

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

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May 2006

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 # STP28

# General Project Overview

## Timeline

- Project start date - FY05
- Project end date - FY09
- Percent complete - 20%

## Budget

- Total funding\* - \$420K (requested)
    - DOE share - \$332K
    - Contractor share - \$88K
  - Funding received FY05 - \$48K<sup>#</sup>
  - Funding for FY06 - \$78K<sup>#</sup>
- (\*over 5 years. <sup>#</sup> includes cost sharing.)

## Barriers

- Weight % H
- Volume % H
- Regeneration

## Partners

- LANL
- PNNL
- Rohm & Haas
- U of Pennsylvania

# Overall Project Objectives

- Safety analysis of amine-borane compounds and dissemination of this information throughout the Chemical Hydrogen Storage Center.
- Evaluation of hydrogen on-board generation and off-board regeneration capability and capacity of N-substituted amine-borane compounds to determine if a system can be developed that safely meets the DOE 2010 target of 6-wt% hydrogen.

# Approach

## Safety Analysis of Amine-Borane Compounds and Safety Guidance for Chemical Hydrogen Storage Center.

- Literature searching for preparation, physical properties, chemical properties and safety aspects of amine-borane adducts and related N-B-H compounds.
- Collection of Material Safety Data Sheets and technical information from manufacturers of amine-borane compounds and borazine.
- Anecdotal observations from organizations and research groups currently or formerly active in amine-borane chemistry.

# Accomplishments

All the information collected about amine-borane compounds has now been compiled in a document entitled:

## **Ammonia-Borane and Related N-B-H Compounds and Materials: Safety Aspects, Properties and Applications**

An electronic version of this document was supplied to all the partners in the Chemical Hydrogen Storage Center of Excellence in April 2006. An electronic database with links to pdf copies of essentially all 440+ references is now ready for distribution.

The following slides provide a greatly condensed version of this survey.

# Introduction

Amine-borane complexes have great potential for use as a key component in hydrogen storage fuels due to their stability and the high gravimetric content of hydrogen in these compounds. For example, the simplest complex, ammonia-borane ( $\text{H}_3\text{NBH}_3$ ), contains 19.5-wt% H. The 2015 DOE goal is to develop and achieve an on-board hydrogen storage system with at least 9-wt% H. Thus, an amine-borane-based system has reasonable potential to meet this goal. However, many issues need to be addressed.

Technical and economic issues related to the possible use of ammonia-borane (AB) for the generation of hydrogen for fuel cell applications were evaluated in prior DOE funded reports.<sup>1</sup> Regardless of the issues, the potential use of AB for hydrogen storage in automobiles has reached the popular scientific press.<sup>2</sup> Also, AB is being investigated as a hydrogen storage material for portable fuel cell powered devices.<sup>3</sup>

Safety may also be an issue. Diborane is an obvious precursor for AB, but  $\text{B}_2\text{H}_6$  is toxic and pyrophoric.<sup>4</sup> The amine adducts of borane have increased stability and reduced reactivity in comparison to  $\text{B}_2\text{H}_6$ , which means the safety concerns may be less than those for  $\text{B}_2\text{H}_6$ . However, the safety of amine-borane complexes must be examined.

# Introduction (continued)

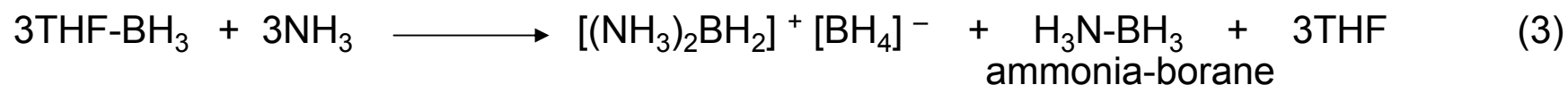
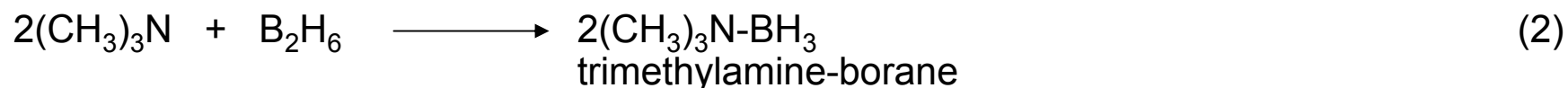
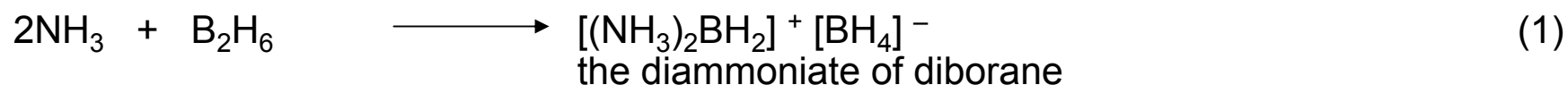
A number of reviews have appeared covering the chemistry of amine-borane adducts.<sup>5</sup> Also, an older survey of synthetic procedures for almost all known boron-nitrogen compounds (except for boron nitrides) is available.<sup>6</sup> The present survey overlaps the earlier reviews as necessary to give a complete picture of the chemistry of AB and related N-B-H containing materials. If a B-N compound does not contain B-H, then it was omitted from the survey.

The amine-cyanoboranes and amine-carboxyboranes were not covered since the main interest in these compounds appears to be related to the physiological activity of various derived boronated biomolecules. A recent theoretical study of the role of a B-N dative bond in the biochemical activity of these boronated biomolecules provides a listing of these B-N compounds and their physiological activity.<sup>7</sup>

Finally, it is interesting to note that the reviews of boron and its commercial uses by the US Geological Survey seldom mention any B-N or B-H compounds.<sup>8</sup> B-O compounds completely dominate the current commercial uses and applications of boron chemistry.

# Introduction (continued)

Before discussing the stability and reactivity (safety aspects) of amine-borane adducts, it is important to consider how the compounds are prepared. The direct reaction of ammonia with diborane does not give a Lewis acid-base complex. Instead an unsymmetrical cleavage occurs. This is in contrast to the direct reaction of trimethylamine with diborane, which gives the expected Lewis acid-base complex. When ammonia is added to a tetrahydrofuran (THF) solution of borane-THF, the result is a 50/50 mixture of the products from symmetrical and unsymmetrical cleavage. These reactions are illustrated in equations 1-3.



Sheldon Shore extensively studied the above chemistry of diborane and ammonia and a review of his work covers all details with references to the literature.<sup>9</sup>



# Safety Aspects

The properties and stability of AB and the diammoniate of diborane are quite different. At ambient temperatures the diammoniate slowly undergoes decomposition with evolution of hydrogen resulting in pressure build-up in storage vessels.<sup>10</sup> The recommendation is to store the compound at  $-78\text{ }^{\circ}\text{C}$ .<sup>10</sup> It is possible to prepare AB from the diammoniate and this is reported to give a material that is somewhat unstable at room temperature.<sup>11</sup> However, when AB is prepared from  $(\text{CH}_3)_2\text{S-BH}_3$  and ammonia and is recrystallized from diethyl ether to remove the diammoniate by-product, then the produced high-purity crystalline AB is found to be stable for 5 days at  $70\text{ }^{\circ}\text{C}$ .<sup>12</sup> Another investigator also found that high purity AB with a sharp melting point did not show any sign of decomposition (no pressure build-up) over a 2 month period at room temperature and could be sublimed at temperatures up to almost  $100\text{ }^{\circ}\text{C}$  under high vacuum with no decomposition.<sup>13</sup> When AB of good apparent purity was prepared by the reaction between  $\text{NaBH}_4$  and an ammonium salt, the solid AB appeared to be stable indefinitely at room temperature.<sup>14</sup>

It appears that high purity AB can be safely stored in a closed vessel at room temperature, but mixtures or solutions need to be vented until the absence of pressure build-up is assured.

## Safety Aspects (continued)

The decomposition of AB at high temperatures with hydrogen evolution is well documented and is reported to become vigorous at near 120 °C.<sup>15</sup> If this thermal decomposition is run in air, then an interesting light emission is observed at 180-190 °C, which is thought to be the result of an oxidation reaction of a decomposition product.<sup>16</sup> Obviously, it seems prudent to use inert atmosphere techniques when doing any work that involves hydrogen generation. It is a good idea to always store AB over an inert atmosphere since a mass spec study of the vapor above solid AB showed the presence of diborane.<sup>17</sup>

Two fires recently occurred during the handling of AB. In January 2005 a sample of AB on mesoporous carbon was observed to inflame in air when contacted with a stainless steel spatula.<sup>18</sup> The best explanation is that this incident may have been caused by a static discharge. In April 2005 a fire occurred in a vendor's packaging department during acetone clean-up of equipment following packaging of AB.<sup>19</sup>

The recommendations here are to avoid initial use of acetone in the open air for clean up of lab equipment that contains residues of AB and to not allow mixtures of finely divided carbon and amine-borane adducts to dry in the open air.

## Safety Aspects (continued)

Ammonium borohydride is closely related to AB, but this salt can only be prepared at low temperatures and decomposes at temperatures above  $-20\text{ }^{\circ}\text{C}$  with evolution of hydrogen.<sup>20</sup> This may be more than a simple thermal decomposition because when ultra-dry solvents are used a mixture of  $(\text{BH}_4)^-$  and  $(\text{NH}_4)^+$  does not react to give hydrogen.<sup>21</sup> Regardless, even though ammonium borohydride appears attractive based on wt% H, it must be treated with caution since it is usually an unstable material.

Another material to treat with caution is hydrazine-bisborane ( $\text{H}_3\text{B-NH}_2\text{NH}_2\text{-BH}_3$ ). It can be prepared from diborane and anhydrous hydrazine at low temperatures, but the white solid product explodes when heated in air.<sup>22</sup> It is also reported to be shock sensitive and will detonate upon impact.<sup>23</sup> Solid pellets of hydrazine-bisborane can be ignited to provide hydrogen gas via a self-sustaining thermal decomposition.<sup>24</sup>

## Safety Aspects (continued)

It is now generally accepted that amine-boranes prepared from primary and secondary amines are stable and do not evolve hydrogen under normal conditions. However, early workers reported that  $(\text{CH}_3)\text{NH}_2\text{-BH}_3$  and  $(\text{CH}_3)_2\text{NH-BH}_3$  decompose slowly even at  $0\text{ }^\circ\text{C}$  with evolution of hydrogen.<sup>25</sup> A later report states that both of these adducts are stable white solids with no tendency to evolve hydrogen at room temperature.<sup>26</sup> This apparent discrepancy is now understood as being due to unsymmetrical cleavage of diborane.<sup>27</sup> Interestingly, a patent claims the manufacture of “stable”  $(\text{CH}_3)_2\text{NH-BH}_3$  which shows no decomposition when heated up to  $110\text{ }^\circ\text{C}$ .<sup>28</sup> More recently, a melt of neat  $(\text{CH}_3)_2\text{NH-BH}_3$  was kept at  $45\text{ }^\circ\text{C}$  for 7 days with no observed decomposition.<sup>29</sup>

It is recommended that all new amine-borane adducts prepared from 1° or 2° amines need to be treated as potentially unstable until tested for the absence of pressure build-up upon storage.

Pyridine-borane is known to be thermally unstable. Early workers observed the adduct decomposing during an attempted vapor pressure measurement.<sup>30</sup> Also, a violent decomposition occurred during an attempted distillation of pyridine-borane.<sup>31</sup> A serious industrial accident resulted when a 55-gal drum of pyridine-borane was moved to a hot room then later **ruptured and started a fire**.<sup>32</sup>

## Safety Aspects (continued)

Although it is not an amine-borane, a discussion of the instability of borane-THF is needed since it does reveal a problem when a system contains an internal route from a reactive B-H to a thermodynamically more stable B-O. Borane-THF, as a 1M solution in THF, is available commercially, but was initially only offered as a  $\text{NaBH}_4$  stabilized solution. Borane-THF undergoes a slow internal reductive ring opening to give butoxy-B compounds,<sup>33</sup> and this reaction can be retarded if a small amount of  $\text{NaBH}_4$  (0.005M) is present.<sup>34</sup> Later it was claimed in a patent that borane-THF can be stored "unstabilized" if never allowed above 20 °C.<sup>35</sup> Unfortunately, whether stabilized with  $\text{NaBH}_4$  or not, this reagent can decompose violently when stored in bulk at ambient temperatures as witnessed by a very serious industrial accident.<sup>36</sup>

The lesson to be learned from the problems with borane-THF is that a mixture of any boron hydride plus an oxygen containing organic needs to be evaluated carefully to see if there is a temperature at which a self-accelerating decomposition can occur. This is especially critical if the mixture is ever produced and shipped in large quantities.

## Safety Aspects (continued)

The generation of hydrogen from AB or other amine-borane adducts may involve the formation of borazine,  $(\text{HNBH})_3$ . Early work on the synthesis of borazine showed that liquid borazine slowly decomposes to give hydrogen and a non-volatile white solid with small amounts of diborane in the volatiles.<sup>37</sup> Later the decomposition of liquid borazine was studied at 50 °C and 100 °C with only about 50% of the borazine being recovered after 160 hours.<sup>38</sup> The recommendation is to store borazine at or below 4 °C.<sup>39</sup>

The toxicity of diborane is well known and well documented.<sup>4</sup> The real question is how toxic are the amine-borane adducts. A review of the MSDS's supplied by the manufacturers seems to indicate that the amine-borane product is only listed as toxic if the free amine is classified as toxic. This probably means that the authors of the MSDS's could not find any reported toxicological studies in the open literature. A search of the government report archives at US Borax uncovered one study from Project ZIP.<sup>40</sup> The acute toxicity of dimethylamine-borane, pyridine-borane and trimethylamine-borane was measured by injection in rats.<sup>41</sup> The  $\text{LD}_{50}$  when expressed as mg B/kg showed that the toxicity of dimethylamine-borane and pyridine-borane is approximately equal to the toxicity of pentaborane while trimethylamine is much less toxic. Pentaborane is known to be highly toxic.<sup>42</sup>

## Safety Aspects (continued)

The safety aspects of amine-borane compounds is not complete without a discussion of handling procedures and techniques. Gases that are reactive to the atmosphere are best handled using vacuum line techniques. Solids that are reactive to the atmosphere are best manipulated in a glove box. Air-sensitive liquids and solutions can be easily handled using syringe and double-ended needle techniques along with appropriate glass ware equipped with sleeve stoppers.<sup>43</sup> Obviously, many of the amine-borane adducts are unreactive to water and oxygen, but it is still a good idea to run all reactions and to handle and store these materials under inert atmospheres.

Care must be taken to properly vent all reaction set-ups and to make sure any generated hydrogen is diluted with nitrogen and vented to an efficient hood. By using aqueous mineral acids, it is possible to completely destroy any B-H bonds in amine-borane adducts with evolution of hydrogen. This can be used to make sure any by-products are safe for proper disposal.

# Additional Information

The balance of the survey covering ammonia-borane and related N-B-H compounds and materials includes the following sections:

- **Synthesis**
- **Physical Properties**
- **Theoretical Studies**
- **Chemical Properties**
- **Synthetic Applications**
- **Industrial Applications**

A copy of the complete survey can be supplied to all interested parties.



# Conclusions

The possible use of boron hydrides for chemical hydrogen storage is just the most current in a long line of government funded projects involving B-H compounds. During World War II a contract was initiated at the University of Chicago with the initial goal to prepare volatile compounds of uranium.<sup>44</sup> The goal was never accomplished, but the research did lead to the development of improved processes for the preparation of  $\text{NaBH}_4$  and  $\text{B}_2\text{H}_6$ . This work led to the next major government funded project which occurred during the Cold War.

In the mid to late 1950's a concerted effort was made to develop a boron-based high-energy fuel for jets and rockets.<sup>45</sup> This project funded many academic investigations and the industrial partners even built pilot-scale production plants.<sup>45</sup> The goal was never accomplished, but the research did result in a wealth of technical information, which was ultimately made public in the 1960's.<sup>46</sup>

Again we have a project where boron hydrides could hold the key to success. However, we must learn from our past mistakes and one of the most serious was the rush to achieve results at the expense of safety. This resulted in a total of five major accidents with eight people being killed during the high-energy fuels projects.<sup>45</sup> All could have been prevented. We must not allow safety to be compromised during our work on Chemical Hydrogen Storage.

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# Summary

The technical information about ammonia-borane and related N-B-H compounds provides the following key safety recommendations:

- Ammonia-borane of unknown purity must be handled carefully and vented until stability is known.
- Mixtures/solutions of ammonia-borane must be vented unless known or determined to be stable.
- Amine-borane adducts prepared from primary or secondary amines must be vented until absence of pressure build-up is assured.
- Mixtures of any boron hydride with an oxygen containing organic must always be evaluated for the possibility of a temperature at which a self-accelerating decomposition can occur.