\text{NH}_2\text{-BH}_3$ and determine solubility and stability.

- Milestone (FY2006) - Stable solution of a substituted borane-amine compound containing (theoretically) at least 9 wt% hydrogen.
- Deliverable - Report on material properties and behavior with a go/no-go decision based on success of reaching milestone.

Task 4 Hydrogen evolution from substituted borane-amine compounds.

- Milestone (FY2007) - Demonstrate production of a stable borazine plus hydrogen.
- Deliverable - Report on results with a go/no-go decision.

Task 5 Prepare $\text{BH}_3\text{-H}_2\text{NCH}_2\text{CH}_2\text{NH}_2\text{-BH}_3$ and determine solubility and stability.

- Milestone (FY2007) - Stable solution of a substituted bis-borane-amine compound containing (theoretically) at least 9 wt% hydrogen.
- Deliverable - Report on material properties and behavior with a go/no-go decision based on success of reaching milestone.

Future Work - Project Task Summary (cont.)

Task 6 Study hydrogen evolution from a solution of $\text{BH}_3\text{-H}_2\text{NCH}_2\text{CH}_2\text{NH}_2\text{-BH}_3$ or related compound.

- Milestone (FY2008) - Demonstrate production of a stable borazine plus hydrogen.
- Deliverable - Report on results with a go/no-go decision.

Task 7 Develop catalytic process for hydrogen evolution from substituted borane-amine compounds.

- Milestone (FY2008) - Demonstrate catalytic production of a stable borazine plus hydrogen.
- Deliverable - Report on catalyzed hydrogen evolution from substituted borane-amine compounds with a go/no-go decision.

Future Work - Project Task Summary (cont.)

Task 8 Prepare a substituted borazine and study reactivity.

- Milestone (FY2009) - Completion of hydrogenation study of a substituted borazine.
- Deliverable - Report on material properties and behavior.

Task 9 Develop catalytic process for hydrogenation of a substituted borazine compound.

- Milestone (FY2009) - Demonstrate catalytic hydrogenation of a substituted borazine to give a stable borane-amine compound.
- Deliverable - Report on catalyzed hydrogenation of a substituted borazine.

Timeline Summary of Project Tasks

Tasks	FY2005	FY2006	FY2007	FY2008	FY2009
Task 1 Evaluation of safe handling for borane-amines.	■				
Task 2 Safety guidance for CHS Center of Excellence.	■				
Task 3 Prepare borane-amine and determine solubility and stability.		■ ■			
Task 4 Hydrogen evolution from substituted borane-amine compounds.			■ ■		
Task 5 Prepare bis-borane-amine and determine solubility and stability.			■ ■		
Task 6 Study hydrogen evolution from solution of bis-borane-amine compounds.				■ ■	
Task 7 Development of a catalytic process for hydrogen evolution from borane-amine compounds.				■ ■	
Task 8 Prepare a substituted borazine and study reactivity.				■	
Task 9 Develop catalytic process for hydrogenation of a substituted borazine compound.					■

■ Go/No-Go decision point based on success of reaching milestone.

Conclusions

This project is part of a multi-site team effort to discover and develop chemical hydrogen storage materials and technology to meet DOE cost and performance targets. The direct use of compressed hydrogen gas seems to offer the simplest solution. However, the major infrastructure costs for hydrogen fueling stations along with the safety issues involved with the handling of hydrogen gas by the general public points to the need for a more advanced concept for on-board hydrogen storage.

Directly reversible dehydrogenation-hydrogenation systems, such as metals hydrides, overcome the need for high-pressure compression of hydrogen gas. However, all of these proposed and studied technologies still require completely redesigned fueling stations and necessitates the handling of hydrogen gas by consumers.

Of all known technologies, it appears that the use of chemical hydrogen storage materials in liquid form has the greatest potential to meet the cost and performance targets while being as safe or safer to handle than gasoline. Numerous chemical hydrogen systems need to be studied and evaluated. One of the more attractive candidates is a system based on borane-amine complexes.

Acknowledgements

The opportunity to participate as a team member in the DOE Chemical Hydrogen Storage Center of Excellence is sincerely appreciated. Many individuals at DOE could be listed, but the following have provided significant assistance:

- Bill Tumas, LANL
- Dave Thorn, LANL
- Tom Baker, LANL
- Carole Read, DOE, Washington DC

Finally, Professor Larry Sneddon, University of Pennsylvania, must be thanked for providing the initial motivation to consider boron-nitrogen chemistry as a means to store hydrogen. This occurred a few years ago and now we are team members in the DOE CHSCoE.

Supplemental Slides

The following three slides are for the purposes of the reviewers only – they will not be presented as part of the poster presentation.

Publications and Presentations

General interest lecture

Department of Chemistry

Arizona State University

Tempe, AZ

February 14, 2005

Hydrogen Safety

The most significant hydrogen hazard associated with this project:

Fire and potential explosions are the most significant hazards. Various borane-amine complexes will be prepared using more reactive borane-Lewis base complexes and/or diborane. The risk of a fire or explosion is always present when handling diborane and other highly active boron hydrides. Air exposure can generate hydrogen and a source of ignition (diborane is pyrophoric) can result in a fire or an explosion of a hydrogen/flammable vapor/air mixture.

Hydrogen Safety

Our approach to deal with this hazard:

All work with the highly active boron hydrides will be carried out on a relatively small laboratory scale (maximum of 100 mmoles of active boron hydride per reaction). In addition, all reactions will be run under an inert atmosphere and all handling and processing will be done in a hood. If utilized, diborane will only be generated as needed and immediately complexed with an amine.