Amineborane Based Chemical Hydrogen Storage

Final Report

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Objectives
- Develop methods for on-demand, low temperature hydrogen release from chemical hydrides that can achieve DOE targets
- Develop high conversion off-board methods for chemical hydride regeneration

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

A. System Weight and Volume
B. System Costs
E. Charging/Discharging Rates
R. Regeneration Processes

Technical Targets
- Gravimetric Density: 0.045 (2007); 0.06 (2010); 0.09 (2015) kg-H₂/kg
- Volumetric Density: 0.036 (2007); 0.045 (2010); 0.081 (2015) kg-H₂/L
- H₂ Flow Rate
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Section 1: Executive Summary

The development of efficient and safe methods for hydrogen storage is a major hurdle that must be overcome to enable the use of hydrogen as an alternative energy carrier. The objectives of the Penn program in the DOE Center of Excellence in Chemical Hydride Storage were both to develop new methods for on-demand, low temperature hydrogen release from chemical hydrides and to design high-conversion off-board methods for chemical hydride regeneration.

Because of their reactive protic (N-H) and hydridic (B-H) hydrogens and high hydrogen contents, amineboranes such as ammonia borane, NH₃BH₃ (AB), 19.6-wt% H₂, and ammonia triborane NH₃B₃H₇ (AT), 17.7-wt% H₂, were initially identified by the Center as promising, high-capacity chemical hydrogen storage materials with the potential to store and deliver molecular hydrogen through dehydrogenation and hydrolysis reactions. In collaboration with other Center partners, the Penn project focused both on new methods to induce amineborane H₂-release and on new strategies for the regeneration the amineborane spent-fuel materials.

The Penn approach to improving amineborane H₂-release focused on the use of ionic liquids, base additives and metal catalysts to activate AB dehydrogenation and these studies successfully demonstrated that in ionic-liquids the AB induction period that had been observed in the solid-state was eliminated and both the rate and extent of AB H₂-release were significantly increased. Several systems were identified that have the potential to meet the DOE total-system targets for chemical hydrogen storage.

Ionic Liquid Promoted Ammonia Borane H₂-Release. While partial AB dehydrogenation has be achieved in the solid-state, milder conditions and more controllable AB H₂-release reactions could, in principle, be attained in solution. However, practical applications of chemical hydrogen storage required a replacement for the volatile organic solvents that have traditionally been employed for reactions of molecular chemical hydrides. The Penn project demonstrated that ionic-liquids, salts that are liquid at low temperatures (< 100 °C), have a number of advantages as reaction media for chemical hydrogen storage systems, including low volatility, nonflammability, high polarity with low coordinating power, and the ability to stabilize ionic intermediates and transition states. As shown in the example H₂-release studies in Figure 1.1, ionic liquids were demonstrated to have an activating effect on AB H₂-release that eliminated the induction period observed in the solid-state H₂-release reactions and increased both the extent and rate of AB H₂-release.

H₂-release studies, such as presented in Figure 1.2 (left), of the temperature dependence of the reactions of 50:50-wt% AB:bmimCl (bmimCl = 1-butyl-3-methylimidazolium chloride) mixtures demonstrated that dramatic rate enhancements for H₂-release were possible with only modest increases in temperature. Thus, at 110 °C, over 2 H₂-equivalents were released in only ~20 min. As can also be seen in Figure 1.2 (right), significantly enhanced H₂-release rates compared to the solid-state were still achieved when employing as little as 20.2-wt% bmimCl, thereby resulting in a H₂-release system with 11.4 materials-wt% H₂-release.

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Figure 1.1 Summary of H₂-release results from 50:50 wt% ammonia-borane/ionic-liquid mixtures at 85 °C.

Figure 1.2 H₂-release measurements of: (left) 50-wt% AB in bmimCl showing the significant increase in H₂-release with increased temperature, and (right) 20-wt% AB in bmimCl at different temperatures showing both their fast rates and higher materials wt-%.

Both solution and solid-state ¹¹B NMR studies of AB H₂-release reactions in progress revealed important details of both the mechanism of H₂-release in ionic liquids and the nature of the final spent fuel products. These studies showed that the diammoniate of diborane (DADB) is the active intermediate in AB dehydropolymerization and that ionic liquids induce the formation of DADB from AB. By increasing the speed of formation of DADB, ionic liquids dramatically improve the AB H₂-release rate. Intermolecular dehydrocoupling reactions between the hydridic B-H hydrogens and protic N-H hydrogens on DADB and/or AB produce polyaminoborane polymers (Figure 1.3), which then undergo further dehydrogenation to ultimately form unsaturated cross-linked polyborazylene spent-fuel materials.
**Figure 1.3** Proposed mechanistic pathways and intermediates for ionic-liquid activated ammonia borane H\(_2\)-release.

**Base Promoted Ammonia Borane H\(_2\)-Release.** The Penn project demonstrated that the addition of small amounts of bases, including LiNH\(_2\), LiH and bis(dimethylamino)naphthalene, (Proton Sponge, PS) to AB reactions carried out in either the solid-state or solution reduced or eliminated the induction period and enhanced the rate and extent of H\(_2\)-release. Reactions with Proton Sponge in either ionic-liquid or tetraglyme solutions were especially effective since they increased both the rate and extent (to over 2 equivalents) of AB H\(_2\)-release while avoiding the formation of the stable borohydride salts that were observed in the LiNH\(_2\) and LiH reactions. H\(_2\)-release studies, such as shown in **Figure 1.4** for 50:50-wt% AB/ionic-liquid mixtures at 85 °C, demonstrated the remarkable effect that addition of Proton Sponge had on increasing the H\(_2\)-release rate with the biggest rate increase being for the release of the 2\(^{nd}\) H\(_2\)-equivalent.

**Figure 1.4** H\(_2\)-release measurements showing the increases in H\(_2\)-release rates achieved by the addition of PS to 50-wt% solutions of AB in ionic-liquid and tetraglyme solvents.
Ionic liquid solvents proved more favorable than tetraglyme for the PS-reactions, since they reduced the formation of undesirable volatile products, such as borazine. Model studies and solid-state and solution $^{11}$B NMR observations of the progress of PS-promoted reactions in ionic-liquids support a unique H$_2$-release pathway involving initial AB deprotonation to form the H$_3$BNH$_2^-$ anion. This anion then initiates AB dehydropolymerization to form anionic polyaminoborane polymers. Subsequent chain-branching and dehydrogenation reactions led ultimately to polyborazylene-type spent-fuel products. PS was also found to have the unanticipated effect of significantly reducing reaction foaming.

**Metal catalyzed Ammonia Borane H$_2$-Release.** At the outset of our project, the use of metal catalysts to induce AB H$_2$-release was identified as an approach having a number of potential advantages that might be complimentary to other H$_2$-release methods. However, practical applications of chemical hydrogen storage required a replacement for the organic solvents that have traditionally been used in catalysis since the volatility of these solvents would result in both their loss to the environment and contamination of the H$_2$-stream. The Penn project demonstrated that, owing to their negligible vapor pressures and ability to stabilize active transition metal intermediates, ionic-liquids are ideal solvents for transition metal catalyzed AB H$_2$-release reactions. Furthermore, the reactions carried out in ionic liquids gave different product structures/compositions than have been obtained in conventional organic solvents.

![Figure 1.5](image)

**Figure 1.5** H$_2$-release measurements of the reactions of 50-wt% AB in bmimCl at 65 ºC with 5-mol% catalysts.

As shown in the examples in **Figure 1.5**, a number of transition metals were found to catalyze H$_2$-release from ammonia borane in ionic-liquid solvents. In situ $^{11}$B NMR studies demonstrated that there are different mechanistic pathways for H$_2$-release in the uncatalyzed and metal-catalyzed reactions in ionic-liquids with the metal catalysts having the biggest effect on the release of the 1$^{st}$ H$_2$-equivalent. Furthermore, since they produced lower amounts of borazine, a potential fuel-cell poison, ionic-liquid solvents were found to be favored over conventional solvents for metal catalyzed AB H$_2$-release.

**Ammonia Triborane (AT) H$_2$-Release.** The high H$_2$-release capacities that could potentially be achieved from ammonia triborane (AT) NH$_3$B$_3$H$_7$ by either hydrolytic (9.8 wt% H$_2$) or thermolytic (17.7 wt% H$_2$) processes also made AT an attractive initial candidate for chemical hydrogen storage. Early work at Penn achieved a convenient and safe method for AT synthesis
that then enabled the first systematic evaluation of its hydrogen storage potential. AT was shown to be both soluble and stable in water, but that upon the addition of an appropriate transition metal catalyst, AT rapidly hydrolyzed to release hydrogen with a rate that was easily controlled by the catalyst loadings and temperature. As indicated in Figure 1.6 (left), H₂-release measurements following periodic AT to solution containing of 5-wt% Rh/Al₂O₃ showed little change in the hydrogen H₂-rates over 11 cycles. Over 6.1 materials-wt% H₂-release was achieved Figure 1.6 (right) from a concentrated 22.7-wt% aqueous AT solution at room temperature in the presence of 5-wt% Rh/Al₂O₃.

Figure 1.6 (left) H₂-release following repeated AT additions to an aqueous solution containing 5-wt% Rh/Al₂O₃. (right) Rhodium (5-wt% Rh/Al₂O₃, 1.0-mol% Rh) catalyzed H₂-release from a 22.7-wt% aqueous AT solution yielding 6.1-wt% H₂ [wt% = H₂-wt/(NH₃BH₃+H₂O+Rh/Al₂O₃-wts)].

While the DOE total-system H₂-storage targets of 9 total-system wt% for transportation will not be attainable with this, or any other, hydrolytic-based system, an AT-based hydrolytic system can provide a means of safe hydrogen generation that should be competitive with either NH₃BH₃ or NaBH₄ based hydrolys for other applications having less stringent weight requirements.

Ammonia Borane Regeneration. The efficient regeneration of ammonia borane from BNHₓ spent fuel is one of the most challenging problems that will have to be overcome in order to utilize AB-based hydrogen storage. Any viable AB regeneration process must be capable of regenerating a variety of molecular, polymeric and/or solid-state spent-fuel materials, while avoiding the formation of difficult to reduce intermediates. Three Center partners, LANL, PNNL and Penn, each took a different complimentary approach to AB regeneration. The Penn approach, outlined in Figure 1.7, focused on a strategy involving spent-fuel digestion with strong acids followed by boron-halide coordination/reduction/displacement processes.
**First Step: Acid Digestion of Spent Fuels**

\[ \text{BNH}_x + 4 \text{HX} \rightarrow \text{BX}_3 + \text{NH}_4\text{X} \]

**Second Step: One-Pot Conversion of BX₃ to AB**

**Coordination of BX₃**

\[ \text{BX}_3 + \text{Base} \rightarrow \text{BaseBX}_3 \]

**BX Reduction**

\[ \text{BaseBX}_3 + 3 \text{HMR}_3 \rightarrow \text{BaseBH}_3 + 3 \text{XMR}_3 \]

\[ \text{M} = \text{Sn}, \text{Si} \]

**Base Displacement by NH₃ to Yield AB**

\[ \text{BaseBH}_3 + \text{NH}_3 \rightarrow \text{H}_3\text{NBH}_3 + \text{Base} \]

**Figure 1.7** Overview of Penn approach to AB regeneration.

Spent fuel materials resulting from AB H₂-release were successfully digested in a number of strong acid systems to produce materials containing tetrahedral boron atoms devoid of remaining hydrogen. The digestate from the reaction of spent fuel with trifluoroacetic acid was found to react with dimethylethylaminoalane to form dimethylethylamine borane; however, the dimethylethylamine could not be displaced by ammonia to produce AB. Digestion of spent fuels resulting from only ~1 equivalent of AB H₂-release with superacidic AlBr₃/HBr/CS₂ solutions yielded BBr₃ which could be distilled out of the reaction mixtures; however, the digestion of more highly dehydrogenated spent fuels with ~2 equivalents of H₂-release could not be attained. While the Penn boron-halide reduction studies successfully demonstrated that a dialkylsulfide-based coordination/reduction/displacement process gave quantitative conversions of BBr₃ to ammonia borane with efficient and safe product separations, the fact that AB spent-fuels cannot as yet be digested in good yields to BX₃ halides has led to a No-Go decision on this overall AB-regeneration strategy.

**Final Conclusions**

Our completed studies have led to both the discovery and continued improvements of promising H₂-release systems based on ammonia borane. These results have clearly shown that, while improvements are still necessary, many of these systems have the potential to achieve DOE hydrogen-storage goals. The high extent of their H₂-release, the tunability of both their H₂-materials weight percents and release rates, and their product control that is attained by either trapping or suppressing unwanted volatile side products, such as borazine, continue to make AB/ionic-liquid based systems attractive candidates for chemical hydrogen storage applications. These studies have also demonstrated that H₂-release from chemical hydrides can occur by a number of different mechanistic pathways and strongly suggest that optimal chemical-hydride based H₂-release systems may require the use of synergistic dehydrogenation methods to induce H₂-loss from chemically different intermediates formed during release reactions.
Section 2: Overview

The development of efficient and safe methods for hydrogen storage is a major hurdle that must be overcome to enable the use of hydrogen as an alternative energy carrier. The objectives of the Penn program in the DOE Center of Excellence in Chemical Hydride Storage were both to develop new methods for on-demand, low temperature hydrogen release from chemical hydrides and to design high-conversion off-board methods for chemical hydride regeneration.

Because of their reactive protic (N-H) and hydridic (B-H) hydrogens and high hydrogen contents, amine boranes such as ammonia borane, NH$_3$BH$_3$ (AB), 19.6 wt% H$_2$, and ammonia triborane NH$_3$B$_3$H$_7$ (AT), 17.7 wt% H$_2$, were initially identified by the Center as promising, high-capacity chemical hydrogen storage materials with the potential ability to store and deliver molecular hydrogen through dehydrogenation and hydrolysis reactions. In collaboration with our other Center Partners, the Penn project focused both on the development of new methods to induce amineborane H$_2$-release and on new strategies for the regeneration their amineborane spent-fuel materials.

Our initial studies, illustrated in Figure 2.1, of solid-state AB dehydrogenation identified three key H$_2$-release problems that would have to be overcome: (1) AB exhibited an initial induction period before any H$_2$-release, (2) the rate of AB H$_2$-release was too slow, and (3) the extent of AB H$_2$-release was too low.

![Figure 2.1](image-url)

**Figure 2.1** Summary of H$_2$-release properties of solid-state ammonia-borane at 85 and 95 °C illustrating the: (1) initial induction period preceding H$_2$-release, (2) slow rate of H$_2$-release and (3) poor extent of H$_2$-release.

At the outset of our work, little was known about the mechanism(s) of amine borane dehydrogenation, the identity of the products that were formed following H$_2$-release, and whether the types of products changed depending upon the methods/conditions of the reactions. As a result, the development of any general amine borane regeneration process was a complex problem since, depending upon the conditions and dehydrogenation method, a wide variety of molecular, polymeric and/or solid-state spent fuel materials with quite different reactivities could be produced. Thus, another primary objective of the Penn program was to develop a fundamental understanding of the possible products and mechanisms of AB dehydrogenation and then use this knowledge as a guide for the development of general methods for amine borane regeneration from spent fuel materials.
As described in the following sections, the Penn approach to improving amine borane H₂-release focused on the use of ionic liquids (Section 3), base additives (Section 4) and metal catalysts (Section 5) to activate AB dehydrogenation and these studies successfully demonstrated that the AB induction period could be eliminated and both the rate and extent of AB H₂-release could be significantly increased. Several systems were identified that have the potential to meet the DOE total-system targets for H₂-release. Section 6 describes our development of an ammonia triborane based hydrolytic H₂-release system that can provide safe hydrogen generation for non-transportation applications. The Penn approach to AB regeneration, which focused on a strategy involving spent-fuel digestion with strong acids followed by boron-halide coordination/reduction/displacement processes, is presented in Section 7.
Section 3. Ammonia Borane Hydrogen Release in Ionic Liquids

Summary

Ionic liquids were found\textsuperscript{1,2,3} to promote the rate and extent of H\textsubscript{2}-release from ammonia borane (AB), a promising, high capacity hydrogen storage material. For example, AB reactions at 85 °C in 1-butyl-3-methylimidazolium chloride (bmimCl) (50:50-wt%) exhibited no induction period and released 1.0 H\textsubscript{2}-equiv. in 67 min and 2.2 H\textsubscript{2}-equiv. in 330 min at 85 °C, whereas comparable solid-state AB reactions had a 180 min induction period and required 360 min to release ~0.8 H\textsubscript{2}-equiv. at 85 °C, with the release of only another ~0.1 H\textsubscript{2}-equiv. at longer times. Significant rate enhancements for the ionic-liquid mixtures were obtained with only moderate increases in temperature, with, for example, a 50:50-wt% AB/bmimCl mixture releasing 1.0 H\textsubscript{2}-equiv. in 5 min and 2.2 H\textsubscript{2}-equiv. in only 20 min at 110 °C. Increasing the AB/bmimCl ratio to 80:20 still gave enhanced H\textsubscript{2}-release rates compared to the solid-state, and produced a system that achieved 11.4 materials-weight percent H\textsubscript{2}-release. Solid-state and solution \textsuperscript{11}B NMR studies of AB H\textsubscript{2}-release reactions in progress support a mechanistic pathway involving: (1) ionic-liquid promoted conversion of AB into its more reactive ionic diammoniate of diborane (DADB) form, (2) further intermolecular dehydrocoupling reactions between hydridic B-H hydrogens and protonic N-H hydrogens on DADB and/or AB to form neutral polyaminoborane polymers and (3) polyaminoborane dehydrogenation to unsaturated cross-linked polyborazylene materials.

3.1 Introduction

The requirement for efficient and safe methods for hydrogen storage is a major hurdle that must be overcome to enable the use of hydrogen as an alternative energy carrier.\textsuperscript{4,5} Owing to its high hydrogen content, ammonia borane (AB) has been identified as one of the leading candidates for chemical hydrogen storage, potentially releasing 19.6 wt% H\textsubscript{2} according to Equation 3.1.\textsuperscript{6}

\[
H_3NBH_3 \rightarrow BN + 3 H_2 \quad (3.1)
\]

Partial dehydrogenation of ammonia borane can be thermally induced in the solid-state,\textsuperscript{1,7} but to be useful for hydrogen storage, milder conditions and more controllable reactions still need to be developed. Such reactions could, in principle, be attained in solution, but practical applications of chemical hydrogen storage would require a replacement for the volatile organic solvents that have traditionally been employed for reactions of molecular chemical hydrides. The work reported in this section demonstrates that ionic liquids provide advantageous media for ammonia borane dehydrogenation in which both the extent and rate of hydrogen release are significantly increased. Solid-state and \textit{in situ} \textsuperscript{11}B NMR studies of reactions in progress are also presented that provide insight into the intermediates and mechanistic steps involved in ionic-liquid promoted AB H\textsubscript{2}-release.

3.2 Experimental Section

All manipulations were carried out using standard high-vacuum or inert-atmosphere techniques as described by Shriver.\textsuperscript{8}
3.2.1 Materials

Ammonia borane (Aviabor 97% minimum purity) was ground into a free flowing powder using a commercial coffee grinder. The diammoniate of diborane (DADB) was synthesized by the literature method.\(^8\) The 1-butyl-3-methylimidazolium iodide (bmimI) was synthesized sonochemically from 1-iodobutane and 1-methyl-imidazole according to literature methods.\(^9\) All ionic liquids, including 1-butyl-2,3-dimethylimidazolium chloride (bmmimCl) (EMD), 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF\(_4\)), 1-butyl-3-methylimidazolium chloride (bmimCl), 1-butyl-3-methylimidazolium triflate (bmimOTf), 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF\(_6\)), 1-ethyl-2,3-dimethylimidazolium ethylsulfate (emmimEtSO\(_4\)), 1-ethyl-2,3-dimethylimidazolium triflate (emmimOTf), 1,3-dimethylimidazolium methylsulfate (mmimMeSO\(_4\)) and 1-propyl-2,3-dimethylimidazolium triflde (pmmimTf\(_3\)C) (Aldrich) were dried by toluene azeotropic distillation to remove any moisture. Tetraethylene glycol dimethyl ether (Sigma 99%) (tetraglyme) and ethylene glycol dimethyl ether (Sigma 99%) (glyme) were distilled from sodium under vacuum with heating.

3.2.2 Physical Measurements

3.2.2.1 H\(_2\)-Release Measured with a Toepler Pump

The Toepler pump system used for hydrogen measurements was similar to that described by Shriver.\(^8\) The Toepler pump (Figure 3.1) system also enabled the trapping of any volatile dehydrogenation products. This method of measuring H\(_2\)-release worked best for reactions with slow H\(_2\)-release rates, since the Toepler pump required several minutes to make each measurement. The released gases from the reaction vessel were first passed through a liquid nitrogen trap before continuing on to the Toepler pump (700 mL). The released H\(_2\) was then pumped into a series of calibrated volumes with the final pressure of the collected H\(_2\) gas measured (±0.5 mm) with the aid of a U-tube manometer. After the H\(_2\) measurement was completed, the in-line liquid nitrogen trap was warmed to room temperature and the amount of any volatiles that had been trapped were then also measured using the Toepler pump.

![Figure 3.1](Image)

**Figure 3.1** Toepler pump system used for H\(_2\)-release measurements.

3.2.2.2 H\(_2\)-Release Measured with an Automated Gas Burette

For reactions with faster rates, an automated gas burette was employed for H\(_2\)-release measurements. The automated gas burette (Figure 3.2) was based on a design reported by Zheng et al.,\(^{11}\) but employed all glass connections with a cold trap (-78 °C) inserted between the
reaction flask and burette to allow trapping of any volatiles that might have been produced during the reaction. The gas burette enabled rapid data collection of H$_2$-release at short time ranges.

**Figure 3.2** Automated gas burette used for H$_2$-release measurements.

Unlike the Toepler pump reactions, which were run under vacuum, reactions carried out with the burette were run under inert gas at atmospheric pressure to mimic real-world conditions. As shown in **Figure 3.2**, the reactions were carried out in the volume-calibrated flask on the right, which was plunged into a pre-heated oil bath to start the reaction. On top of the reaction flask was an air condenser to keep most of the volatiles in the reaction flask. The H$_2$ stream, along with any additional volatiles, passed through the -78 °C trap and flowed into the bottom of the oil-filled burette. As H$_2$ collected at the top of the burette, the oil flowed into a reservoir kept at atmospheric pressure (measured with pressure gauge). The pressure difference in the burette was tracked with a vacuum transducer and the temperature was tracked at multiple locations with thermocouples. All data were collected and processed on a program written in LabVIEW 8.5 by Zheng et al.$^{11}$

For reactions using the automated gas burette, the AB (150 mg, 4.87 mmol) samples were loaded into ~100 mL flasks with calibrated volumes, along with the ionic liquid (150 mg) or tetraglyme (150 mg). Under a flow of helium, the flask was attached to the burette system. The system was evacuated for 30 min for reactions with the ionic liquid solutions and for 5 min for reactions with tetraglyme. The system was then backfilled with helium and allowed to equilibrate to atmospheric pressure for ~30 min. Once the system pressure equalized, the data collection program was started and the flask was immersed in the preheated oil bath. The product residues were extracted with dry glyme and analyzed by $^{11}$B NMR. The data are reported from the point where the flask was initially plunged into the oil bath, but H$_2$-release was not observed until the ionic-liquid/AB mixture melted. Data were recorded at 2-5 second intervals depending on the speed of the reaction. The data sets for the gas burette graphs presented in this section are available on a CD that was submitted with this report.

### 3.2.2.3 Procedures for $^{11}$B NMR Studies of Reaction Products

Solid-state and ionic liquid reactions carried out using either the Toepler pump or gas burette measurements were extracted with pyridine at various points in the reactions. The reaction flask was removed from the oil bath and cooled to room temperature, then dry pyridine
was added to the reaction flask under N$_2$ flow. The pyridine solution was extracted by syringe and then the $^{11}$B NMR was taken.

While bmimCl is a liquid at 85 °C, it is a solid at room temperature; therefore, solid-state $^{11}$B NMR analyses (at Pacific Northwest National Laboratories: 240 MHz machine spun at 10 kHz) were used to monitor the products of reactions carried out in bmimCl. All solid-state $^{11}$B chemical shifts were measured relative to external NaBH$_4$ (-41 ppm) and then referenced to BF$_3$O(C$_2$H$_5$)$_2$ (0.0 ppm).

The solution $^{11}$B NMR (128.4 MHz Bruker DMX-400) studies in the room temperature ionic-liquid bmimOTf were carried out by heating reaction mixtures composed of 50 mg of AB (1.6 mmol) or 50 mg of DADB (0.8 mmol) and 450 mg of ionic liquid at 85 °C in a sealed NMR tube, with the tube periodically removed from the heating bath to collect $^{11}$B NMR spectra of the reaction mixture (recorded at 25 °C).

All solid-state and solution $^{11}$B NMR chemical shifts are referenced to external BF$_3$O(C$_2$H$_5$)$_2$ (0.0 ppm) with a negative sign indicating an upfield shift.

### 3.3 Results and Discussion

Utilization of waste heat from a PEM fuel cell can provide for AB H$_2$-release reaction temperatures near 85 °C. However, at 85 °C, H$_2$-release from solid-state AB has been shown to exhibit an induction period of up to 3 h. After hydrogen release begins, only the release of ~0.9 equiv. of H$_2$ can be achieved, rather than the 3 equiv. predicted by Equation 3.1, even with prolonged heating at 85 °C.$^{1,7}$ As a result, a number of approaches are now being explored to induce efficient AB H$_2$-release, including, for example, activation by transition metal catalysts,$^{12-27}$ acid catalysts,$^{28}$ base catalysts,$^{29}$ and nano and meso-porous scaffolds.$^{30-32}$ Most of these additives use organic solvents either as the reaction medium or as the AB transport and loading method. The use of organic solvents is not desirable due to their high volatility, which would result in their loss to the environment as well as their contamination of the H$_2$-stream. An alternative solvent system is necessary.

#### 3.3.1 Why Use Ionic Liquids?

Ionic liquids are generally defined as salts that are relatively low viscosity liquids at temperatures below 100 °C. These salts have a number of unique properties that make them attractive substitutes for traditional organic solvents in hydrogen storage systems, including: (1) negligible vapor pressures, (2) stability to elevated temperatures, (3) the ability to dissolve a wide range of compounds and (4) a polar reaction medium that can stabilize ionic transition states and intermediates. The low volatility of these systems makes them superior to organic solvents and they have been used in a broad range of applications.$^{33-36}$ Their ability to stabilize ionic intermediates is critical to AB dehydropolymerization initiation as discussed in section 3.3.7.

Another promising application in ionic liquid technology is in transition-metal catalyst immobilization. Many industrial processes use heterogeneous catalysts despite more efficient, cheaper homogenous catalysts being available due to separation issues. Ionic liquids promise to become an immobilizing solvent system for catalysis where the catalyst is solubilized in the ionic liquid while the reagents and products are held in the organic layer (biphasic system) and can therefore be easily separated. Other uses for ionic liquids include solvation for radical polymerization and catalytic cracking of polyethylene as well as electrochemical reactions.$^{33}$
Ionic liquids are often air and moisture stable though many are hygroscopic, needing drying before use in reactions. Traditional synthetic methods for ionic liquids require long, high temperature reaction conditions whereas new methods utilize sonication and significantly shorter reaction times.10

Some of the most common ionic liquids are composed of inorganic anions, $X^-$, BF$_4^-$, PF$_6^-$, and nitrogen-containing organic cations, such as RN,R’N-imidazolium or RN-pyridinium. Figure 3.3 shows the structures, acronyms, and melting points of the variety of ionic liquids used in these studies. The ionic liquids can be grouped into solids or liquids at room temperature. The two position of the imidazolium ring in ionic liquids is susceptible to attack, since the hydrogen at this position is acidic. Reactions at this hydrogen can lead to solvent degradation and/or the formation of carbene borane adducts (most often during transition-metal catalyzed reactions). Replacing the hydrogen with a methyl group eliminates this issue and these ionic liquids are termed ‘protected.’ The protected ionic liquids can be obtained as either solids or liquids.

Solid ionic liquids have the advantage of being easily weighed and have a wider variety of protected imidazolium rings. Room temperature liquids, such as bmimI, bmimOTf, and mmimMeSO$_4$, are particularly useful for running in situ $^1$B NMR experiments. Since it showed good activity and was inexpensive and easy to handle, 1-butyl-3-methylimidazolium chloride, bmimCl, was used in many of the studies reported herein. The melting point of BmimCl is above room temperature, but it forms a stirrable liquid at room temperature when mixed with AB.

![Figure 3.3 Structures of ionic liquids used in these studies.](image)

### 3.3.2 Procedures for AB H$_2$-release reactions

For the experiments where the released H$_2$ was measured with the Toepler pump, the AB (250 mg, 8.1 mmol) was loaded under N$_2$ into ~100 mL single neck round bottom flasks with the ionic liquid (250 mg). The flasks were then evacuated, sealed, and placed in a hot oil bath preheated to the desired temperature. The flasks were opened at the indicated times and the released H$_2$ was quantified using the Toepler pump system. Post reaction, the flasks were evacuated for 30 min through the cold trap to remove any volatile products from the reaction.
The product residues and volatiles in the cold trap were extracted with dry glyme and analyzed by $^{11}$B NMR.

For reactions using the automated gas burette, the AB (150 mg, 4.87 mmol) samples were loaded into ~100 mL flasks with calibrated volumes, along with the ionic liquid (150 mg) or tetraglyme (0.15 mL) solvents. Under a flow of helium, the flask was attached to the burette system. The system was evacuated for 30 min for reactions with the ionic liquid solutions, and for 5 min for tetraglyme solutions. The system was then backfilled with helium and allowed to equilibrate to atmospheric pressure for ~30 min. Once the system pressure equalized, the data collection program was started and the flask was immersed in the preheated oil bath. The data are reported from the point where the flask was initially plunged into the oil bath, but H$_2$-release was not observed until the ionic-liquid/AB mixture melted. Data were recorded at 2-5 second intervals depending on the speed of the reaction. The product residues were extracted with dry glyme and analyzed by $^{11}$B NMR.

### 3.3.3 Solid-State vs. Ionic Liquid H$_2$-release

Our initial$^1$ AB H$_2$-release measurements for solid-state H$_2$-release were periodic values obtained using a Toepler pump, but the new studies reported herein use the automated gas burette.$^{11}$ This method has provided both more precise and continuous release data for these reactions. A comparison of the 85 °C H$_2$-release data, measured with the automated gas burette, obtained from solid-state AB versus AB dissolved in the 1-butyl-3-methyl-imidazolium chloride (bmimCl) ionic liquid (50:50- wt%) is presented in Figure 3.4. For the solid-state AB reaction, there was negligible hydrogen production after 180 min and only 0.81 equivalents of H$_2$ after 360 min. Other samples heated for longer times (67 h) showed that a total of only 0.9 H$_2$-equivalents could ultimately be obtained from the solid-state AB reactions at 85 °C. In contrast, the AB/bmimCl mixture exhibited no induction period, with H$_2$-release beginning immediately after the solution melted, to give release of 1.0 H$_2$-equiv. in 67 min and 2.2 H$_2$-equiv. in 330 min. The released H$_2$ was passed through a -78 °C trap before entering the gas burette. When the reaction was complete, the contents of the trap were extracted with glyme solvent, but $^{11}$B NMR analyses of the solution showed only trace amounts of borazine.

![Figure 3.4](image)

**Figure 3.4** H$_2$-release measurements (gas burette) at 85 °C of: (A) 50-wt% AB (150 mg) in bmimCl (150 mg,) and (B) solid-state AB (150 mg).

The AB/bmimCl H$_2$-release plot in Figure 3.4 also clearly shows that release appears to occur in at least two steps with the release rate for the 2$^{nd}$ H$_2$-equiv. being significantly slower
than for the 1st equiv. Dramatic increases (Figure 3.5) in the rate of H$_2$-release of the 50:50-wt% AB/bmimCl mixture for both H$_2$-equivalents were observed as the temperature was increased with the release of 1.0 H$_2$-equiv. in 37 min and 2.2 H$_2$-equiv. in 161 min at 95 °C, 1.0 H$_2$-equiv. in 9 min and 2.2 H$_2$-equiv. in 45 min at 105 °C, and 1.0 H$_2$-equiv. in 5 min and 2.2 H$_2$-equiv. in 20 min at 110 °C. The 75 °C reaction did not reach 2 H$_2$-equiv.

Figure 3.5 H$_2$-release measurements (gas burette) of 50-wt% AB (150 mg) in bmimCl (150 mg) at: (A) 110 °C, (B) 105 °C, (C) 95 °C, (D) 85 °C and (E) 75 °C.

The U.S. Department of Energy (DOE) has set a 2015 gravimetric total-system target for H$_2$-storage of 9.0 total-system-wt%.$^{35}$ The release of 2.2 H$_2$-equiv. from a 50:50 AB/bmimCl mixture corresponds to a release of 7.2 mat-wt% H$_2$ [mat-wt% H$_2$ = H$_2$-wt/(AB+bmimCl-wts)]. In order for an AB/ionic-liquid system to attain the DOE total-system targets, an increase in the mat-wt% by reduction of the weight of the ionic-liquid component is necessary. As can be seen in Figure 3.6, it was found that significantly enhanced H$_2$-release rates compared to the solid-state could still be obtained when employing as little as 20.2-wt% bmimCl. Thus, 2.0 H$_2$-equiv. were released from 80:20 AB/bmimCl solutions in only 52 min and 157 min at 120 °C and 110 °C, respectively, with both solutions then ultimately giving 2.2 H$_2$-equiv. at longer times. The final release observed for these mixtures corresponds to an 11.4 mat-wt% H$_2$-release.

The 85 °C H$_2$-release data (Toepler pump measurements) in Figure 3.7 show that AB H$_2$-release is activated in a variety of 50:50-wt% AB/ionic-liquid mixtures, but that these mixtures exhibit a range of H$_2$-release extents and rates. The biggest differences were observed for the release of the 2nd equivalent. The bmimCl, bmimMeSO$_4$, mmimMeSO$_4$ and emmimEtSO$_4$ (refer to Figure 3.3 for structures) mixtures all yielded over 2 H$_2$-equiv. at reasonably comparable rates, while the other mixtures showed greatly decreased release rates beyond the 1st equiv. For the pmmmimTf$_3$C mixture, H$_2$-release stopped, as was observed for the AB solid-state reactions at 85 °C, after only ~0.9 H$_2$-equiv. As shown in Figure 3.8, the H$_2$-release rates were significantly decreased upon lowering the temperature with the mmimMeSO$_4$ and emmimEtSO$_4$ mixtures being the most active. At 45 °C, bmimCl and bmmimCl showed little activity.
**Figure 3.6** H₂-release measurements (gas burette) of AB (150 mg) in 20.2-wt% bmimCl (38 mg): (A) 120 °C, (B) 110 °C, (C) 105 °C, (D) 95 °C, (E) 85 °C and (F) 75 °C. (The early spike in the data is caused by the initial delay of the burette to respond to H₂-release)

**Figure 3.7** H₂-release measurements (Toepler pump) of the reaction of 50-wt% AB (250 mg) at 85 °C in 250 mg of: (A) bmimCl, (B) bmimCl, (C) emmimEtSO₄, (D) bmimBF₄, (E) mmimMeSO₄, (F) bmimOTf, (G) emmimOTf, (H) bmimI, (I) bmimPF₆ and (J) pmmimTf₂C.
3.3.4 $^{11}$B NMR Characterization of Reaction Products and Pathways

The bmimCl ionic liquid is a solid at room temperature, but the 50:50-wt% AB/bmimCl mixtures formed a viscous, stirrable room temperature liquid. However, as the H$_2$-release reaction began, the mixture foamed. As the H$_2$-release neared the loss of ~1 H$_2$-equiv., the foam began to convert to a white solid. The entire AB/bmimCl mixture ultimately became solid as the reaction reached over 2 H$_2$-equiv. Similar behavior was seen for the other 50:50-wt% AB/ionic-liquid mixtures, but with some differences in their liquid ranges. On the other hand, the 80:20-wt% AB/bmimCl mixtures formed a moist paste at room temperature. Upon initial heating, this paste melted, but then rapidly solidified after the onset of H$_2$-release. Solid formation was likewise observed in H$_2$-release reactions of 50:50-wt% AB/tetraglyme systems (discussed later) to produce a final two-phase liquid/solid mixture.

3.3.4.1 $^{11}$B NMR of Pyridine Extracts from Reaction Products

The $^{11}$B NMR spectra of the pyridine soluble products produced at different stages in the AB solid-state and AB/bmimCl reactions are compared in Figure 3.9. Consistent with the observed absence of H$_2$-loss, the spectrum (Figure 3.9a) of the residue of the 1 h solid-state AB reaction showed only unreacted AB (quartet, -22.3 ppm$^{38}$), whereas the spectrum (Figure 3.9c) of the 1 h AB/bmimCl mixture clearly showed multiple resonances indicating a significant reaction that was consistent with its measured 0.52 equiv. of H$_2$-release. As shown in Figures 3.9b and 3.9d, the spectra of the pyridine soluble residues of the AB solid-state and AB/bmimCl
reactions obtained after the reactions had released 0.83 and 0.95 H₂-eqv., respectively, were similar, each showing that the AB resonance had decreased and the growth of new resonances arising from the diammoniate of diborane (which forms without the loss of H₂), [(NH₃)₂BH₂]⁺BH₄⁻, (DADB) (-13.3 (overlapped) and -37.6 ppm)¹⁸ and branched-chain polyaminoborane polymers (PAB) (-7, -13.3 and -25.1 ppm).¹ As dehydrogenation progressed past 1 equivalent, only a small amount of material was pyridine soluble; therefore, solid-state NMR was also used to analyze these materials.

Figure 3.9 Top: DFT/GIAO/NMR characterizations of AB dehydrogenation products. Bottom: Solution ^{11}B NMR (128.4 MHz) spectra of the residues (extracted in pyridine) of the 85 °C reaction of: (Left) solid-state AB (250 mg) after H₂-release of: (a) 0.04 equiv. and (b) 0.83 equiv. (Right) 50-wt% AB (250 mg) in bmimCl (250 mg) after H₂-release of: (c) 0.52 equiv. and (d) 0.95 equiv. AB ●, DADB ( ★ BH₄⁻ ▲ BH₂⁺), PAB ▲, B=N ■.
Figure 3.10 Solid-state $^{11}$B NMR (240 MHz) spectra recorded at 25 °C of the reaction of 50-wt% AB (150 mg) in bmimCl (150 mg) at 110 °C after the release of: (a) 1 equiv. and (b) 2 equiv.

3.3.4.2 Solid-State $^{11}$B NMR Studies

Consistent with both the H$_2$-release measurements and the $^{11}$B NMR analyses of the pyridine extracts, the solid-state $^{11}$B spectrum (Figure 3.10) of the reaction of a 50:50-wt% bmimCl/AB mixture heated at 110 °C also showed the presence of DADB after 1.0 equiv. of H$_2$-release. The solid-state $^{11}$B NMR spectrum of the final product after the release of 2 H$_2$-equiv. showed a broad downfield resonance characteristic of the sp$^2$ boron-nitrogen framework of cross-linked polyborazylene structures,$^{39,41}$ indicating that AB dehydrogenation ultimately produced B=N unsaturated products. NMR studies of the dehydrogenated products of AB H$_2$-release promoted by solid-state thermal reactions,$^7,40$ have likewise shown the formation of B=N unsaturated final products after the release of more than 2 H$_2$-equiv.

3.3.4.3 In Situ $^{11}$B NMR Studies in Ionic Liquids

In situ $^{11}$B NMR studies (Figure 3.11) of AB H$_2$-release at 85 °C in a solution of the room temperature ionic liquid bmimOTf (10:90 AB/bmimOTf mixture) exhibited features similar to those observed in the solid-state NMR spectra of the more concentrated AB/bmimCl reactions. Initially, only the AB resonance was present, but the appearance, after 10 min, of the well resolved quintet resonance near -38 ppm indicated significant AB conversion to DADB. After 30 min, 0.5 H$_2$-equiv. had been released, but the NMR spectrum (Figure 3.11c) indicated that the AB was completely consumed to produce a mixture of DADB and PAB polymer. Once the reaction reached the release of 0.9 H$_2$-equiv., the spectrum (Figure 3.11d) of the mixture showed a decrease in the DADB resonance along with a corresponding increase in the PAB resonances. The spectrum taken after the release of 1.5 H$_2$-equiv. (Figure 3.11e) showed that the DADB had been almost completely consumed and a new downfield resonance near 16 ppm had appeared. This 16 ppm resonance continued (Figure 3.11f) to grow and the PAB resonances continued to decrease as the reaction achieved the release of 2.0 H$_2$-equiv.

The solid-state $^{11}$B NMR spectrum, discussed earlier (Figure 3.10), of the product of the AB/bmimCl reaction after the release of 2 H$_2$-equiv. showed the broad downfield resonance near 30 ppm that is characteristic of unsaturated sp$^2$ boron-nitrogen frameworks. On the other hand,
the *in situ* NMR studies of the AB/bmimOTf reactions, as well as similar NMR studies of the 85 °C H₂-release from AB/mmmMeSO₄ and AB/bmil reactions, showed the growth of a 16 ppm resonance after the release of 2 H₂-equiv. The 16 ppm resonance in these ionic liquid reactions is thus shifted almost 14 ppm upfield relative to that normally found for polyborazylene⁴⁻⁵⁴ or borazine.⁴² This suggests that if either of these unsaturated species were formed in these solutions, the observed chemical shift change could result from interactions with the ionic liquid solvent.

![Figure 3.11](image)

**Figure 3.11** Solution¹¹B NMR (128.4 MHz) spectra recorded at 25 °C of the reaction of 10-wt% AB (50 mg) in bmimOTf (450 mg) at 85 °C after the release of: (a) 0.0 equiv. (0 min), (b) 0.1 equiv. (10 min), (c) 0.5 equiv. (30 min), (d) 0.9 equiv. (60 min), (e) 1.5 equiv. (180 min) and (f) 2.0 equiv. (360 min). (The broad DADB resonance at -13 ppm is obscured by the AB and PAB resonances)

Given both their polar compositions and planar aromatic like structures and properties, a variety of ionic liquid interactions would be possible for borazine and polyborazylene, including the formation of ionic liquid hydrogen-bonded and/or clathrated⁴³⁻⁴⁸ species. Holbrey et al. have shown that ionic liquids can clathrate aromatic species such as benzene, toluene, and *o-* *m-* *p-* xylene. A crystallographic determination (Figure 3.12.) of a benzene/1,3-dimethylimidazolium hexafluorophosphate clathrate showed that the benzene form a layered complex with the imidazolium rings. The aromatic is encapsulated in a cation-anion cage with the cation imidazolium methyl groups having strong π-interactions with the aromatic.⁴⁶

![Figure 3.12](image)

**Figure 3.12** Crystallographically determined structure of 1,3-dimethylimidazolium hexafluorophosphate with 0.5 mol benzene included as a clathrate.⁴⁶
Similar interactions would be expected to occur in the isoelectronic BN analogue borazine. Several $^{11}$B NMR studies specifically probing this phenomenon showed interactions like that found by Holbrey and others. These interactions are expected to decrease as the temperature is increased and, as shown in the $^{11}$B NMR spectra in Figure 3.13, it was found that upon recording the NMR spectrum of the final AB/bmimOTf sample with the NMR probe heated at 100 °C instead of 27 °C, the resonance at 16 ppm disappeared and was replaced by a resonance in the more normal 30 ppm region of borazine. It was likewise found that when glyme (1:10 glyme) was added to an AB/bmimOTf reaction sample exhibiting a 16 ppm resonance, this resonance disappeared and was replaced by a 30 ppm resonance. Additional evidence that borazine could give rise to a shift in this region in ionic liquid solutions was obtained by recording the spectra of a pure sample of borazine dissolved in 90 wt% bmimI. The initial spectrum showed only a broad downfield peak (Figure 3.14a), but this resonance then shifted to 16 ppm after the solution was heated at 85 °C (Figure 3.14b). The borazine could then be recovered from the bmimI solution by extraction with toluene (Figure 3.14c). These results are thus all consistent with a significant interaction between borazine and the ionic liquids. Some ionic liquids required initial heating to form these interactions, whereas the less viscous ionic liquids formed them at room temperature. Such interactions may play a key role in retarding the loss of borazine, a likely fuel cell catalyst poison, during AB H$_2$-release.

**Figure 3.13** Solution $^{11}$B NMR (128.4 MHz) of the reaction of 10-wt% AB (50 mg) in bmimOTf (450 mg) at 85 °C for 6 h: (a) NMR probe at 27 °C and (b) NMR probe at 100 °C.

**Figure 3.14** Solution $^{11}$B NMR (128.4 MHz) spectra recorded at 25 °C of 10-wt% borazine (50 mg) in bmimI (450 mg) after: (a) initial mixing at 25 °C, (b) 19 h at 85 °C and (c) the toluene extraction after heating.
3.3.5 Why do Ionic Liquids Accelerate AB H₂-release? What is the Role of DADB?

The $^{11}$B NMR spectra of the pyridine extracts (Figure 3.9) of both solid-state and ionic liquid H₂-release reactions at different times and the in situ NMR experiments in ionic liquids (Figure 3.11) clearly showed the initial formation of diammoniate of diborane (DADB) (Equation 3.2) resulting from the reaction of two equivalents (without H₂-loss) of AB.

$$2 \text{NH}_3\text{BH}_3 \rightarrow [(\text{NH}_3)_2\text{BH}_2]^+\text{[BH}_4^-] \quad (3.2)$$

The fact that the DADB is a precursor to the formation of the polyaminoboranes, rather than just a side reaction, was demonstrated by H₂-release and $^{11}$B NMR studies of DADB reactivity in ionic liquids. These studies showed that the 85 °C reaction of a pre-synthesized$^{9,38}$ pure sample of DADB dissolved in bmimOTf (10-wt% DADB) yielded the same type of polyaminoborane products, but with faster H₂-release rates, as those found in the AB/bmimOTf reactions.

$$0.5 [(\text{NH}_3)_2\text{BH}_2]^+\text{[BH}_4^-] \rightarrow \text{BN} + 3 \text{H}_2 \quad (3.3)$$

The theoretical DADB H₂-release reaction in terms of AB equiv. is given by Equation 3.3. The H₂-release rates for separate 10 wt% DADB and AB samples in bmimOTF are compared in Figure 3.15, where the faster rate of the DADB reaction is clearly apparent. While AB/bmimOTF required 96 min to release 1.0 H₂-equiv. and 274 min for 1.5 H₂-equiv., the DADB required only 28 min for 1.0 H₂-equiv. and 94 min for 1.5 H₂-equiv. At 400 min, the DADB/bmimOTF reaction had already released 2.09 H₂-equiv., while the AB/bmimCl reaction was still at 1.76 H₂-equiv. These rates are also faster than DADB H₂-release from the solid state.$^{49}$ As can be seen in the NMR studies in Figure 3.16, the initial $^{11}$B NMR spectrum obtained from a 10-wt% DADB/bmimOTF sample showed only the broad resonances expected for the DADB $(\text{NH}_3)_2\text{BH}_2^+$ (-13.3 ppm) and $\text{BH}_4^-$ (-37.6 ppm) components. However, after heating for only 10 min at 85 °C, most of the DADB had been converted to PAB. At 30 min, 0.9 H₂-equiv. had been released and the $^{11}$B NMR spectrum at this point (Figure 3.16c) showed that the DADB had been completely consumed. As the reaction proceeded beyond the release of 1 H₂-equiv., a new resonance grew in that was also at the 16 ppm shift observed in the AB/bmimOTf reactions (Figure 3.16d-f).

![Figure 3.15](image-url) H₂-release measurements (gas burette) of bmimOTf (450 mg) and 10-wt% (50 mg) of: (A) DADB and (B) AB.

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Figure 3.16 Solution $^{11}$B NMR (128.4 MHz) spectra recorded at 25 °C of the reaction of 10-wt% DADB (50 mg) in bmimOTf (450 mg) at 85 °C after the release of: (a) 0.0 equiv. (0 min), (b) 0.9 equiv. (10 min), (c) 1.1 equiv. (30 min), (d) 1.3 equiv. (60 min), (e) 1.6 equiv. (180 min) and (f) 1.9 equiv. (360 min).

Figure 3.17 Possible pathway for ionic-liquid promoted H$_2$-release from AB.

The combined solid-state and solution $^{11}$B NMR studies of AB/ionic-liquid and DADB/ionic-liquid H$_2$-release reactions in progress support a AB dehydrogenation pathway in ionic liquids (Figure 3.17) involving: (1) ionic-liquid promoted conversion of AB into its more
reactive ionic DADB form, (2) further intermolecular dehydrocoupling reactions between hydridic B-H hydrogens and protonic N-H hydrogens on DADB and/or AB to form polyaminoborane polymers and (3) polyaminoborane dehydrogenation to unsaturated cross-linked polyborazylene materials. The initial formation of DADB has also been proposed as a key step in thermally-induced AB H$_2$-release reactions in the solid state$^{7,49}$ and in organic solvents,$^{50}$ but the highly polar medium provided by ionic liquids promotes DADB formation and appears to be the key activating feature of these ionic liquid reactions.

### 3.3.6 H$_2$-Release Reactions in Tetraglyme

The AB H$_2$-release observed in the ionic liquid solvents was also compared with that obtained for the conventional polar organic solvent, tetraglyme. The H$_2$-release data for a 50:50 wt% ratio AB/tetraglyme mixture showed that both the extent and rate of H$_2$-release were comparable to that of the AB/bmimCl reactions (Figure 3.18). However, the $^{11}$B NMR spectra of the AB/tetraglyme reactions showed that, unlike in the ionic liquids, there was little evidence of PAB formation, with the major product being instead borazine (30.1 ppm)$^{42}$ along with smaller amounts of BH$_4^-$ (-36.8 ppm)$^{42}$ and µ-aminodiborane (-27.5 ppm)$^{42}$ (Figure 3.19). Thus, ionic liquid solvents are favored for AB H$_2$-release since they suppress or retard the formation of these undesired products.

![H$_2$-release measurements (gas burette) of 50-wt% AB (150 mg) in tetraglyme (150 mg) at: (A) 95 °C, (B) 85 °C and (C) 75 °C.](image-url)
Figure 3.19 Solution $^{11}\text{B}\{^{1}\text{H}\}$ NMR (128 MHz) spectra recorded at 80 °C of the reaction of 10-wt% AB (50 mg) in tetraglyme (450 mg) at 85 °C after: (a) 1.1 equiv. (60 min), (b) 1.7 equiv. (180 min) and (c) 1.9 equiv. (360 min). Inset shows $^{1}\text{H}$ coupled spectra.

3.4 Conclusions

The results described in this section have demonstrated that ionic liquids have an activating effect on ammonia borane H$_2$-release. Unlike the solid-state H$_2$-release reactions, AB H$_2$-release reactions in ionic liquids do not exhibit an induction period. $^{11}\text{B}$ NMR and H$_2$-release studies showed that DADB is the active intermediate in AB dehydropolymerization and that ionic liquids induce the formation of DADB from AB. By increasing the speed of formation of DADB, ionic liquids dramatically improve the H$_2$-release rate from AB. The high extent of their H$_2$-release, the tunability of both their H$_2$-materials weight percents and release rates, and their product control that is attained by either trapping or suppressing unwanted volatile side products make AB/ionic-liquid based systems attractive candidates for chemical hydrogen storage applications.
Section 4. Base Promoted Ammonia Borane H$_2$-Release

Summary

The addition of small amounts of bases, including LiNH$_2$, LiH and bis(dimethylamino)naphthalene, (Proton Sponge, PS) was found$^{2,51,29,52}$ to reduce or eliminate the induction period and to enhance the rate and extent of H$_2$-release from ammonia borane (AB). For example, while H$_2$-release from pure AB at 85 °C stops after only ~0.9 equivalents, AB reactions with the addition of 8 mol% of LiNH$_2$ or 17 mol% LiH at 85 °C yielded ~1.5 equivalents of H$_2$ (corresponding to ~9.5 materials-wt % H$_2$). Nevertheless, more detailed studies of the LiNH$_2$/AB and LiH/AB reactions showed that it was not possible for these reactions to release additional hydrogen owing the formation of the thermally stable LiBH$_4$ product. On the other hand, the reactions with Proton Sponge were found to promote the rate and extent (to over 2 equivalents) of H$_2$-release from ammonia borane (AB) in both the solid state and in ionic-liquid and tetrylgyme solutions without the formation of stable borohydride salts. For example, AB reactions in 1-butyl-3-methylimidazolium chloride (bmimCl) containing 5.3 mol% PS released 2 equivalents of H$_2$ in 171 min at 85 °C and only 9 min at 110 °C, whereas comparable reactions without PS required 316 min at 85 °C and 20 min at 110 °C. Ionic liquid solvents proved more favorable than tetrylgyme since they reduced the formation of undesirable products, such as borazine. Solid-state and solution$^{11}$B NMR studies of PS-promoted reactions in progress support a reaction pathway involving initial AB deprotonation to form the H$_3$BNH$_2^-$ anion. This anion can then initiate AB dehydropolymerization to form polyaminoborane polymers. Subsequent chain-branching and dehydrogenation reactions lead ultimately to a cross-linked polyborazylene-type product. Model studies of the reactions of [Et$_3$BNH$_2$BH$_3$]$^+$Li$^+$ with AB show evidence of chain-growth providing additional support for a PS-promoted AB anionic dehydropolymerization H$_2$-release process.

4.1 Introduction

In the preceding section, it was shown that the addition of ionic liquids to ammonia borane dramatically increased the extent and rate of H$_2$-release and eliminated the induction period that had been observed in solid-state reactions. These studies also showed that ionic liquids induce the formation of diammoniate of diborane, [(NH$_3$)$_2$BH$_2$]$^+$BH$_4^-$, (DADB) from AB and that DADB is the key intermediate for H$_2$-release in these systems. In this section, the activating effect of base additives will be described for AB reactions in the solid-state, ionic liquids, and tetrylgyme and it is shown that these bases enhance H$_2$-release from AB via a very different mechanistic pathway involving anionic AB dehydropolymerization initiated by the H$_3$BNH$_2^-$ anion.

4.2 Experimental Section

All manipulations were carried out using standard high vacuum or inert atmosphere techniques, as described by Shriver.$^8$

4.2.1 Materials

Ammonia borane (AB) (Aviabor, 97% minimum purity) was ground into a free flowing powder using a commercial coffee grinder. The 1-butyl-3-methylimidazolium chloride (bmimCl), 1,3-dimethylimidazolium methylsulfate (mmimMeSO$_4$),
1-butyl-2,3-dimethylimidazolium chloride (bmmimCl), and 1-ethyl-2,3-dimethylimidazolium ethylsulfate (edmimEtSO₄) ionic liquids (Fluka) were dried by toluene azeotropic distillation. Tetraethylene glycol dimethyl ether (Sigma 99%) (tetraglyme) and ethylene glycol dimethyl ether (Sigma 99%) (glyme) were vacuum distilled from sodium with heating. Lithium amide and lithium hydride were used as received from Aldrich. Aldrich bis(dimethylamino)naphthalene (Proton Sponge, PS) was sublimed and stored under inert atmosphere and light free conditions.

4.2.2 Physical Measurements

The Toepler pump system, used for hydrogen measurements, was similar to that described by Shriver and was diagramed in Figure 3.1 of section 3. The released gases from the reaction vessel were first passed through a liquid nitrogen trap before continuing on to the Toepler pump (700 mL). The released H₂ was then pumped into a series of calibrated volumes with the final pressure of the collected H₂-gas measured (±0.5 mm) with the aid of a U-tube manometer. After the H₂-measurement was completed, the in-line liquid nitrogen trap was warmed to room temperature and the amount of any volatiles that had been trapped was then also measured using the Toepler pump.

The automated gas burette Figure 3.2 of section 3 was based on the design reported by Zheng et al., but employed all glass connections with a cold trap (-78 °C) inserted between the reaction flask and burette to allow trapping of any volatiles that might have been produced during the reaction. A more complete description of both the Toepler pump and automated gas burette is available in section 3.

Differential scanning calorimetry was carried out on a Setaram C80 calorimeter at Pacific Northwest National Laboratories. Samples containing 50 mg of AB and 50 mg of bmimCl, without and with 5 mol% (18 mg) of PS were loaded into the cells under a N₂ atmosphere. The ramp rate was 1 °C/min and samples were taken to either 85 °C or 110 °C.

Solid-state reactions carried out with the Toepler pump were extracted with pyridine at various points in the reactions and monitored by ¹¹B NMR. The reaction flask was removed from the oil bath and cooled to room temperature, then dry pyridine was added to the reaction flask under N₂ flow. The pyridine solution was extracted by syringe and then the ¹¹B NMR was taken.

While bmimCl is a liquid at 85 °C, it is a solid at room temperature; therefore, solid-state ¹¹B NMR analyses (at Pacific Northwest National Laboratories: 240 MHz machine spun at 10 kHz) were used to monitor the products of reactions carried out in bmimCl. All solid state ¹¹B chemical shifts were measured relative to external NaBH₄ (-41 ppm).

The solution ¹¹B NMR (128.4 MHz Bruker DMX-400) studies in the room temperature ionic liquid mmimMeSO₄ were carried out by heating the reaction mixtures in sealed NMR tubes at 85 °C for the indicated times with the spectra taken at 25 °C. The ¹¹B NMR spectra of the reactions in tetraglyme were collected with the NMR probe heated at 80 °C.

All solid-state and solution ¹¹B NMR chemical shifts are referenced to external BF₃•O(C₂H₅)₂ (0.0 ppm) with a negative sign indicating an upfield shift.

4.2.3 Procedures for AB H₂-Release Reactions

For the experiments where the released H₂ was measured with the Toepler pump, the AB (250 mg, 8.1 mmol) was loaded into the reaction flasks under N₂. The solid-state reactions of
AB/PS, AB/LiH, and AB/LiNH₂ mixtures were carried out in evacuated 500 mL break-seal flasks that were heated in an oven preheated to the desired temperature. The solids were initially crudely mixed, since upon heating the solid mixtures were found to form a melt before the onset of H₂-release. Reactions in solution were loaded into ~100 mL flasks with the ionic liquid and PS in the amounts given in the tables. The flasks were then evacuated, sealed, and placed in a hot oil bath preheated to the desired temperature. The flasks were opened at the indicated times and the released hydrogen quantified using the Toepler pump system. Post reaction, the flasks were evacuated for 30 min through the cold trap to remove any volatile products from the reaction residue. The product residues and volatiles in the cold trap were extracted with dry glyme and analyzed by ¹¹B NMR.

For reactions using the automated gas burette, the AB (150 mg, 4.87 mmol) samples were loaded into ~100 mL flasks with calibrated volumes, along with the ionic liquid (150 mg) or tetraglyme (0.15 mL) solvents and PS. Under a flow of helium, the flask was attached to the burette system. The system was evacuated for 30 min for reactions with the ionic liquid solutions, and for 5 min for tetraglyme solutions. The system was then backfilled with helium and allowed to equilibrate to atmospheric pressure for ~30 min. Once the system pressure equalized, the data collection program was started and the flask was immersed in the preheated oil bath. The product residues were extracted with dry glyme and analyzed by ¹¹B NMR. The data are reported from the point where the flask was initially plunged into the oil bath, but H₂-release was not observed until the ionic-liquid/AB mixture melted. Data were recorded at 2-5 second intervals depending on the speed of the reaction. The data sets for the gas burette graphs presented in this section are available on a CD that was submitted with this report.

Reactions of bmimCl and bmimCl/PS with partially dehydrogenated AB followed the procedures for the automated gas burette. Initially, two separate samples of neat AB (150 mg, 4.87 mmol) were heated for 23 h at 85 °C to release ~1 equivalent of H₂. The reaction flasks were removed from the gas burette system under a flow of helium and then taken into a glove box where bmimCl (150 mg, 50 wt%) was added to one sample and bmimCl (150 mg, 50 wt%) and PS (55 mg, 5 mol%) added to the second. After thorough mixing, the flasks were reattached to the gas burette system and heated again at 85 °C. Data were recorded on the gas burette system until H₂-release stopped.

4.2.4 Computational Methods
DFT/GIAO/NMR calculations were performed using the Gaussian 03 program. Geometries were fully optimized at the B3LYP/6-31G(d) level without symmetry constraints. The ¹¹B NMR chemical shifts were calculated at the B3LYP/6-311G(d) level using the GIAO option within Gaussian 03. The ¹¹B NMR GIAO chemical shifts are referenced to BF₃•OEt₂ using an absolute shielding constant of 101.58, which was obtained from the GIAO NMR calculated shift of BF₃•OEt₂ at the B3LYP/6-311G(d)//B3LYP/6-31G(d) level of theory.

4.3 Results and Discussion

4.3.1 Ammonia Borane H₂-Release Reactions Promoted by Lithium Amide and Lithium Hydride
Our initial studies of base promoted AB H₂-release²,52 showed that the addition of small amounts of either LiH or LiNH₂ to AB in the solid state eliminated the induction period and
increased both the rate and extent of H\textsubscript{2}-release at 85 °C. Comparisons of the dehydrogenation of pure ammonia borane versus the reactions having added lithium amide or lithium hydride are depicted in Figure 4.1. For the pure ammonia borane reaction at 85 °C, there was negligible hydrogen production after 3 h, but after 15 h, 0.9 equivalents of H\textsubscript{2} were produced. Even with prolonged heating (67 h) at this temperature no further H\textsubscript{2}-release was observed. However, the AB reactions with the addition of 8 mol% of LiNH\textsubscript{2} (18 mg) or 17 mol% LiH (13 mg) at 85 °C led to significant increases in the extent of H\textsubscript{2}-release (~1.5 equivalents in both cases at 15 h). In both cases, these values correspond to the release of ~9.5 materials-wt % H\textsubscript{2}. 

**Figure 4.1** H\textsubscript{2}-release measurements (Toepler pump) of the reaction of pure solid-state AB (250 mg) and with 8 mol% LiNH\textsubscript{2} and 17 mol% LiH at 85 °C.

**Figure 4.2** shows comparisons of the \textsuperscript{11}B NMR spectra of the pyridine-extracted products from an AB/ionic-liquid reaction with those obtained from the AB/lithium-base reactions. At the earlier times, where less than 1 equivalent of H\textsubscript{2} was released, the spectra appear similar. However, at the later times where more H\textsubscript{2} was released, it was evident that while the quintet peak near -37 ppm in the ionic liquid reaction (top right) has been completely lost, the -39 quintet peaks in the LiNH\textsubscript{2} and LiH reactions remained. As discussed in section 1, the -37 ppm resonance in the spectrum of the ionic-liquid promoted AB release products was assigned to the BH\textsubscript{4}\textsuperscript{-} component of the diammoniate of diborane [(NH\textsubscript{3})\textsubscript{2}BH\textsubscript{2}]\textsuperscript{+}BH\textsubscript{4}\textsuperscript{-} (DADB), which was found to be a key intermediate in the ionic-liquid promoted reactions. However, the -39 ppm quintet resonance in the spectra of the LiNH\textsubscript{2} and LiH reactions was found not to be from DADB, but instead to arise from an undesirable product, LiBH\textsubscript{4}. Unfortunately, since LiBH\textsubscript{4} does not decompose until >350 °C, its formation in the AB/lithium-base reactions prevents further AB H\textsubscript{2}-release beyond at 85 °C.
Our studies of the roles of LiNH$_2$ and LiH in inducing H$_2$-release from solid-state AB indicated a different type of dehydrogenation mechanism than was observed in either the solid-state or ionic liquids. As outlined in Equations 4.1 and 4.2, the initial step in the AB/lithium-base reactions is proposed to be AB deprotonation to produce the H$_3$BNH$_2^-$ anion, with this anion then inducing anionic dehydropolymerization of AB to produce a growing polyaminoborane polymer (Equation 4.3).

$$\text{H}_3\text{BNH}_3 + \text{Li}^+\text{NH}_2^- \rightarrow \text{H}_3\text{BNH}_2^\text{-Li}^+ + \text{NH}_3 \quad (4.1)$$

$$\text{H}_3\text{BNH}_3 + \text{Li}^+\text{H}^- \rightarrow \text{H}_3\text{BNH}_2^\text{-Li}^+ + \text{H}_2 \quad (4.2)$$

$$\text{H}_3\text{BNH}_2^\text{-Li}^+ + \text{H}_3\text{BNH}_3 \rightarrow \text{H}_3\text{BNH}_2\text{BH}_2\text{NH}_2^\text{-Li}^+ + \text{H}_2 \quad (4.3)$$

Our studies also showed that the undesirable LiBH$_4$ product could form in these systems via reactions such as shown in Equations 4.4 and 4.5.

$$\text{H}_3\text{BNH}_2^\text{-Li}^+ \rightarrow -(\text{H}_2\text{BNH}_2) + \text{Li}^+\text{H}^- \quad (4.4)$$

$$\text{H}_3\text{BNH}_3 + \text{Li}^+\text{H}^- \rightarrow \text{Li}^+\text{BH}_4^- + \text{NH}_3 \quad (4.5)$$
4.3.2 Ammonia Borane H$_2$-Release Reactions Promoted by Proton Sponge

In order to avoid the formation of stable alkali-metal borohydrides during base promoted AB H$_2$-release, we investigated the use of alternative nitrogen-based deprotonating agents to induce AB polymerization. As discussed in the following sections, we have demonstrated that the strong (pKa ~12), non-nucleophilic base, bis(dimethylamino)naphthalene (Proton Sponge, PS),$^{54}$ can also induce AB H$_2$-release via an anionic dehydropolymerization mechanism with the advantage that the formation of a stable BH$_4^-$ salt is avoided.

4.3.2.1 H$_2$-Release from AB/PS Solid-State Reactions

As shown in Figure 4.3a, initial H$_2$-release measurements using the Toepler pump of the solid-state reactions of AB in the presence of 1.0 and 5.2 mol% PS at 85 °C clearly demonstrated the activating effect of PS on AB H$_2$-release. While the reaction with 1.0 mol % PS still showed an induction period with no H$_2$-released after 1 h, the extent of release was significantly increased at 3 h (0.65 equiv.) compared to that from pure AB at the same time (0.34 equiv.). The data for the 5.2 mol % PS reaction indicated both a shortened induction period, with 0.35 equiv. already released at 1 h, and significantly increased amounts of H$_2$-release at both 3 h (0.93 equiv.) and 20 h (1.12 equiv.) compared to those of either the pure AB or 1.0 mol% PS reactions. However, the solid-state AB/PS reactions stopped just after the release of ~1.1 H$_2$-equivalents.

More detailed H$_2$-release data collected (Figure 4.3b) for the 5.2 mol% PS reaction with the automated gas burette again clearly demonstrated that the induction period was shortened and that the rate of H$_2$-release was increased upon the addition of 5.2 mol% PS.

**Figure 4.3** H$_2$-release measurements (a) (Toepler pump) for solid state AB (250 mg) reactions with 0, 1.0 and 5.2 mol% PS (18 and 91 mg) at 85 °C, (b) (gas burette) for solid state AB (150 mg) reactions with 0 and 5.2 mol% PS (55 mg) at 85 °C.

The NMR spectra in Figure 4.4 of the glyme-soluble residues from the solid-state AB/PS reactions showed features similar to those of the pure AB reactions. Thus, as the reaction progressed, the AB resonance (-23.5 ppm)$^{38}$ decreased and was replaced by resonances arising from both the diaminonitrate of diborane, [(NH$_3$)$_2$BH]$^+$BH$_4^-$, (DADB) (-13.3 (overlapped) and -37.6 ppm)$^{9,38}$ and branched-chain polyaminoborane polymers (-7, -13.3 and -25.1 ppm)$^1$ with the observed shift in good agreement with the calculated shifts given in section 3, Figure 3.9. Consistent with the faster H$_2$-release found for the PS/AB mixtures, the spectra show that after 22 h the amount of unreacted AB was less in the PS/AB reactions than in that of the pure AB reaction. The solid-state $^{11}$B NMR spectra in Figure 4.5 of the final products of the reactions showed an additional broad resonance centered near ~23 ppm that is characteristic of the sp$^2$
boron-framework of cross-linked polyborazylene structures,\textsuperscript{39-41} thus indicating that AB dehydrogenation ultimately produces B=N unsaturated products. Consistent with this conclusion, the \textsuperscript{11}B NMR spectra of the volatile products of the PS/AB reactions collected in the cold trap through which the released H\textsubscript{2} had been passed, also indicated some borazine (B\textsubscript{3}N\textsubscript{3}H\textsubscript{6}) formation with the amount of the volatiles (ranging from 0.04 to 0.25 mmol depending upon the particular experiment) corresponding to less than 10\% of the AB converting to borazine.

\textbf{Figure 4.4} \textsuperscript{11}B\{\textsuperscript{1}H\} NMR (128.4 MHz) spectra (insets show \textsuperscript{1}H coupled spectra) recorded at 25 °C of the glyme extract of the reaction of: (a) AB (150 mg) and 5.3 mol\% PS (55 mg) at 85 °C for 22 h and (b) AB (150 mg) at 85 °C for 22 h. (The broad DADB resonance at -13 ppm is obscured by the PAB resonance)

\textbf{Figure 4.5} Solid-state \textsuperscript{11}B NMR (240 MHz) spectra recorded at 25 °C of the reaction of: (a) AB (150 mg) and 5.3 mol\% PS (55 mg) at 85 °C until 1 H\textsubscript{2}-equivalent was released and (b) AB (150 mg) at 85 °C until 1 H\textsubscript{2}-equivalent was released. (The broad DADB resonance at -13 ppm is obscured by the AB resonance) *Borate resonances at 17 and 2 ppm result from air exposure.
4.3.2.2 H₂-Release from AB/PS Solution Reactions

4.3.2.2.1 Initial Reactions Measured with the Toepler Pump

Figure 4.6 H₂-release measurements (Toepler pump) of the reaction of AB (250 mg) in bmimCl (250 mg) with 0, 1.0 and 5.2 mol% PS (18 and 91 mg) at 85 °C.

The work described in section 3 showed that polar solvents, especially ionic liquids such as 1-butyl-3-methylimidazolium chloride (bmimCl), can activate H₂-release from AB at 85 °C, with over 2 equivalents being produced in ~5 h from a 50/50 weight% AB/bmimCl mixture. Comparisons of the H₂-release rates using Toepler pump measurements of AB dissolved in bmimCl with different amounts of added PS at 85 °C are summarized in Figure 4.6. In the absence of PS, only 0.69, 1.00, 1.28 and 1.97 H₂-equiv. were released at 1, 3, 6 and 23 h, respectively. In contrast, a similar reaction of AB in bmimCl containing 5.2 mol% PS showed a significantly increased H₂-release rate, with 1.40 H₂-equiv. released by 1 h and 2.10 H₂-equiv. released after only 3 h. Even when the amount of PS was decreased to only 0.5 mol% PS, there were still significant increases in the H₂-release found at 1 h (0.83 equiv.), 3 h (1.65 equiv.) and 6 h (2.10 equiv.) compared to those of the reaction without PS.

The plots in Figure 4.6 show that the biggest differences in the H₂-release rates of the bmimCl reactions with and without PS occurred following the release of the first equivalent of H₂. For the reaction without PS, the first equivalent was released in 3 h, and even after 23 h only 1.97 equiv was released. On the other hand, by 3 h the reactions with 5.2 and 1.0 mol% PS had already released 2.10 and 1.75 equiv., respectively, and at 6 h, 2.18 and 2.01 equiv. Thus, PS appears to have significantly enhanced the release rate of the second H₂-equivalent from AB.

Differential scanning calorimetry measurements also support this conclusion. The black curve in Figure 4.7a shows a single well-defined exotherm for the release of the first H₂-equivalent from the reaction of an AB/bmimCl mixture. The blue curve, which is from the reaction of a similar mixture containing 5.3 mol% of added PS, clearly exhibits a second exotherm indicating the release of additional H₂ by a different process. Consistent with the H₂-release measurements that showed significant rate enhancements for the 2nd H₂-equivalent as the temperature was raised, when the upper temperature of the DSC analysis was raised from 85 °C to 110 °C (Figure 4.7b), the second exotherm grew and shifted to shorter times such that it overlapped the first isotherm.
Figure 4.7 Differential Scanning Calorimetry analyses of the reactions of AB (150 mg) in bmimCl (150 mg) with 5.3 mol% PS (55 mg) at: (a) 85 °C and (b) 110 °C. *Initial exotherm is apparatus artifact.

4.3.2.2.2 H₂-Release Reactions Measured with the Automated Gas Burette

In order to better quantify the effects of both PS-loading and temperature, more detailed H₂-release data on a series of 50/50 wt% AB/bmimCl systems containing from 0 to 24.9 mol% PS at 75, 85, 95 and 110 °C were collected on the automated gas burette (Figure 4.8). The rate of H₂-release increased as the mol% of PS in the mixture was increased. For example, as shown in Figure 4.8a, while the reaction at 85 °C without PS required 84 min and 316 min to liberate the 1st and 2nd equivalents of H₂, the reactions with 0.96 (1st 74, 2nd 179 min), 5.3 (1st 61, 2nd 171 min) and 24.9 (1st 41, 2nd 77 min) mol% PS were all significantly faster, with the fastest rate found for the highest loading. Substantial rate increases were observed for all reactions when the reaction temperature was increased. Thus, as illustrated in the plots in Figure 4.8b, at 110 °C the reaction without PS required only 7.4 min and 20 min to liberate the 1st and 2nd equivalents of H₂, but the reactions with 0.96 (1st 5.9, 2nd 13 min), 5.3 (1st 4.3, 2nd 9 min) and 24.9 (1st 4.3, 2nd 7 min) mol% PS were all again significantly faster. It is also noteworthy that at 95 °C and 110 °C, unlike at 85 °C, the rate of H₂-release for the 5.3 and 24.9 mol% PS reactions were similar; indicating that less PS is required to induce H₂-release at higher temperatures.

The above studies all indicate that both bmimCl and PS promote the loss of more than one equivalent of H₂ with the combination of PS in bmimCl being the most effective. To further test this conclusion, two samples of neat AB were first heated at 85 °C for 23 h to produce a partially dehydrogenated material where only ~1.0 H₂-equivalent had been released. To the first sample bmimCl was added and to the second sample both PS and bmimCl. The flasks were then reheated at 85 °C to produce liquid suspensions, and any additional H₂-release was measured. While the heating of AB in the solid state at 85 °C for more extended periods (~48 h) gave no further H₂-release, both Toepler pump and gas burette measurements (Figure 4.9) showed that the addition of either bmimCl or bmimCl/PS to the partially dehydrogenated AB caused H₂-release to resume, ultimately yielding an additional ~0.7 equivalent of H₂ from both samples, with the bmimCl/PS reaction exhibiting the fastest rate.
Figure 4.8 H₂-release measurements (gas burette) of the reaction of AB (150 mg) in bmimCl (150 mg) with 0, 0.96, 5.3 and 24.9 mol% PS (10, 55 and 260 mg) at: (a) 85 °C and (b) 110 °C.

Figure 4.9 H₂-release measurements (gas burette) of partially dehydrogenated AB (150 mg) where 1 H₂-equivalent was initially released at 85 °C, then bmimCl (150 mg) and bmimCl (150 mg)/PS (55 mg/5.2 mol%) were added to separate samples and heating resumed at 85 °C. The dashed line shows the observed AB H₂-release when IL and/or PS are not added.

4.3.3 ¹¹B NMR Studies of Reaction Pathways and Intermediates

4.3.3.1 Solid-State ¹¹B NMR Studies

While bmimCl is a liquid at 85 °C, it is a solid at room temperature; therefore, solid-state NMR was used to monitor the bmimCl/AB/PS reactions at different stages by heating the liquid mixtures at 85 °C, then quenching the reactions at the indicated times by cooling to room temperature, with subsequent analyses of the resulting solid materials by solid-state ¹¹B NMR. Consistent with the H₂-release measurements and ¹¹B NMR studies of solid-state PS/AB reactions, the solid-state ¹¹B spectrum of the reaction of a 50/50 wt% bmimCl/AB mixture containing 5.2 mol% PS showed after 0.5 equiv. of H₂-release, the resonances of both DADB⁹,³⁸ and branched chain polyaminoboranes (Figure 4.10).¹ The small signal (-21.2 ppm) that is apparent just downfield of the AB (-23.2 ppm) resonance has a chemical shift value consistent
with that previously reported\textsuperscript{55-58} for the H$_3$BNH$_2$ anion (-21.49 ppm) and with its DFT/GIAO calculated value (-20.6 ppm) (Figure 4.11).

As the reaction continued, the resonances broadened and diminished and a new resonance centered at 25.9 ppm grew in that is characteristic of unsaturated sp$^2$-hybridized boron. As shown in the spectrum in Figure 4.12, after prolonged reaction (23 h) only the 25.9 ppm resonance remained, indicating that all final products had unsaturated sp$^2$-hybridized structures. NMR studies of the dehydrogenated products of AB H$_2$-release promoted by solid-state thermal reactions\textsuperscript{7} have likewise shown the formation of similar types of B=N unsaturated final products after more than 2 equivalents of H$_2$-release.

**Figure 4.10** Solid-state $^{11}$B NMR (240 MHz) spectra recorded at 25 °C of the reaction of AB (150 mg) and 5.3 mol\% PS (55 mg) in bmimCl (150 mg) at 85 °C after the H$_2$-release of: (a) 0.5 equiv. (30 min), (b) 1 equiv. (61 min), (c) 1.5 equiv. (95 min) and (d) 2 equiv. (171 min). (The broad DADB resonance at -13 ppm is obscured by the AB and PAB resonances)

**Figure 4.11** DFT optimized geometries (B3LYP/6-31G(d)) and GIAO calculated (B3LYP/6-311G(d)) $^{11}$B NMR chemical shifts. The shifts for the corresponding neutral species are given in section 3, Figure 3.9.
Figure 4.12 Solid-state $^{11}$B NMR (240 MHz) spectrum recorded at 25 °C of the reaction of AB (250 mg) and 5.2 mol% PS (91 mg) in bmimCl (150 mg) at 85 °C for 23 h.

4.3.3.2 **In Situ** $^{11}$B NMR Studies of Reaction Progress in Ionic Liquids

*In situ* solution $^{11}$B NMR studies of the PS promoted H$_2$-release from AB in the room temperature ionic liquid mmimMeSO$_4$ at 85 °C also exhibited features similar to those observed in the solid-state NMR spectra of the bmimCl reactions. It is significant that the $^{11}$B NMR spectra of the reactions with and without PS in mmimMeSO$_4$ (**Figure 4.13**) showed the formation of similar types of products. In both reactions, DADB and polyaminoborane polymers were formed initially, then at the longer times where more H$_2$ was released, the DADB and polyaminoborane resonances decreased and insoluble materials formed. Only a small intensity resonance was observed near 25 ppm indicating that if unsaturated B=N products, such as borazine or polyborazylene, were formed they must have reacted rapidly to form the final insoluble product.

Figure 4.13 Solution $^{11}$B NMR (128 MHz) spectra recorded at 25 °C of the reaction of AB (50 mg) in mmimMeSO$_4$ (450 mg) at 85 °C, (right) with 5.2 mol% PS (18 mg) after the release of: (a) 0.03 equiv., (b) 0.08 equiv., (c) 0.32 equiv., (d) 1.14 equiv. and (e) 1.63 equiv.; (left) without PS after the release of: (a*) 0.03 equiv., (b*) 0.08 equiv., (c*) 0.29 equiv., (d*) 1.07 equiv. and (e*) 1.62 equiv. (The broad DADB resonance at -13 ppm is obscured by the AB and PAB resonances)
4.3.4 Proton Sponge Reduces Foaming During AB Thermolysis

One of the barriers to the utilization of AB H\textsubscript{2}-release for hydrogen storage, is that AB dehydrogenation in either the solid state or in solution normally produces considerable foaming. However, as shown in the photographs in Figure 4.14, Proton Sponge, besides increasing both the rate and extent of H\textsubscript{2}-release, was found to have the unanticipated, but highly beneficial, effect of significantly reducing foaming during AB H\textsubscript{2}-release in the bmimCl/PS reactions.

![Figure 4.14](image)

Figure 4.14 Foaming resulting from the reaction of 250 mg AB in 250 mg bmimCl after 1 h at 100 °C: (a) without PS, (b) with 5.2 mol% PS (91 mg).

4.3.5 H\textsubscript{2}-Release in Other Ionic Liquids and Tetraglyme

PS was also found to increase AB H\textsubscript{2}-release in both other ionic liquids and tetraglyme, with both the extent and rate of H\textsubscript{2}-release comparable to that of the PS/bmimCl reactions (Figure 4.15). Gas burette data at 85 °C for the tetraglyme reactions showed that fast rates could be achieved with only 1 mol% of PS. The \textsuperscript{11}B NMR spectra of the tetraglyme/PS reactions also showed evidence for the initial formation of the H\textsubscript{3}BNH\textsubscript{2}– anion, followed by the appearance of the resonances for polyaminoborane polymers. However, at longer times, unlike in the ionic liquids, the major product was borazine (30.1 ppm \textsuperscript{42} along with smaller amounts of BH\textsubscript{4}– (-36.8 ppm) \textsuperscript{42} and µ-aminodiborane (-27.5 ppm) \textsuperscript{42} (Figure 4.16). Thus, ionic liquid solvents are favored for AB H\textsubscript{2}-release since they suppress or reduce the formation of these products.

![Figure 4.15](image)

Figure 4.15 H\textsubscript{2}-release measurements (Toepler pump) of the reaction of AB (250 mg) in ionic liquids or tetraglyme (250 mg) with 5.2 mol% PS (91 mg) at 85 °C.
4.3.6 Why Does Proton Sponge Induce H$_2$-Release from AB?

In Section 3, it was proposed that the AB activation for H$_2$-release that is observed in ionic liquids may occur by a mechanistic pathway (section 3, Figure 3.16) involving: (1) ionic-liquid promoted conversion of AB into its more reactive ionic DADB form ([BH$_2$(NH$_3$)$_2$]BH$_4^-$), (2) further intermolecular dehydrocoupling reactions between hydridic B-H hydrogens and protonic N-H hydrogens on DADB and/or AB to form neutral polyaminoborane polymers and (3) polyaminoborane dehydrogenation to unsaturated cross-linked polyborazylene materials. The initial formation of DADB has also been proposed as a key step in thermally-induced AB H$_2$-release reactions in the solid state and in organic solvents. While a DADB pathway may contribute to the H$_2$-release observed in the bmimCl/PS solutions, the observed rate enhancements and DSC properties of the Proton Sponge reactions suggest that there is also another mechanistic pathway for H$_2$-release in these systems.

Proton Sponge (Equation 4.6) is a strong base and because of its low nucleophilicity is frequently used as a deprotonating agent in organic and inorganic syntheses that can eliminate the undesirable side reactions often found with more coordinating bases. PS gains its low nucleophilicity from the hindered lone pairs that are partially protected by the methyl groups. A
contributing factor to the high basicity found in PS is the naphthalene backbone strain. Free PS has a strained naphthalene backbone due to the lone-pair/lone-pair repulsion and methyl group steric strain. The protonated form is less strained because the lone pairs swing into the naphthalene plane to bond making the PSH⁺ more stable than would be expected without the strain relief. The observation of a $^{11}$B NMR signal near -21.0 ppm and a $^1$H NMR signal at -18.9 ppm, characteristic of AB deprotonation to form the H$_3$BNH$_2^-$PSH$^+$ ion, at the beginning stages of the reactions of AB with PS, strongly supports a PS-promoted AB H$_2$-release reaction pathway.

Deprotonation of AB by bases is well-known. For example, the H$_3$BNH$_2^-$Li$^+$ salt has previously been prepared in situ from AB and n-BuLi at 0 °C. More recently, ball milling and solution reactions of AB with metal hydrides have been used to generate H$_3$BNH$_2^-M^+$ (M = Li and Na) and (H$_3$BNH$_2$)$_2$Ca$^{2+}$. We found that AB deprotonation could also be easily achieved by its reaction with either lithium or potassium triethylborohydride (Equation 4.7), but that in these cases, a Et$_3$B-stabilized anion was formed, with the observed resonances in the $^{11}$B NMR spectra of the Li$^+$ (-7.5 (s) and -23.8 (q) ppm) and K$^+$ (-7.8 (s) and -23.6 (q) ppm) compounds being assigned based on the DFT/GIAO calculations to the BEt$_3$- (calc -10.6) and terminal -BH$_3$ (calc -25.3) units in the anion.

$$\text{H}_3\text{BNH}_3 + M^+\text{BEt}_3\text{H}^- \rightarrow [\text{Et}_3\text{BNH}_2\text{BH}_3]^M^+ + \text{H}_2 \quad (M = \text{Li or K})$$ (4.7)

Figure 4.17 Crystallographically determined structure of [Et$_3$BNH$_2$BH$_3$]$^- \cdot K^+$•18-crown-6

The structures of H$_3$BNH$_2^-M^+$ (M = Li and Na) and (H$_3$BNH$_2$)$_2$Ca$^{2+}$ have recently been established from the analyses of their high resolution powder diffraction data, and that of (H$_3$BNH$_2$)$_2$Ca$^{2+}$$\cdot$2THF by a single-crystal X-ray determination. The crystallographic determination of the [Et$_3$BNH$_2$BH$_3$]$^- \cdot K^+$•18-crown-6 complex in Figure 4.17 confirmed that following AB nitrogen-deprotonation by the triethylborohydride, the Lewis-acidic triethylborane group coordinated at the nitrogen.
Electronic structure calculations on \([\text{H}_2\text{NBH}_3]\)M\(^+\) have predicted\(^{59,61}\) that the B-H hydrogens in these complexes will be much more negatively charged and, as a result, have a higher bascity than in AB. This increases the ability of these anions to release \(\text{H}_2\) by the intermolecular reaction of their hydridic B-H hydrogens with an N-H proton on an adjacent complex. Thus, the most likely second step in PS-promoted \(\text{H}_2\)-release is the intermolecular dehydrocoupling of one of the hydridic B-H hydrogens of \([\text{H}_2\text{NBH}_3]\)\(\text{PSH}^+\) with a \(\text{H}_3\text{NBH}\) to produce, as shown in Figure 4.18, a growing anionic polyaminoborane polymer. DFT/GIAO calculations of model anionic polymers showed that their \(^{11}\text{B}\) NMR chemical shifts (Figure 4.11) would be indistinguishable from those of the corresponding neutral polyaminoborane polymers,\(^1\) thus explaining the similarity of the spectra for the reactions with and without PS in Figure 4.13.

The expected decreased acidity of the internal \(\text{NH}_2\) hydrogens of a polyaminoborane polymer relative to those on terminal \(\text{NH}_3\) units should result in the \(\text{NH}_2\) protons being less reactive for dehydrocoupling reactions that could liberate more than one-equivalent of \(\text{H}_2\). Thus, the increased release-rate for the second equivalent of \(\text{H}_2\) observed for the PS-induced reactions of AB may result from the greater ability of the more basic B-H hydrogens of an anionic polyaminoborane to induce \(\text{H}_2\)-elimination reactions with the protons at these \(\text{NH}_2\) sites.

![Figure 4.18](image-url) Possible anionic polymerization pathway for PS-promoted \(\text{H}_2\)-release from AB.

Support for the proposed anionic polymerization pathway for the AB/PS reaction was obtained from our studies of the reaction (Equation 4.8) of \([\text{Et}_3\text{BH}_2\text{BH}_3]\)\(\text{Li}^+\) with AB.\(^{29}\) The higher Lewis acidity of the BH\(_3\) group compared to the Et\(_3\)B unit should significantly increase
the nucleophilic character of the boron-hydrogens and enhance the ability of this anion to undergo dehydropolymerization with AB. In agreement with this expectation, Toepler pump measurements confirmed the loss of H$_2$ during the reaction of equal equivalents of NH$_3$BH$_3$ with [Et$_3$BNH$_2$BH$_3$]$_{-}$Li$^{+}$ at 23 °C and an electrospray mass spectrum indicated formation of Et$_3$BNH$_2$BH$_2$NH$_2$BH$_3$$. The $^{11}$B NMR spectra was in good agreement with the calculated $^{11}$B NMR shifts for the DFT optimized geometry of the chain growth product Et$_3$BNH$_2$BH$_2$NH$_2$BH$_3$$. given in Figure 4.19. These results provide additional strong support for a PS-induced H$_2$-release mechanism involving an intermolecular anionic dehydropolymerization pathway initiated by the NH$_2$BH$_3$$^{-}$ anion.

![Figure 4.19](image)

**Figure 4.19** DFT (B3LYP/6-31G(d)) optimized geometry and GIAO (B3LYP/6-311G(d)) calculated $^{11}$B NMR shifts for [Et$_3$BNH$_2$BH$_2$NH$_2$BH$_3$]$^{-}$.

### 4.4 Conclusions

The work described in this section demonstrated base-activation of AB H$_2$-release in the solid-state and in ionic-liquid and tetraglyme solution reactions. The experimental observations and model studies support an anionic dehydropolymerization mechanism initiated by the H$_3$BNH$_2$ anion. For the bmimCl/PS reactions, significantly increased rates of AB H$_2$-release, yielding over 2 equivalents of H$_2$, were achieved with as little as 1 mol% Proton Sponge. PS was also found to have the unanticipated effect of significantly reducing reaction foaming. These studies further demonstrate that H$_2$-release from chemical hydrides can occur by a number of different mechanistic pathways and strongly suggest that optimal chemical-hydride based H$_2$-release systems may require the use of synergistic dehydrogenation methods to induce H$_2$-loss from chemically different intermediates formed during release reactions.
Section 5. Metal-Catalyzed Ammonia Borane H₂-Release in Ionic Liquids

Summary

A number of transition metals were found to catalyze H₂-release from ammonia borane and Me₂NHBH₃ in ionic-liquid solvents. While significant increases in the initial H₂-release rates of the catalyzed reactions 50-wt% AB/ionic-liquids solutions were observed at 65 °C, H₂-release from these concentrated solutions essentially stopped after the release of only ~1 H₂-equivalent. A higher degree of AB H₂-release was observed for the metal-catalyzed reactions with more dilute (~10-wt%) AB/ionic-liquid solutions with the release of over 2 H₂-equivalents at 65 °C. In situ ¹¹B NMR studies demonstrated that there are different mechanistic pathways for H₂-release in the uncatalyzed and metal-catalyzed reactions in ionic-liquids and since the reactions in ionic-liquids yield lower amounts of borazine, a potential fuel-cell poison, ionic-liquid solvents are favored over conventional solvents for metal catalyzed AB H₂-release.

5.1 Introduction

The results discussed in sections 3 and 4 of this report demonstrated that both ionic-liquids and bases can activate ammonia borane (AB) H₂-release. The use of metal catalysts to induce AB H₂-release as an alternative activation approach could have a number of potentially complimentary properties, including (1) faster initial H₂-release, (2) better control of release rates, (3) lower temperature reactions, and (4) better control of product structure/composition. As a result, numerous examples have now been reported of metal-catalyzed H₂-release from ammonia borane. However, practical applications of chemical hydrogen storage will require a replacement for the organic solvents that have traditionally been used in these earlier reports, since the volatility of these solvents would result in both their loss to the environment and contamination of the H₂-stream. As discussed in section 3, ionic-liquids have a number of potential advantages as reaction media for chemical hydrogen storage systems, including low volatility, nonflammability, high polarity with low coordinating power, and the ability to stabilize reactive metal-catalyst intermediates. We report in this section our work that has demonstrated that transition metal catalysts can also be used in ionic liquids to induce H₂-release from amine boranes and that these reactions gave different product structures/compositions than have been obtained in conventional organic solvents.

5.2 Experimental Section

All manipulations were carried out using standard high-vacuum or inert-atmosphere techniques as described by Shriver.

5.2.1 Materials

Ammonia borane (Aviabor 97% minimum purity) was ground into a free flowing powder using a commercial coffee grinder. Me₂NHBH₃ (Aldrich) was sublimed and stored under an inert atmosphere. The 1-butyl-3-methylimidazolium iodide (bmimI) was synthesized sonochemically from 1-iodobutane and 1-methyl-imidazole according to literature methods. All ionic liquids, including 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄), 1-butyl-3-methylimidazolium chloride (bmimCl), 1-butyl-3-methylimidazolium triflate (bmimOTf), 1-butyl-2,3-dimethylimidazolium chloride (bmmimCl), 1-ethyl-2,3-dimethylimidazolium ethylsulfate (emmimEtSO₄), 1-ethyl-2,3-dimethylimidazolium triflate (emmimOTf), and 1,3-
dimethylimidazolium methylsulfate (mmimMeSO₄) were dried by toluene azeotropic distillation to remove any moisture. The [Rh(COD)Cl₂] (Aldrich), RhCl₃ (Strem), NiCl₂ (Aldrich), Ru(COD)Cl₂ (Strem), and RuCl₃ (Strem), Pd(DBA)₂ (Acros), Pd₂(DBA)₃ (Aldrich), and Ni(COD)₂ (Strem) were anhydrous and handled under inert atmosphere.

5.2.2 Physical Measurements

The Toepler pump system used for hydrogen measurements was similar to that described by Shriver⁸ and was diagramed in Figure 3.1 of section 3. The released gases from the reaction vessel were first passed through a liquid nitrogen trap before continuing on to the Toepler pump (700 mL). The released H₂ was then pumped into a series of calibrated volumes with the final pressure of the collected H₂-gas measured (±0.5 mm) with the aid of a U-tube manometer. After the H₂-measurement was completed, the in-line liquid nitrogen trap was warmed to room temperature and the amount of any volatiles that had been trapped was then also measured using the Toepler pump.

The automated gas burette shown in Figure 3.2 of section 3 was based on the design reported by Zheng et al.,¹¹ but employed all glass connections with a cold trap (-78 °C) inserted between the reaction flask and burette to allow trapping of any volatiles that might have been produced during the reaction. A more complete description of both the Toepler pump and automated gas burette is available in section 3.

Differential scanning calorimetry was carried out on a Setaram C80 calorimeter at Pacific Northwest National Laboratories. Samples containing 50 mg of AB and 50 mg of bmimCl, without and with 5 mol% metal catalyst were loaded into the cells under a N₂ atmosphere. The ramp rate was 1 °C/min and samples were taken to either 85 °C or 110 °C.

The solution ¹¹B NMR (128.4 MHz Bruker DMX-400) studies in the room temperature ionic liquid bmimOTf were carried out by heating the reaction mixtures in sealed NMR tubes at the desired temperatures/times with the spectra taken at 25 °C.

Solid-state ¹¹B NMR analyses (at Pacific Northwest National Laboratories: 240 MHz machine spun at 10 kHz) were used to monitor the products of reactions carried out in bmimCl. All solid state ¹¹B chemical shifts were measured relative to external NaBH₄ (-41 ppm).

All solid-state and solution ¹¹B NMR chemical shifts are referenced to external BF₃•O(C₂H₅)₂ (0.0 ppm) with a negative sign indicating an upfield shift.

5.2.3 Procedures for AB H₂-Release Reactions

5.2.3.1 H₂-Release Measured with a Toepler Pump

For the experiments where the released H₂ was measured with the Toepler pump, the AB (250 mg, 8.1 mmol) was loaded into the reaction flasks under N₂. Reactions in solution were loaded into ~100 mL flasks with the ionic liquid and metal. The flasks were then evacuated, sealed, and placed in a hot oil bath preheated to the desired temperature. The flasks were opened at the indicated times and the released hydrogen quantified using the Toepler pump system. Examples of typical H₂-release data obtained for uncatalyzed, and Rh- and Pd-catalyzed reactions at different temperatures are given in Table 5.1. Post reaction, the flasks were evacuated for 30 min through the cold trap to remove any volatile products from the reaction residue. The product residues and volatiles in the cold trap were extracted with dry glyme and analyzed by ¹¹B NMR.
Table 5.1 Typical H\textsubscript{2}-Release Data for uncatalyzed, Rh-catalyzed and Pd-catalyzed NH₃BH₃ reactions in 50-wt % ionic liquid at 85, 65 and 45 °C.

<table>
<thead>
<tr>
<th>Time [h]</th>
<th>Temp [°C]</th>
<th>H\textsubscript{2}-Release</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Uncatalyzed\textsuperscript{a}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>equiv. (mmol)</td>
</tr>
<tr>
<td>1</td>
<td>85</td>
<td>1.00 (8.09)</td>
</tr>
<tr>
<td>3</td>
<td>85</td>
<td>1.32 (10.7)</td>
</tr>
<tr>
<td>6</td>
<td>85</td>
<td>1.64 (13.3)</td>
</tr>
<tr>
<td>23</td>
<td>85</td>
<td>2.20 (17.8)</td>
</tr>
<tr>
<td>1</td>
<td>65</td>
<td>0.19 (1.51)</td>
</tr>
<tr>
<td>3</td>
<td>65</td>
<td>0.60 (4.87)</td>
</tr>
<tr>
<td>5</td>
<td>65</td>
<td>0.75 (6.08)</td>
</tr>
<tr>
<td>23</td>
<td>65</td>
<td>1.01 (8.19)</td>
</tr>
<tr>
<td>1</td>
<td>45</td>
<td>0.003 (0.028)</td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>0.01 (0.083)</td>
</tr>
<tr>
<td>5</td>
<td>45</td>
<td>0.02 (0.19)</td>
</tr>
<tr>
<td>23</td>
<td>45</td>
<td>0.34 (2.77)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 250 mg NH₃BH₃ (8.1mmol) and 250 mg emmimEtSO₄; \textsuperscript{b} 100 mg [Rh(COD)Cl]₂ (5mol% Rh); \textsuperscript{c} 150 mg NH₃BH₃, 150 mg bmimCl, and 140 mg Pd(DBA)₂.

5.2.3.2 H\textsubscript{2}-Release Measured with an Automated Gas Burette

For reactions using the automated gas burette, the AB (150 mg, 4.87 mmol) or Me₂NHBH₃ (150 mg, 2.55 mmol) samples were loaded into ~100 mL flasks with calibrated volumes, along with the ionic liquid (150 mg) or tetraglyme (0.15 mL) solvents and any metal catalysts. Under a flow of helium, the flask was attached to the burette system. The system was evacuated for 30 min for reactions with the ionic liquid solutions, and for 5 min for tetraglyme solutions. The system was then backfilled with helium and allowed to equilibrate to atmospheric pressure for ~30 min. Once the system pressure equalized, the data collection program was started and the flask was immersed in the preheated oil bath. The product residues were extracted with dry glyme and analyzed by \textsuperscript{11}B NMR. The data are reported from the point where the flask was initially plunged into the oil bath, but H\textsubscript{2}-release was not observed until the ionic-liquid/AB mixture melted. Data were recorded at 2-5 second intervals depending on the speed of the reaction.

5.3 Results and Discussion

Manners has previously reported that while ammonia borane is stable in tetraglyme solutions at 45 °C, the addition of the chloro(1,5-cyclooctadiene)rhodium(I) complex ([Rh(COD)Cl]₂) precatalyst induced H\textsubscript{2}-release to form cyclotriborazane, \textmu-aminodiborane, borazine and insoluble BNH₆ oligomers.\textsuperscript{14} He also showed that Rh catalyzed Me₂NHBH₃
dehydrogenation in toluene to form the (Me$_2$NBH$_2$)$_2$ cyclic dimer. Although ionic liquids have been used for a wide variety of metal-catalyzed chemical reactions, our work demonstrating that [Rh(COD)Cl]$_2$ also catalyzed AB H$_2$-release in emmimEtSO$_4$, was the first report of metal-catalyzed AB H$_2$-release in an ionic liquid. The quantitative H$_2$-evolution measurements summarized in Figure 5.1 provide comparisons of the rates of AB H$_2$-release for 50-wt% AB/emmimEtSO$_4$ solutions with and without 2.5-mol% of [Rh(COD)Cl]$_2$ (5-mol% Rh) at different temperatures. At 45 °C, the uncatalyzed reaction released little hydrogen within the first 6 h, while the catalyzed reaction released almost 0.6 equivalents. At both 65 °C and 85 °C, there were again significant increases in the initial H$_2$-release rates of the catalyzed reactions up to ~1 H$_2$-equivalent, but the H$_2$-release rates after this point were comparable for both the catalyzed and uncatalyzed reactions.

![Graph](image1)

**Figure 5.1** Comparisons of the H$_2$-release activities at different temperatures (Toepler pump measurements) of the reactions of AB (250 mg) in 50-wt% emmimEtSO$_4$ with and without 2.5-mol% of [Rh(COD)Cl]$_2$.

As shown in **Figure 5.2**, the [Rh(COD)Cl]$_2$ complex was also found to be quite active in 50-wt% bmimCl for the catalyzed dehydrocyclization of Me$_2$NHBH$_3$ to (Me$_2$NBH$_2$)$_2$.

![Graph](image2)

**Figure 5.2** H$_2$-release measurements on the automated gas burette of the reaction of Me$_2$NHBH$_3$ (150 mg) in 50-wt% bmimCl at 65 °C with 2.5-mol% [Rh(COD)Cl]$_2$. 

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Differential scanning calorimetric studies carried out at PNNL, demonstrated that the Rh-catalyst significantly lowered the temperature required for H$_2$-release. **Figure 5.3** shows DSC plots of equal mass AB/bmimCl mixtures heated to 85 °C at 1°C/min and then held at 85 °C. The exotherm resulting from AB H$_2$-release in the sample containing the [Rh(COD)Cl]$_2$ precatalyst is clearly shifted to lower temperatures.

**Figure 5.3** DSC analysis of 50-wt% NH$_3$BH$_3$ in bmimCl with and without 5 mol% Rh.

As presented in **Figure 5.4**, the AB H$_2$-release rate was found to be dependent on the Rh catalyst concentration, but again, in each case, H$_2$-release from these concentrated (50-wt%) solutions at 65 °C essentially stopped after the release of only ~1 H$_2$-equivalent.

**Figure 5.4** H$_2$-release measurements using the automated gas burette of the 65 °C reaction of AB (150 mg) in 50-wt% bmimCl with different mol% Rh.

As shown in **Figures 5.5** and **5.6**, a higher degree of AB H$_2$-release was observed for the metal-catalyzed reactions with more dilute (~10-wt%) AB solutions in emmimEtSO$_4$. Thus, the release of over 2 H$_2$-equivalents was obtained in the Rh (4 h), Ru (6 h) and Ni (12h) catalyzed reactions, whereas the comparable uncatalyzed reaction released only 0.4, 0.6 and 0.8 H$_2$-equivalents at these times.
Figure 5.5 H₂-release measurements using the automated gas-burette of the reaction of AB (150 mg) in 90-wt% bmmOTf at 65 °C with 5-mol% catalysts.

The $^{11}$B-NMR spectra of monoglyme extracts of the 50-wt% AB/emimEtSO$_4$ Rh-catalyzed reaction mixtures showed the -5 and -12 ppm resonances characteristic of polyaminoborane formation. Significant borazine resonances (+30 ppm) were also observed in the extracts from catalyzed reactions that had released >1 equiv. of H$_2$. Most significantly, unlike in the uncatalyzed reactions, there was no evidence for the formation of DADB in the extracts from the catalyzed reactions.

The in-situ solution $^{11}$B-NMR observations presented in Figure 5.6 of the reactions of 10-wt% AB in bmmOTf confirmed the absence of DADB in the catalyzed reactions. Thus, in the spectra on the left, the formation of DADB is clearly indicated in the uncatalyzed reaction by the appearance of the quintet resonance near -36 ppm, whereas this resonance is absent in the spectra of corresponding rhodium-catalyzed reaction shown on the right. As can also be observed in these spectra, polyaminoborane is clearly the dominant product in the uncatalyzed reaction, whereas borazine appears to be the major product of the catalyzed reaction. These observations all indicate that there are different mechanistic pathways for H$_2$-release in the uncatalyzed and metal-catalyzed reactions in ionic-liquids.

Figure 5.6 In situ solution $^{11}$B NMR spectra of the reaction of 10-wt% AB in bmmOTf at 85 °C: (left) uncatalyzed; (right) with 2.5-mol% [Rh(COD)Cl]$_2$. 
The \( \text{H}_2 \)-release measurements summarized in **Figures 5.7** and **5.8**, demonstrated that a number of metals catalyze \( \text{H}_2 \)-release from both AB and \( \text{Me}_2\text{NHBH}_3 \) in the bmimCl ionic-liquid, including Rh, Ni, Pd and Ru based catalysts.

**Figure 5.7** \( \text{H}_2 \)-release measurements using the automated gas burette of the reactions of 50-wt\% AB (150 mg) in bmimCl at 65 °C with 5-mol\% catalysts.

**Figure 5.8** \( \text{H}_2 \)-release measurements using the automated gas burette of the reactions of 50-wt\% \( \text{Me}_2\text{NHBH}_3 \) in bmimCl at 65 °C with 5-mol\% catalysts.

In situ solution \(^{11}\text{B} \) NMR studies of the Ni and Ru-catalyzed AB \( \text{H}_2 \)-release reactions showed that while these metals were somewhat less active than the Rh-catalysts, borazine formation appeared to be suppressed in these reactions.

**Figure 5.9** In situ solution \(^{11}\text{B} \) NMR spectra of the progress of the reactions of 10-wt\% AB in bmimOTf at 65 °C with: (left) 5-mol\% RuCl\(_3\); (right): 5-mol\% NiCl\(_2\).
The Pd(DBA)$_2$ complex proved to have the highest rates for AB H$_2$-release and showed excellent activity in a range of ionic-liquid and conventional solvents with a release rate that increased with the catalyst loading (Figure 5.10).

![Figure 5.10 AB H$_2$-release rates at 65 °C measured with the automatic gas burette for the Pd(DBA)$_2$ catalyst with different ionic-liquids, wt%-AB and catalyst-concentrations.](image)

In situ solution $^{11}$B NMR studies (Figure 5.11) of the Pd(DBA)$_2$-catalyzed AB H$_2$-release reactions in tetraglyme and bmimOTf revealed that, unlike in the bmimOTf reaction, there was little evidence of polyaminoborane formation in the tetraglyme reaction, with the major product being instead borazine (30.1 ppm). Thus, since they suppress the formation of borazine, a potential fuel-cell poison, ionic-liquid solvents are clearly favored over conventional solvents for metal catalyzed AB H$_2$-release.

![Figure 5.11 In situ solution $^{11}$B NMR studies monitoring the progress of H$_2$-release at 65 °C from: (left) 10-wt% AB in tetraglyme with 1 mol% Pd(DBA)$_2$ (the peak at 30.1 ppm is from borazine) and (right) 10-wt% AB in bmimOTf with 1 mol% Pd(DBA)$_2$.](image)

The solid-state $^{11}$B NMR spectra (Figures 5.12 and 5.13) of the insoluble AB spent-fuel products of the metal-catalyzed H$_2$-release in ionic liquids were similar to those obtained from the uncatalyzed reactions with each spectrum exhibiting a broad downfield resonance.
characteristic of cross-linked polyborazylene structures.\textsuperscript{39-41} Thus, even though the uncatalyzed and metal-catalyzed AB H\textsubscript{2}-release reactions in ionic liquids appear to go by different mechanistic pathways and intermediate species, both reactions ultimately produce similar spent fuel materials composed of an sp\textsuperscript{2} boron-nitrogen framework with B=N units.

**Figure 5.12** Solid State \textsuperscript{11}B NMR spectrum of the reaction of 50-wt\% AB in bmimCl at 65°C for 23 h with 5-mol\% Rh.

**Figure 5.13** Solid State \textsuperscript{11}B NMR of the reaction of 50-wt\% AB in bmimCl at 65 °C with 5-mol\% of Pd(DBA)\textsubscript{2} after the release of only 0.5, 1.0 and 1.2 H\textsubscript{2}-equivalents.

### 5.4 Conclusions

The results presented in this section have demonstrated that metal catalysts can be used to alter both the rates and mechanisms of ammonia borane H\textsubscript{2}-release in ionic liquid media. A number of transition metals were found to catalyze AB H\textsubscript{2}-release in ionic-liquids with the rhodium and palladium metals showing the highest activities. In situ \textsuperscript{11}B NMR studies demonstrated that there are different mechanistic pathways for H\textsubscript{2}-release in the uncatalyzed and metal-catalyzed reactions in ionic-liquids with the metal catalysts having the biggest effect on the release of the 1\textsuperscript{st} H\textsubscript{2}-equivalent. Furthermore, since they produced lower amounts of borazine, a potential fuel-cell poison, ionic liquids were found to be favored over conventional solvents for metal catalyzed AB H\textsubscript{2}-release reactions.
Section 6. Synthesis and Hydrolytic H$_2$-Release from Ammonia Triborane

Summary

Our studies$^{65,66}$ demonstrated that iodine oxidation of B$_3$H$_8^-$ in glyme solution produced (glyme)B$_3$H$_7$. Subsequent displacement of the coordinated glyme by reaction with anhydrous ammonia provided a safe and convenient preparation of ammonia triborane, NH$_3$B$_3$H$_7$ (1). Studies of ammonia triborane hydrolytic H$_2$-release reactions showed that upon the addition of acid or an appropriate transition metal catalyst, aqueous solutions of 1 rapidly release hydrogen, with 6.1 materials-wt% H$_2$-release being achieved from a 22.7-wt% aqueous solution of 1 at room temperature in the presence of 5-wt% Rh/Al$_2$O$_3$ (1.1 mol% Rh). The rate of H$_2$-release was controlled by both the catalyst loadings and temperature. While the DOE total-system H$_2$-storage targets for transportation will not be attainable with this, or any other, hydrolytic-based system, an ammonia triborane based hydrolytic system can provide a means of safe hydrogen generation that should be competitive with both the NH$_3$BH$_3$ and NaBH$_4$ based hydrolyses for other applications having less stringent weight requirements.

6.1 Introduction

The high hydrogen release capacity that could potentially be achieved by ammonia triborane oxidative-hydrolysis, Equation 6.1, (9.7 materials-wt% H$_2$) or thermolysis, Equation 6.2, (17.7 materials-wt% H$_2$) makes it an attractive candidate for chemical hydrogen storage.

\[
\text{NH}_3\text{B}_3\text{H}_7 + 6 \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + 3 \text{BO}_2^- + 2\text{H}^+ + 8 \text{H}_2 \quad (9.8 \text{ wt\% H}_2) \quad (6.1)
\]

\[
\text{NH}_3\text{B}_3\text{H}_7 \rightarrow \text{“B}_3\text{N”} + 5 \text{H}_2 \quad (17.7 \text{ wt\% H}_2) \quad (6.2)
\]

Although Kodama first synthesized$^{67}$ NH$_3$B$_3$H$_7$ over 50 years ago, owing to the lack of a suitable method for its efficient and safe synthesis, its reactivities and properties had not been intensively explored. Of the fewer than 30 previous publications on 1, many were stimulated by the apparent contradiction between the computational studies$^{68-74}$ that predict a symmetric single hydrogen-bridged C$_5$-symmetric structure, and the early single crystal X-ray determination$^{75}$ of 1 that showed an asymmetric structure with perhaps two bridging-hydrogens.

In this section we describe: (1) a new, efficient preparation of 1 that now makes this compound easily available; (2) a description of the hydrolytic hydrogen release properties of 1.

6.2 Experimental Section

All manipulations were carried out using standard high-vacuum or inert-atmosphere techniques as described by Shriver.$^8$

6.2.1 Materials

Aldrich NaBH$_4$ (98%), iodine, 18-crown-6, RhCl$_3$, [Rh(COD)(μ-Cl)]$_2$ (COD = 1,5-cyclooctadiene), Pd/Al$_2$O$_3$, Pt/C, Pt (nanosize, activated), Pd (submicron), Ru powder, and NiCl$_2$ and Aldrich or Strem Rh/Al$_2$O$_3$, Ru/Al$_2$O$_3$, and RuCl$_3$ were stored under inert atmosphere and used as received. Diglyme (Acros Organics) was distilled over Na prior to use. Glyme, dimethoxyethane, (Aldrich) was dried by passing through an activated alumina column prior to use. Bu$_4$N$^+$B$_3$H$_8^-$ was prepared according to the procedure described by Ryschkewitsch.$^{76,77}$
6.2.2 Physical Measurements

$^{11}$B NMR spectra at 128.4 MHz and $^1$H NMR spectra at 400.1 MHz were obtained on a Bruker DMX-400 spectrometer equipped with appropriate decoupling accessories. $^1$H NMR spectra at 500.1 MHz were obtained on a Bruker AM-500 spectrometer. All $^{11}$B chemical shifts are referenced to external BF$_3$·O(C$_2$H$_5$)$_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All $^1$H chemical shifts were measured relative to internal residual protons from the lock solvents (99.9% CD$_2$Cl$_2$ or 99.5% C$_6$D$_6$) and are referenced to (CH$_3$)$_4$Si (0.0 ppm). Diffuse reflectance infrared Fourier transform (DRIFT) spectra were obtained on a Perkin-Elmer 100 FT-IR spectrometer with DRIFT accessory. Melting points were determined using a standard melting point apparatus and are uncorrected. All pH measurements were performed using an Orion 230 pH meter.

6.2.3 Preparation of NH$_3$B$_3$H$_7$ (1) from Bu$_4$N$^+$B$_3$H$_8^-$

After a solution of Bu$_4$N$^+$B$_3$H$_8^-$ (1.0 g, 3.53 mmol) in dry glyme (10.0 mL) was cooled at -70 °C for 15 min under an inert atmosphere, a solution of iodine (0.44 g, 1.73 mmol) in dry glyme (10.0 mL) was added, and the resulting solution stirred for 10 min at this temperature. The reaction mixture was then allowed to warm to room temperature, during which time the purple color of the solution faded indicating consumption of the I$_2$. Analysis of the solution by $^{11}$B NMR showed the formation of (glyme)B$_3$H$_7$. The solution was again cooled at -70 °C and anhydrous ammonia was bubbled through the solution with vigorous stirring. The solution was then warmed slowly to room temperature and the white precipitate that had formed was removed by filtration. The filtrate was dried in vacuo and separation of the resulting residue by silica gel chromatography with CH$_2$Cl$_2$ as an eluent gave a white crystalline powder, NH$_3$B$_3$H$_7$ (0.16 g, 2.83 mmol) in 80% yield. The melting point and spectroscopic data match the literature values for NH$_3$B$_3$H$_7$. $^1$H NMR (400.13 MHz, CD$_2$Cl$_2$) 3.58 (t, 3, NH$_3$), 1.62 (br, 7, B$_3$H$_7$). $^1$H NMR (500.14 MHz, C$_6$D$_6$) 2.00 (br, 7, B$_3$H$_7$), 1.01 (t, 3, NH$_3$). $^{11}$B NMR (128.4 MHz, CD$_2$Cl$_2$) -7.7 (br, s, 2, B$_2$ and B$_3$), -32.8 (br, s, 1, B1). IR (cm$^{-1}$) 3321(m), 3251(w), 2494(s), 2435(s), 1599(m), 1388(s), 1164(m), 1122(w), 1011(w), 882(w).

The reaction residue after the ammonia treatment could be alternatively purified by sublimation at 50 °C under reduced pressure, but this method took longer and afforded lower yields (< 50%). (CAUTION: after sublimation, immediate deactivation of the oily residue is required; otherwise the residue and/or gases from the oily residue can enflame upon exposure to air).

6.2.4 General Procedures for Hydrolytic H$_2$-Release Measurements from Aqueous NH$_3$B$_3$H$_7$ Solutions

Samples of 1 were added to neutral water in a two-necked round bottom flask equipped with a side arm containing acid or metal catalysts. The flask was connected to a gas burette via the second arm, closing the system. When the side arm was inverted, the acid or catalyst was mixed with the aqueous NH$_3$B$_3$H$_7$ solution and H$_2$ was evolved. The volume of evolved H$_2$ was quantitatively measured versus time employing the gas burette with pressure equalization against atmospheric pressure. For the reactions at 30 °C and 50 °C, the final volumes were measured after cooling the reaction mixtures to room temperature.
6.2.4.1 Stability of Solid and Aqueous Ammonia Triborane

Solid 1 stored in air at room temperature showed no changes by $^{11}$B NMR analysis after 2 months. The stability of a 33-wt% (8.8 M) aqueous solution (prepared by dissolving 0.33 g of 1 in 0.66 mL of distilled water) of 1 was determined by comparing the integration ratio of 1 (-32.9 ppm) and its NH$_3$BH$_3$ (-22.0 ppm) decomposition product in the $^{11}$B NMR spectra taken versus time.

For the 0.5-wt% solutions (0.09 M) with various pH values, a series of 10.0 mg samples of 1 were dissolved in 2.0 mL of distilled water or the desired buffers. The initial pH of the unbuffered 1 (0.5-wt%) solution was 8.7 by pH meter. The phosphate buffers (sodium dihydrogenphosphate, 99%, Aldrich) of 1.0 M concentrations were prepared by dissolving 12.0 g of NaH$_2$PO$_4$ and 14.6 g of NaCl in 90.0 mL of CO$_2$-free distilled water in a volumetric flask, and then adjusting the solution to the desired pH’s using a minimum amount of HCl and/or NaOH. Additional CO$_2$-free distilled water was added into the volumetric flask to 100.0 mL. The degree of degradation of 1 was again measured by integrating the ratio of 1 and NH$_3$BH$_3$ in the $^{11}$B NMR spectrum at each time.

6.2.4.2 Hydrolysis of 1 with HCl

Conc. HCl (11.8 N, 1.0 mL) was added to solid 1 (12.0 mg, 0.212 mmol) at room temperature and the evolved hydrogen was quantitatively measured versus time with the gas burette. In separate experiments, 1.9 mL of each of the standardized 0.93 M (1.0 eq), 2.79 M (3.0 eq), and 4.66 M (5.0 eq) solutions of HCl was added to the three samples of 1 (0.1 g, 1.77 mmol) and the released hydrogen was quantitatively measured versus time with the gas burette.

6.2.4.3 Hydrolysis of 1 with Metal Catalysts

Experiments were carried out at room temperature by adding the desired amounts of the metal catalysts to samples of 1 dissolved in neutral water (1.0 or 2.0 mL) and then measuring the evolved hydrogen versus time with the gas burette.

6.2.4.3.1 Extended Catalyst Lifetime Studies of [Rh(COD)(μ-Cl)]$_2$ (22.7 and 7.9 mol%) in the absence of buffer solutions

The [Rh(COD)(μ-Cl)]$_2$ (12 mg, 0.024 mmol, 22.9 mol%) precatalyst was added to 1.0 mL of the neutral water containing 4.6 mg (0.081 mmol) of 1 and the evolved H$_2$ was measured with the gas burette. More 1 was then added to the solution at 4 additional times and the evolved hydrogen measured. In a separate experiment, the [Rh(COD)(μ-Cl)]$_2$ (3.6 mg, 0.0073 mmol, 7.9 mol%) catalyst was added to 1.0 mL of neutral water containing 4.8 mg (0.085 mmol) of 1. More 1 was then added to the solution at 3 additional times and the evolved hydrogen measured.

6.2.4.3.2 Extended Catalyst Lifetime Studies of 5wt%-Rh/Al$_2$O$_3$ (7 mol% Rh) in the presence of buffer solutions

A borate buffered solution was prepared by adding CO$_2$-free distilled water to a volumetric flask containing 3.05 g of Na$_2$B$_4$O$_7$·10H$_2$O, and then adjusting the pH of the solution to 7.2. The 5-wt% Rh/Al$_2$O$_3$ (1.25 mg Rh, 0.0121 mmol Rh) catalyst was added to 2.0 mL of the buffer solution containing 9.0 mg (0.159 mmol) of 1 and the evolved H$_2$ was measured with the gas burette. More 1 was periodically added to the solution at 10 additional times and the evolved hydrogen measured.
6.2.4.3.3 Hydrolysis of 1 with Rh/Al₂O₃ at Different Temperatures

In separate experiments, 40 mg samples of Rh/Al₂O₃ (5-wt% Rh/Al₂O₃, 0.019 mmol Rh, 1.1 mol% Rh) were added to 4.9-wt% aqueous solutions of 1 (0.1 g NH₃B₃H₇ + 1.9 mL H₂O + 40 mg Rh/Al₂O₃) at 0, 20, 35 and 50 °C and the evolved hydrogen was then measured versus time.

6.2.4.4 Hydrolysis of a Concentrated Aqueous NH₃B₃H₇ Solution

A 40 mg sample of Rh/Al₂O₃ (5-wt% Rh/Al₂O₃, 0.019 mmol Rh, 1.1 mol% Rh) was added to a 22.7-wt% aqueous solution of 1 (0.1 g NH₃B₃H₇ + 0.3 mL H₂O + 40 mg Rh/Al₂O₃) at room temperature. The evolved hydrogen was quantitatively measured versus time with the gas burette. The weight percent of the hydrogen produced was calculated by: materials-wt% H₂ released = [H₂-wt produced/(NH₃B₃H₇ + H₂O + Rh/Al₂O₃-wt%)] x 100.

6.3 Results and Discussion

6.3.1 Synthesis

Kodama⁶⁷ originally synthesized ammonia triborane (1) by a two-step process (Equations 6.3-6.4) involving (1) the cleavage reaction of tetraborane, B₄H₁₀, with ethers to initially form LB₂H₇ (L = tetrahydrofuran or tetrahydropyran) adducts (plus B₂H₆), followed by (2) displacement of the ethers by reaction with anhydrous ammonia. Unfortunately, since tetraborane is both thermally unstable and explosive in air, a large-scale synthesis based on this method is not feasible.

\[ \text{B}_4\text{H}_{10} + \text{L} \rightarrow \text{LB}_2\text{H}_7 + \frac{1}{2} \text{B}_2\text{H}_6 \]  
\[ \text{LB}_2\text{H}_7 + \text{anhydrous NH}_3 \rightarrow \text{NH}_3\text{B}_3\text{H}_7 + \text{L} \]

Equations 6.3

Equations 6.4

Kodama also showed 1 could be obtained from the reaction of Na⁺B₃H₈⁻ with NH₄Cl, but in much lower yields (typically 20-30%) than the tetraborane-based route. The air and moisture stable B₃H₈⁻ anion is an attractive starting material since it can be readily made by the iodine oxidation of sodium borohydride (Equation 6.5).⁷⁶,⁷⁷ Binder⁷⁹ previously reported that I₂ oxidation of Me₄N⁺B₃H₈⁻ in noncoordinating solvents (e.g. CH₂Cl₂) yielded the B₃H₅-dimer, B₃H₁₄. We found that iodine oxidation (with slow warming from -70 to 20 °C) of the air stable Bu₄N⁺B₃H₈⁻ salt in glyme (1,2-dimethoxyethane) provided an efficient method for preparing solutions of the (glyme)B₃H₇ adduct (Equation 6.6).

\[ 3\text{Na}^+\text{BH}_4^- + \text{I}_2 \xrightarrow{\text{glyme} \quad 110 \degree \text{C}} \text{Na}^+\text{B}_3\text{H}_8^- + 2\text{NaI} + 2\text{H}_2 \]

Equation 6.5

\[ \text{NBu}_4^+\text{B}_3\text{H}_8^- + 1/2\text{I}_2 \xrightarrow{\text{glyme} \quad -70-23 \degree \text{C}} (\text{glyme})\text{B}_3\text{H}_7 + 1/2\text{H}_2 + \text{NBu}_4\text{I} \]

Equation 6.6

\[ (\text{glyme})\text{B}_3\text{H}_7 + \text{NH}_3(\text{g}) \xrightarrow{\text{glyme} \quad -70-23 \degree \text{C}} \text{NH}_3\text{B}_3\text{H}_7 + \text{glyme} \]

Equation 6.7
As shown in Figure 6.1, upon treatment with iodine at low temperature, the B₃H₇⁻ anion was oxidized to give a new compound that exhibited broad ¹¹B NMR resonances in a 2:1 ratio at -6.8 and -9.5 ppm, respectively, in agreement with the DFT/GIAO calculated chemical shifts for (glyme)B₃H₇: -3.6 (B2,3) and -11.1 (B1) ppm. Treatment of the glyme solution with anhydrous ammonia at -70 °C then afforded 1. Any unreacted B₃H₇⁻ was easily removed by filtration of the reaction solution through silica gel to give pure 1 in 80% yield. 1 could also be purified by vacuum sublimation at 50 °C, but some decomposition occurred lowering the yield to less than 50%. All spectroscopic data for 1 are in agreement with the literature values.⁷⁸

![Figure 6.1 ¹¹B{¹H} NMR spectra for the reaction progression leading to the formation of 1: (a) B₃H₇⁻; (b) (glyme)B₃H₇ formed after I₂ oxidation of B₃H₇⁻ in glyme; (c) 1 formed following ammonia displacement of the coordinated glyme (before purification), and (d) 1 after silica gel filtration.](image)

### 6.3.2 Hydrolytic Hydrogen Release

As described earlier by Equation 6.1, oxidative hydrolysis of 1 could release 8 equivalents of H₂ making such a process potentially competitive with either NaBH₄ or NH₃BH₃ based hydrolytic H₂-release systems. Two factors that are critical for such applications are aqueous solubility and stability. In this regard, owing most probably to its N-H-O hydrogen-bonding properties discussed in the previous section, 1 proved to be remarkably soluble in water, with solutions of at least 33-wt% being attained. Furthermore unlike aqueous NaBH₄, which is stable only in strongly alkaline solutions,⁸⁰,⁸¹ NH₃B₃H₇ was reasonably stable in neutral aqueous solutions, as evidenced by the ¹¹B NMR studies shown in Figure 6.2 of a 20-wt% solution of 1 which showed that, even after 11 days, only a small amount had decomposed to ammonia borane and borates. Likewise, in agreement with Kodama’s previous report of the air stability of 1,⁶⁷ ¹¹B NMR studies showed solid 1 stored in air was not changed even after 2 months at room temperature.
Figure 6.2 $^{11}$B NMR spectra of a 20-wt% aqueous solution of 1 at room temperature after (a) 0 h; (b) 24 h; (c) 96 h; (d) 147 h; (e) 11 days (● NH$_3$B$_3$H$_7$; ▼ NH$_3$BH$_3$).

Efficient H$_2$-release from aqueous solutions of 1 was obtained upon the addition of either acids or appropriate metal-catalysts. Acid hydrolysis of NH$_3$BH$_3$ has previously been demonstrated$^{65,82-94}$ and, as shown by the quantitative gas burette measurements of H$_2$-release presented in Figure 6.3a, analogous reactions of 12 mg (0.21 mmol) of 1 with an excess of aqueous HCl (1 mL of 12.1 M HCl) gave a near theoretical value (Equation 6.8) of 7.85 H$_2$-equivalents (1.65 mmol) over ~1 h.

$$\text{NH}_3\text{B}_3\text{H}_7 + \text{HCl} + 6 \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{Cl}^- + \text{“3 BO}_2^- + 3\text{H}^+” + 8 \text{H}_2 \quad (6.8)$$

The rate of acid hydrolysis was dependent upon the amount of acid used. Thus, when 5.0 eq. of HCl was reacted with a 4.9-wt% solution of 1, 7.0 H$_2$-equivalents were liberated in 95 min (Figure 6.3b), whereas a reaction with 3.0 eq. of HCl liberated 5.7 H$_2$-equivalents after 310 min and a reaction with only 1.0 eq. of HCl gave less than 1.0 H$_2$-equivalents after 350 min.

Figure 6.3 Hydrogen release from (a) a 0.45-wt% aqueous solution of 1 upon reaction with excess HCl and (b) a 4.9-wt% aqueous solution of 1 upon reaction with ■ 5.0 eq.; ● 3.0 eq.; or ▲ 1.0 eq. of hydrochloric acid.
Previous computational studies of the acid-induced dehydrogenation of ammonia borane and ammonia triborane both support a mechanism involving the initial elimination of one equivalent of H₂ via the reaction of the acid proton with a hydridic B-H hydrogen of the amine boranes. In aqueous solutions, subsequent electrophilic association of the resulting cationic species (i.e. NH₃BH₂⁺ and NH₃B₃H₆⁺) with water would then be expected to lead to the observed rapid H₂-release and formation of borates.

More rapid hydrogen release was achieved without acids by using metals to catalyze the hydrolysis reaction (Equation 6.9).

\[
\text{NH}_3\text{B}_3\text{H}_7 + 6\text{H}_2\text{O} \xrightarrow{\text{Metal catalyst}} \text{NH}_4^+ + "3\text{BO}_2^- + 2\text{H}^+ + 8\text{H}_2(\text{g}) \quad (6.9)
\]

Hydrogen release from NaBH₄ and NH₃BH₃ has previously been attained by metal-catalyzed hydrolysis, with Ru-catalysts for NaBH₄ and Pt-catalysts for NH₃BH₃ exhibiting the highest reactivities. A variety of these and other potential catalysts were screened for activating the hydrolysis of 1, including Rh(0), Ru(0), Pd(0), and Pt(0) supported on alumina or carbon; RhCl₃, [Rh(COD)(µ-Cl)]₂, RuCl₃, and NiCl₂ metal halides; and nano- or micro-sized metal or NiB₂ powders. As shown in the examples in Figure 6.4, catalytic activity was found to be highly dependent upon the particular metal, kind of supports, and degree of dispersed catalytic sites.

The rhodium-based systems, Rh(0) supported on alumina and RhCl₃, proved to be the most active. For example, 5-wt% Rh(0) supported on alumina gave over 7.5 H₂-equivalents in 15 min, while with higher catalyst loadings, RhCl₃ yielded ~7 H₂-equivalents in only 1.5 min. Although they were unchanged upon initially dissolving in water, both [Rh(COD)(µ-Cl)]₂ and RhCl₃ appeared to undergo reduction upon addition of 1 suggesting that Rh clusters and/or colloids may be the active catalytic species in these systems. In contrast, neither 5-wt% Rh supported on carbon nor 5-wt% Ru supported on alumina afforded a measurable amount of hydrogen in 2 h. Although 5-wt% Pd/Al₂O₃, Ru(0) supported on an ion exchange resin and nickel boride also showed significant catalytic activity, their reactivities were much less than either 5-wt% Rh/Al₂O₃ or RhCl₃, with less than 7.0 H₂-equivalents being evolved in 40 min. Ru powder (22.6 mol%) was much less active, exhibiting less than 3 H₂-equivalents in 400 min. Ni, Pd, and Pt powders and NiCl₂ showed negligible H₂-release in 2 h.

Unlike the immediate reaction observed with RhCl₃, the hydrolysis reaction of 1 with 7.1 mol% of RuCl₃ showed an induction period of ~5-10 min. The formation of black particles during this time suggests reduction of the RuCl₃ to form catalytically active Ru(0). A similar induction period was previously observed for NaBH₄ catalyzed by Ru supported on carbon (2-wt% Ru).
Figure 6.4  Metal-catalyzed hydrolytic H\textsubscript{2}-release from aqueous (0.45-wt\%) solution of 1 containing (■) RhCl\textsubscript{3} (6.9 mol\%); (●) 5-wt\% Rh/Al\textsubscript{2}O\textsubscript{3} (7.0 mol\%-Rh); (▼) RuCl\textsubscript{3} (7.1 mol\%); ([Rh(COD)\mu-Cl]\textsubscript{2} (7.1 mol\%); (★) Ni\textsubscript{3}B (35-41 mol\%); (◆) 5-wt\% Ru supported on ion exchange resins (6.3 mol\%); (▲) 5-wt\% Pd/Al\textsubscript{2}O\textsubscript{3} (6.7 mol\%); (●) Ru powder (22.6 mol\%); (●) 5-wt\% Rh/C (5.3 mol\%); NiCl\textsubscript{2} (6.9 mol\%), Ni powder (nanosize, 38.6 mol\%), Pd powder (submicron size, 9.0 mol\%), Pt powder (nanosize, 6.5 mol\%), 5-wt\% Ru/Al\textsubscript{2}O\textsubscript{3} (7.3 mol\%), or no catalyst. † For these metal catalysts, the amount of hydrogen was measured up to 120 min.

The pH of a 0.45-wt\% aqueous solution of 1 increased to above 8 after hydrolysis in the presence of [Rh(COD)Cl]\textsubscript{2}, and if more 1 was then added to this solution, then a decrease in the rate of H\textsubscript{2}-release was observed. On the other hand, if a borate buffer was used to maintain the solution pH, then the Rh/Al\textsubscript{2}O\textsubscript{3} catalyst exhibited an extended lifetime. As indicated in Figure 6.5, hydrogen evolution measurements following periodic additions of ~9 mg (~0.16 mmol) of solid 1 to a 2 mL aqueous borate-buffered (pH maintained between 7.2 and 8.0) solution containing 1.3 mg (0.012 mmol Rh) of 5-wt% Rh/Al\textsubscript{2}O\textsubscript{3} showed little change in the hydrogen release rates over 11 cycles.

The "BO\textsubscript{2}⁻" product shown in Equation 6.8 is only a hypothetical formulation, with the actual borate products of these reactions depending upon the final solution concentration and pH. The \textsuperscript{11}B NMR spectrum in Figure 6.6a of a solution obtained after the metal catalyzed hydrolysis of a 0.45-wt\% solution of 1, exhibits a signal in the 15-17 ppm range resulting from a fast-exchanging equilibrium mixture of B(OH)\textsubscript{3}/B(OH)\textsubscript{4}⁺, along with a weak signal at 12.4 ppm from B\textsubscript{3}O\textsubscript{3}(OH)\textsubscript{4}⁻.\textsuperscript{98-100} With more concentrated solutions of 1 (Figure 6.6b (4.9-wt\%) and 6.6c (22.7-wt\%)), the signals for the condensed-borates B\textsubscript{3}O\textsubscript{3}(OH)\textsubscript{4}⁻ and B\textsubscript{5}O\textsubscript{6}(OH)\textsubscript{4}⁻ were dominant.\textsuperscript{98-100} Thus, although the 5-wt% Rh/Al\textsubscript{2}O\textsubscript{3} showed extended catalytic activity for the hydrolysis of the diluted solution of 1, more concentrated solutions will probably not exhibit such extended activity because the borates will precipitate from the solutions and coat the catalyst surface.
Figure 6.5 Hydrogen evolution following repeated additions (11 cycles) of 1 to a borate buffered solution containing 5-wt% Rh/Al₂O₃.

Figure 6.6 ¹¹B NMR spectra of aqueous 1 solutions (a) after hydrolysis of 0.45-wt%; (b) after hydrolysis of 4.9-wt%; (c) after hydrolysis of 22.7 wt% aqueous solution; • an equilibrium mixture of B(OH)₃ and B(OH)₄⁻; ⋆ B₃O₃(OH)₄⁻; ★ B₅O₆(OH)₄⁻.

Similar to the results previously observed for the catalyzed NaBH₄⁸⁰,⁹⁷,¹⁰¹ and NH₃BH₃⁸³,⁸⁵ hydrolysis reactions, the H₂-release rate appeared to be independent of the concentration of 1 with, for example, identical rates observed for 4.9-wt% and 22.7-wt% solutions of 1 with 5-wt% Rh/Al₂O₃ (1.1 mol% Rh). However, the H₂-release rates of the 5-wt% Rh/Al₂O₃ and RhCl₃ could be effectively controlled and tuned by adjusting the catalyst loadings and reaction temperatures. As illustrated in Figure 6.7a for 5-wt% Rh/Al₂O₃-catalyzed reactions, while a 1.4 mol% Rh loading gave 5.4 H₂-equivalents in 3 h, 7.0 mol% of Rh gave 7.6 H₂-equivalents in only 17 min. For a RhCl₃ catalyzed reaction, 1.4 mol% Rh gave 5.6 H₂-equivalents in 40 min, while 6.9 mol% Rh gave 7.0 H₂-equivalents in only 2 min.
Figure 6.7 (a) the effect of catalyst loadings on H₂-release rates from a 0.45-wt% aqueous solution of 1 with different amounts of 5-wt% Rh/Al₂O₃ (■ 7.0 mol%; ● 2.9 mol%; ▲ 1.4 mol%); (b) the effect of temperature on H₂-release from a 4.9 wt% aqueous solution of 1 catalyzed by 5-wt% Rh/Al₂O₃ (1.1 mol% Rh). (▼, 50; ▲, 35; ●, 25; ■, 0 °C).  

As shown in Figure 6.7b, at 50 °C over 7 H₂-equivalents were produced in 25 min from a 4.9-wt% aqueous solution of 1 catalyzed by 5-wt% Rh/Al₂O₃ (1.1 mol% Rh). Decreased rates were observed at lower temperatures, but even at 0 °C, 6 H₂-equivalents were released in 17 h. An Arrhenius plot of the H₂-release rate data from a 5-wt% Rh/Al₂O₃ (1.1 mol%-Rh) catalyzed reaction of a 4.9-wt% 1 solution at different temperature yielded an activation energy (13.4 kcal/mol) in the range found for metal-catalyzed NaBH₄ hydrolysis (~9 to 18 kcal/mol, depending on the catalyst⁹⁷,¹⁰²,¹⁰³).

Calculations of the standard heats of hydrolysis from the standard enthalpies of formation, using Dixon's value for the heat of formation of solid NH₃B₃H₇ (-24.2 kcal/mol),⁶⁹ indicate that H₂-release from NH₃B₃H₇ is slightly more exothermic (18.9 kcal/mol-H₂) than from either NaBH₄ (14.9 kcal/mol-H₂) or NH₃BH₃ (12.7 kcal/mol-H₂) but is much less exothermic than the hydrolytic reactions of metal hydrides (LiAlH₄ (29.0 kcal/mol-H₂), MgH₂ (33.5 kcal/mol-H₂), and LiH (31.6 kcal/mol-H₂))⁴⁰⁴,¹⁰⁵.

The hydrolysis reaction of a highly concentrated 22.7 wt% sample containing 0.30 g of H₂O, 0.10 g of 1 (1.8 mmol) and 0.04 g of 5-wt% Rh/Al₂O₃ (0.02 mmol of Rh) produced 0.027 g (13.5 mmol, 7.5 equivalents) of H₂ over 3 h at 21 °C. Since the excess water solvent and catalyst must also be included as a material weight, this mixture corresponds to a 6.1 materials-wt% H₂ [i.e., mat-wt% H₂ = H₂-wt/(NH₃B₃H₇+H₂O+Rh/Al₂O₃-wts)].
6.4 Conclusions

While the DOE total-system H₂-storage targets for transportation (2015, 9.0 total system wt% H₂)\textsuperscript{37} will not be attainable with this, or any other, hydrolytic-based system, an ammonia triborane based hydrolytic system can provide a means of safe hydrogen generation that should be competitive with both the NH₃BH₃ and NaBH₄ based hydrolys for other applications having less stringent weight requirements.
Section 7. Regeneration of Spent Ammonia Borane Hydrogen Fuels

Summary
Spent fuel materials resulting from ammonia borane H₂-release were successfully digested in a number of strong acid systems to produce, according to ¹¹B NMR analysis, materials containing tetrahedral boron atoms devoid of remaining hydrogen. The digestate from the reaction of spent fuel with trifluoroacetic acid was found to react with dimethylethylaminoalane to form dimethylethylamine borane; however, the dimethylethylamine could not be displaced by ammonia to produce AB. Digestion of spent fuels resulting from only ~1 equivalent of AB H₂-release with superacitic AlBr₃/HBr/CS₂ solutions yielded BBr₃ which could be distilled out of the reaction mixtures; however, the digestion of more highly dehydrogenated spent fuels with ~2 equivalents of H₂-release could not be attained. Boron-halide reduction studies demonstrated that complexes readily formed upon reaction of BBr₃ with dialkylsulfides and that these R₂S-BBr₃ adducts could be quantitatively reduced to R₂S-BH₃ with either tin hydrides or silanes. The dialkylsulfides were then easily displaced from R₂S-BH₃ by ammonia to yield ammonia borane.

7.1 Introduction
The efficient regeneration of ammonia borane from spent fuel BN₃Hₓ is one of the most challenging problems that will have to be overcome in order to utilize ammonia borane based hydrogen storage systems. The development of a general AB regeneration process is made complicated by the fact that, depending upon the conditions and extent of AB H₂-release, a variety of molecular, polymeric and/or solid-state materials with very different chemical reactivities are formed (Figure 7.1).

![Figure 7.1](attachment:image.png) Possible spent-fuel products of ammonia borane H₂-release.
Any viable process must be capable of regenerating all of these spent-fuel materials and, in addition, avoid the formation of difficult to reduce intermediates. This section discusses an approach to AB regeneration from spent fuels involving: (1) the digestion of the spent AB fuels by strong acids to form BX$_3$ species; (2) base coordination of BX$_3$ and subsequent reduction of the base-BX$_3$ adduct to base-BH$_3$; and finally (3) displacement of the base from the base-BH$_3$ adduct by ammonia to produce AB.

7.2 Experimental Section

Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen or argon atmosphere using the high vacuum or inert-atmosphere techniques described by Shriver.

7.2.1 Materials

Ammonia borane (AB) was purchased from Aviabor and milled to a fine powder in a commercial coffee grinder. Trifluoroacetic acid (TFA) was purchased from Fisher and used as received. Aluminum bromide, aluminum chloride, HBr (anhydrous), and HCl (anhydrous), BB$_3$ (neat), BCl$_3$ (1 M in heptane), triethylsilane (TES), tributyltin hydride (TBTH), N,N-diethylaniline (DEA), and alane-N,N-dimethylethylamine (0.5 M in toluene) and hexagonal boron nitride (h-BN) were purchased from Aldrich and used as received. The dimethyl-, diethyl-, dibutyl-, dihexyl-, diisopropyl and diisobutyl-sulfides and tetrahydrothiophene were obtained from Aldrich and used as received. 1-Butyl-3-methyl imidazolium chloride (BmimCl) was purchased from Aldrich and dried azeotropically with toluene. Ammonia (anhydrous) was purchased from Air Gas and used as received. Triethylamine, CS$_2$, and CH$_2$Cl$_2$ were purchased from Fisher and dried as described elsewhere. Polyborazylene was synthesized via the controlled thermal polymerization of borazine.

7.2.2 Physical Methods

$^{11}$B NMR at 128.3 MHz and $^1$H NMR at 400.1 MHz spectra were obtained on a Bruker DMX-400 spectrometer equipped with appropriate decoupling accessories. All $^{11}$B chemical shifts are referenced to BF$_3$·OEt$_2$ (0.0 ppm), with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to internal residual protons from the lock solvents (99.9% CDCl$_3$) and then referenced to (CH$_3$)$_4$Si (0.0 ppm).

7.2.3 Synthesis of Spent Fuel at 85 °C (SF1)

In a typical experiment, AB (200 mg, 6.49 mmol) was loaded into a round-bottom flask equipped with a sidearm and Teflon stopcock. The flask was evacuated on a high-vacuum line and sealed. The flask was then heated at 85 °C under static vacuum for 14 h. The flask was opened to the high-vacuum line and evacuated for 12 h, yielding a white solid with its observed weight (198 mg) corresponding to the loss of 11 mg of H$_2$ (5.50 mmol, 0.85 eq). The $^{11}$B NMR of SF1 is shown in Fig. 7.3.

7.2.4 Synthesis of Spent Fuel at 120 °C (SF2)

Using an identical setup as in the 85 °C experiment, the flask containing AB was heated at 120 °C under static vacuum for 12 h, opened, and then held under dynamic vacuum on a high-vacuum line for 12 h. In a typical experiment, 200 mg of AB (6.49 mmol) yielded 180 mg of
SF2, with the observed weight corresponding to a loss of 20 mg of H₂ (9.74 mmol, 1.5 eq). SF2 was insoluble in all common solvents, so no ¹¹B NMR spectrum of this material could be obtained.

7.2.5 Acid Digestions of Spent Fuels

7.2.5.1 Digestion of Spent Fuels with Oxyacids

7.2.5.1.1 Digestion of Spent Fuels with Trifluoroacetic Acid (TFA)

(a) SF1 (150 mg) was loaded into a 100 mL round-bottom flask equipped with a sidearm and stirbar. The flask was connected to a high-vacuum line and TFA (~6 mL) was vacuum transferred into the flask. The mixture was heated at 60 °C for 12 h, during which time the solid SF1 dissolved to give a monophasic, pale yellow solution. The TFA was removed in vacuo, yielding 803 mg of a yellow solid. (b) Using an identical setup, SF2 (100 mg) was stirred in ~6 mL of TFA at 60 °C for 12 h. All of the SF2 dissolved to produce products having ¹¹B NMR spectra identical to those found in (a). The TFA was removed in vacuo yielding 538 mg of a yellow solid. ¹¹B NMR (128.3 MHz, TFA): δ -0.40 (s), -1.60 (s).

7.2.5.1.2 Digestion of Spent Fuels with Other Oxyacids

SF1 and SF2 were digested in a number of other oxygen-containing acids of varying strength. The conditions and results of these experiments are summarized in Table 7.1.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Spent Fuel Digested</th>
<th>Conditions</th>
<th>Product ¹¹B NMR Resonances</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFA</td>
<td>SF1 and SF2</td>
<td>Neat, 55 °C, 4-5 h</td>
<td>-0.4, -1.6</td>
</tr>
<tr>
<td>Triflic Acid</td>
<td>SF1 and SF2</td>
<td>Neat, 0 °C, mins</td>
<td>-3.88</td>
</tr>
<tr>
<td>Glacial Acetic Acid</td>
<td>SF1</td>
<td>4:1 pyridine: acetic acid, 4 days</td>
<td>2.81, -0.06, -0.57</td>
</tr>
<tr>
<td>Glacial Acetic Acid</td>
<td>SF1</td>
<td>neat, 60 °C, not fully solubilized</td>
<td>-0.06, -0.59</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>SF1</td>
<td>THF, excess formic acid</td>
<td>1.5</td>
</tr>
<tr>
<td>Chlorosulfonic</td>
<td>SF2</td>
<td>Neat, 1h, 50 °C</td>
<td>-3.1, -4.6</td>
</tr>
</tbody>
</table>

7.2.5.2 Digestion of Spent Fuels with Haloacids

7.2.5.2.1 Digestion Reactions with Anhydrous HCl

(a) In separate experiments, SF1(50 mg), SF2 (50 mg) and h-BN (50 mg) were stirred in liquid anhydrous HCl (~7 mL) in a closed Fischer and Porter thick-walled pressure vessel at -78 °C for 4 h. The HCl was removed in vacuo and the product was pumped to dryness through a trap held at -90 °C. In each case, no boron containing species could be observed by ¹¹B NMR in the material in the cold trap and gravimetric analysis of the solids remaining in the flasks indicated no reaction had occurred. (b) Polyborazylene (97 mg) was stirred in liquid anhydrous HCl (~10 mL) in a closed pressure vessel at -78 °C for 4 h. The HCl was removed in vacuo...
yielding 231 mg of a white material that was insoluble in common solvents. The observed gravimetric uptake of the solid corresponded to an approximate formula \((B_3N_3H_3Cl_3)_x\) which would be consistent with the addition of one HCl molecule to 91% of all the unsaturated B-N units in polyborazylene. The material slowly lost HCl when held at room temperature.

**7.2.5.2.2 Digestion Reactions with Superacidic HCl in Ionic Liquids**

An acidic AlCl\(_3\)/BmimCl solution was prepared by the addition of AlCl\(_3\) (473 mg, 3.5 mmol, 55 mol%) to BmimCl (500 mg, 2.9 mmol) as described elsewhere.\(^{107}\) In two separate experiments, SF1 (50 mg) samples were added to AlCl\(_3\)/BmimCl solutions in reaction vessels equipped with a gas inlet and outlet. The reactions were heated at (a) 65 °C and (b) 90 °C, respectively while anhydrous HCl was flowed through the reaction vessels with the exit gases being passed through -78 °C traps before being vented to the atmosphere through bubblers. After 2 h, the solutions were monophasic and all SF1 had dissolved. No boron-containing species were found in the cold traps. The \(^{11}\)B NMR analyses of the AlCl\(_3\)/BmimCl solutions diluted with CH\(_2\)Cl\(_2\) showed new peaks at: (a) \(\delta -31.2 \text{ (s)}, 0.2 \text{ (s)}, 0.0 \text{ (s)}\). (b) \(\delta 1.3 \text{ (s)}, 0.2 \text{ (s)}, -0.8 \text{ (s)}, -1.3 \text{ (s)}\). Attempts to separate the products from the AlCl\(_3\)/BmimCl solutions by distillation and/or extraction were unsuccessful.

**7.2.5.2.3 Digestion Reactions with Superacidic AlBr\(_3\)/HBr/CS\(_2\)\(^{108}\)**

(a) SF1 (50 mg) and AlBr\(_3\) (2.5 g, 9.36 mmol) were dissolved in ~12 mL of dry CS\(_2\) in a 100 mL Schlenk flask equipped with a gas inlet. The mixture was stirred while the flask was filled with gaseous HBr. Stirring was continued for 4 h, with fresh HBr being added to the system every 20 min. The white solid SF1 gradually dissolved, yielding a dense, bubbling yellow oil. The \(^{11}\)B NMR spectra of the clear CS\(_2\) layer revealed the presence of BBr\(_3\). The mixture was fractionated on a high-vacuum line through consecutive -95 °C and -198 °C traps. Dry triethylamine (TEA) (~5 mL) was vacuum transferred to the -95 °C trap and the mixture allowed to warm to room temperature. The BBr\(_3\)-TEA adduct\(^{109}\) was concentrated in vacuo, yielding 228 mg (0.65 mmol, a 40% yield based on a NH\(_2\)BH\(_2\) formula for SF1) and was identified by its characteristic \(^{11}\)B NMR spectrum (128.3 MHz, CDCl\(_3\)): \(\delta -6.1 \text{ (s)}\). The yellow oil that had separated from the CS\(_2\) layer was analyzed by \(^{11}\)B NMR (128.3 MHz, neat): \(\delta -9.4 \text{ (s)}\). (b) SF2 (50 mg) and AlBr\(_3\) (2.5 g, 9.36 mmol) were dissolved in ~12 mL of dry CS\(_2\) and similarly treated with HBr. No formation of BBr\(_3\) could be observed in the CS\(_2\) solution by \(^{11}\)B NMR.

**7.2.5.2.4 Digestion Reactions with Superacidic AlCl\(_3\)/HCl/CS\(_2\)**

(a) SF1 (50 mg) was added to a solution of AlCl\(_3\) (200 mg, 1.50 mmol) in CS\(_2\) (~8 mL). Anhydrous HCl was bubbled into the reaction mixture for 3 h at room temperature with the exit gases passing through a -78 °C trap before being vented to the atmosphere through a bubbler. No dissolution of SF1 was observed and analysis of the CS\(_2\) layer by \(^{11}\)B NMR showed no formation of soluble boron containing species. No boron containing products were found in the cold trap. (b) Using an identical setup, SF1 and AlCl\(_3\) were treated with HCl in toluene instead of CS\(_2\). Again, no dissolution of SF1 was observed, and no new boron containing species were found by \(^{11}\)B NMR. (c) Liquid anhydrous HCl (~7 mL) was condensed into a Fischer and Porter thick-walled pressure vessel containing SF1 (50 mg) and AlCl\(_3\) (100 mg, 0.75 mmol). The mixture was stirred at -78 °C for 4 h. The volatiles were removed in vacuo, and \(^{11}\)B NMR analysis of
these volatiles showed no boron-containing species. Likewise, no soluble boron containing species were found in the remaining solids by $^{11}$B NMR.

7.2.6 Reduction Studies of Digestates of Spent Fuels

7.2.6.1 Reduction of TFA-Digestated Spent Fuels

The TFA-digestate (43 mg) from 7.2.5.1.1 was treated with 10 mL of a 0.5 M solution of alane-N,N-dimethylethylamine complex in toluene at room temperature. The solid digestate dissolved with vigorous bubbling. After the reaction was stirred for 3 h, $^{11}$B NMR analysis showed the formation of N,N-diethylmethylamine borane. The mixture was fractionated on a high-vacuum line through consecutive 0 °C, -40 °C, and -198 °C traps. Toluene and the new Et$_2$MeNBH$_3$ adduct were retained at -40 °C, but attempts to quantitatively separate these were unsuccessful. $^{11}$B NMR (128.3 MHz, CDCl$_3$): $\delta$ -9.6 (q, $J$ = 99 Hz).

7.2.6.2 Complexation of BX$_3$, Reduction of B-X and Base-Displacement to Reform AB

7.2.6.2.1 Triethylamine (TEA) BX$_3$ Complexation and B-X Reduction by Tributyltin Hydride (TBTH)

(a) The addition of TEA (1.3 mL, 9.6 mmol) to a stirred 1 M solution of BCl$_3$ in heptane (8 mL, 8 mmol) at 0 °C resulted in the immediately formation of a white precipitate. Volatiles were removed in vacuo, and $^{11}$B NMR analysis of a CH$_2$Cl$_2$ solution of the white solid indicated the formation of the TEA-BCl$_3$ adduct. $^{11}$B NMR analysis indicated that the reaction of the solids in a stirred CH$_2$Cl$_2$ (~15 mL) solution with TBTH (7.74 mL, 28.8 mmol) at 60 °C for 3 days resulted in only partial reduction. Addition of TBTH (10 mL, 37.1 mmol) with further reaction for 12 h at 60 °C brought the reaction to ~95% TEA-BH$_3$. Attempts to separate the adduct from the tributyltin chloride and residual TBTH were unsuccessful. For TEA-BCl$_3$: $^{11}$B NMR: $\delta$ 7.7; TEA-BH$_3$: -13.6 (q, $J$ = 87 Hz). (b) TEA (0.43 mL, 3.0 mmol) was added to a solution of BBr$_3$ (640 mg, 2.64 mmol) in CH$_2$Cl$_2$ (~10 mL) and stirred for 5 min at room temperature at which point $^{11}$B NMR analysis showed the quantitative formation of TEA-BBr$_3$. For TEA-BBr$_3$: $^{11}$B NMR: $\delta$ -6.2. This mixture was then treated with additional TBTH (6.34 mL, 23.8 mmol) for 1 h at room temperature, but $^{11}$B NMR analysis showed no reaction. The reaction was then heated at 45 °C for 2 h, leading to quantitative conversion to TEA-BH$_3$.

The TEA-BH$_3$ adduct was independently synthesized by the addition of TEA to an equimolar amount of BH$_3$-THF. The solvent was removed in vacuo, at which point anhydrous liquid ammonia (~8 mL) was condensed onto the adduct and the mixture stirred for 2 h at -78 °C. The ammonia was removed in vacuo, but analysis by $^{11}$B NMR showed no displacement of TEA by NH$_3$.

7.2.6.2.2 N,N-Diethylaniline (DEA) BBr$_3$ Complexation, B-Br Reduction with Triethylsilane (TES) and NH$_3$ Displacement to Produce Ammonia Borane

A sample of BBr$_3$ (1.21 g, 4.7 mmol) was reacted with DEA (0.84 mL, 4.7 mmol) in CH$_2$Cl$_2$ (~10 mL) at 0 °C. Analysis by $^{11}$B NMR showed a new peak at -25.2 ppm, indicative of adduct formation. TES (6.0 mL, 37.5 mmol) was then added and the mixture stirred at room temperature for 5 min. Analysis by $^{11}$B NMR showed quantitative conversion to DEA-BH$_3$. Ammonia was then bubbled though the reaction mixture for 40 min, causing the precipitation of
a large amount of white solid. The reaction flask was closed and the mixture stirred for 2 additional hours under an ammonia atmosphere. The precipitate was filtered and washed 3 times with hexanes, and then extracted with ether until further ether washes showed no traces of products in the $^{11}\text{B}$ NMR. The combined ether washes were concentrated in vacuo to yield AB (121 mg, 3.9 mmol, 84%). Examination of the reaction solution by $^1\text{H}$ NMR also revealed the formation of small amounts of para-bromodiethylaniline as a result of bromination of DEA.

7.2.6.2.3 Complexation of BBr$_3$ with Dialkylsulfides and Reduction of Adducts

The reactions of BBr$_3$ in CH$_2$Cl$_2$ with equimolar amounts of a number of dialkylsulfides, including dimethyl, diethyl, dibutyl, dihexyl, disopropyl and diisobutyl-sulfides and tetrahydrothiophene, resulted in the clean formation of their corresponding sulfide-BBr$_3$ adducts. The adducts all showed a single $^{11}\text{B}$ NMR resonance near -12 ppm. Each adduct could then be reduced with just over 3 molar equivalents of TES yielding BH$_3$-adducts with a single $^{11}\text{B}$ NMR resonance near -21 ppm. Complete reductions of the (n-alkyl)$_2$S-BBr$_3$ adducts with TES at 55 °C took 12-15 h, while the TES reductions of the R$_2$S-BBr$_3$ (R = isopropyl, isobutyl) adducts took 4 h at 55 °C to complete. As presented in the following two sections, the dialkylsulfide properties were selected to give the appropriate vapor pressure for efficient vacuum fractionation.

7.2.6.2.3.1 Synthesis of AB from BBr$_3$-Adducts with Triethylsilane (TES)

BBr$_3$ (4.43 g, 17.7 mmol) and CH$_2$Cl$_2$ (~ 8 mL) were vacuum transferred into a 100 mL round-bottom flask equipped with a sidearm, stopcock and stirbar. The mixture was put under dry N$_2$ on a Schlenk-line and held at 0 °C while dihexyl sulfide (21.3 mmol, 5.06 mL) was added. The mixture was brought to room temperature and triethylsilane (68.3 mmol, 10.9 mL) was added under flowing N$_2$. The vessel was sealed and heated with stirring at 55 °C for 4 h at which point $^{11}\text{B}$ NMR analysis showed complete reduction of the BBr$_3$ to form the Hex$_2$S-BH$_3$ adduct. The mixture was fractionated on a high-vacuum line through consecutive -25 °C, -78 °C and -196 °C traps. The Hex$_2$S-BH$_3$ adduct was retained in the reaction flask (4.65 g, 17.7 mmol, ~100%), while triethylsilyl bromide (10.7 g, 5.2 mmol, 98%) was trapped at -25 °C and excess TES (1.6 g, 14.1 mmol, 96%) was trapped at -78 °C. The reaction flask was put back under N$_2$ and held at -78 °C while anhydrous NH$_3$ (8-10 mL) was condensed in. The mixture was stirred at -78 °C for 10 min, then the excess NH$_3$ was removed in vacuo. The resulting slurry was taken up in hexanes (~10 mL), filtered, washed 2 times with hexanes and dried in vacuo to yield AB (0.5 g, 16.9 mmol, 96%).

7.2.6.2.3.2 Synthesis of AB from BBr$_3$-Adducts with Tributyltin Hydride (TBTH)

BBr$_3$ (1.41g, 5.6 mmol) was vacuum transferred into a two-neck, round-bottom flask equipped with a septum, vacuum adapter and stirbar. The flask was held at -78 °C while diethyl sulfide (0.91 mL, 8.4 mmol) was added. The mixture was warmed to 0 °C, then TBTH (4.75 mL, 17.6 mmol) was added and the reaction stirred for 10 min. The mixture was fractionated on a high-vacuum line through consecutive -78 °C and -198 °C traps. All tin products (6.4 g, 16.8 mmol tributyltin bromide + 0.8 mmol TBTH) remained in the reaction vessel while the Et$_2$S-BH$_3$ adduct (0.6 g) was collected at -78 °C. The adduct was vacuum transferred back into a round-bottom flask, and anhydrous NH$_3$ was condensed into the flask at -78 °C. The reaction was stirred for 10 min, then all excess NH$_3$ and diethyl sulfide were removed in vacuo, leaving behind AB (0.17 g, 5.6 mmol, ~100%).

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7.3 Results and Discussion

At the outset of this project a possible general scheme, summarized in Figure 7.2, for the regeneration of ammonia borane from spent BNH$_x$ fuels was proposed. The two key steps in the process were: initial digestion of the AB spent-fuel with strong acids to form BX$_3$, followed by a second reduction-process to be carried out in one reaction vessel, involving coordination of the BX$_3$ to a base, reduction of the coordinated boron-X bonds, and finally exchange of the base by ammonia to regenerate NH$_3$BH$_3$.

**First Step: Acid Digestion of Spent Fuels**

\[ \text{BNH}_x + 4 \text{HX} \rightarrow \text{BX}_3 + \text{NH}_4\text{X} \]

**Second Step: One-Pot Conversion of BX$_3$ to AB**

**Coordination of BX$_3$**

\[ \text{BX}_3 + \text{Base} \rightarrow \text{BaseBX}_3 \]

**BX Reduction**

\[ \text{BaseBX}_3 + 3 \text{HMR}_3 \rightarrow \text{BaseBH}_3 + 3 \text{XMR}_3 \]

\[ \text{M} = \text{Sn}, \text{Si} \]

**Base Displacement by NH$_3$ to Yield AB**

\[ \text{BaseBH}_3 + \text{NH}_3 \rightarrow \text{H}_3\text{NBH}_3 + \text{Base} \]

**Figure 7.2** Overview of Penn approach to AB regeneration.

The results of our studies of the AB acid-digestion and BX$_3$-conversion processes are summarized in sections, 7.3.1 and 7.3.2, respectively.

7.3.1 Digestion of Ammonia Borane Spent Fuels with Strong Acids

The first step envisioned in the proposed regeneration process was the acid digestion of the spent fuel materials with their resulting conversion to molecular BX$_3$ and NH$_4$X species. Two types of spent fuels were generated for use in the digestion studies. Spent-fuel SF1 was produced from AB by the thermally (85 °C) induced loss of ~1 H$_2$-equivalent, while the more highly dehydrogenated SF2, with ~2-equivalent of H$_2$-loss, was generated by AB thermolysis at 120 °C. As discussed in the following sections, the use of both strong oxy- and halo-acids to digest these fuels was explored.

7.3.1.1 Digestion of Spent AB Fuel with Oxyacids

As summarized in Table 7.1, a number of oxy-acids, including trifluoroacetic (TFA), triflic, formic and chlorosulfonic acid, were found to completely digest both the SF1 and SF2 spent fuels. These acid/spent-fuel reactions all yielded monophasic solutions with products, as illustrated in Figure 7.3 for the reaction of SF1 with trifluoroacetic acid, having upfield singlet resonances in their $^{11}$B NMR spectra indicating tetrahedrally coordinated boron.
Figure 7.3 $^{11}$B NMR analysis of the digestion of spent-fuel SF1 with trifluoroacetic acid.

Separation of the digestion-products from the oxyacids proved difficult for most of the oxyacid reactions. However, owing to the higher volatility of TFA, excess TFA could be removed in vacuo from the TFA/spent-fuel digestions, allowing the isolation of the non-volatile digestion product as a yellow oil that eventually solidified. This species was reduced by tin hydrides (as discussed in section 7.3.2.1) whereas the isolated digestates from the other volatile acids (formic acid and glacial acetic acid) could not be reduced.

7.3.1.2 Digestion of AB Spent Fuels with Haloacids

As summarized in Figure 7.4, neither the sent-fuels (SF1 and SF2) nor h-BN could be digested with anhydrous HCl. Polyborazylene did react with anhydrous HCl, but was not converted to molecular species. The observed HCl-uptake in the polyborazylene reaction instead suggested the production of a chlorinated cyclotriborazane polymer, such as shown in Figure 7.3, resulting from HCl-addition to the polyborazylene B=N units.

Figure 7.4. Summary of the results of the reactions of anhydrous HCl with AB spent-fuels, polyborazylene and boron nitride.
While the AB spent-fuels proved to be unreactive toward anhydrous haloacids, several superacidic systems gave complete spent-fuel digestion. The addition of 55 mol% AlCl$_3$ to the 1-butyl-3-methylimidazolium chloride (bmimCl) ionic-liquid has previously been shown to greatly enhance the acidity and the reactivity of dissolved HCl as a result of the reactions given in Eqs. 7.1 and 7.2.$^{107}$

$$\text{BmimX} + 2\text{AlX}_3 \rightleftharpoons [\text{Al}_2\text{X}_7][\text{Bmim}^+] \quad (7.1)$$

$$\text{Al}_2\text{X}_7^- + \text{HX} \rightleftharpoons 2\text{AlX}_4^- + \text{H}^+ \quad (7.2)$$

When either SF1 or SF2 was stirred at 65 °C in an AlCl$_3$/bmimCl mixture saturated with flowing HCl, the spent-fuels readily dissolved with vigorous bubbling. After a few minutes, the bubbling stopped and the solutions were monophasic. The $^{11}$B NMR analysis shown in Figure 7.5 indicated complete spent-fuel digestion to form (H$_2$NBCl)$_3$ (3.7 ppm$^{112}$), NH$_3$BCl$_3$ (3.28$^{113}$) and (HNBCl)$_3$ (30.3 ppm$^{114}$). For reactions at 90 °C, the downfield resonance disappeared indicating further B-trichloroborazine degradation.

**Figure 7.5** $^{11}$B NMR analysis of the 65 °C digestion of spent-fuel SF1 with superacidic bmimCl/AlCl$_3$/HCl.

In these reactions, it was not possible to separate the chloroborane products from the BmimCl ionic-liquid, leading us to investigate alternative superacidic systems, such as superacidic HBr/AlBr$_3$/CS$_2$ solutions,$^{108}$ that could potentially allow product separation. When 50 mg of SF1 was added to a mixture of 2.5 g of AlBr$_3$ in CS$_2$, and the system exposed to ~1 atm of HBr, the white SF1 solid bubbled slowly, and then eventually formed a yellow, immiscible oil at the bottom of the reaction vessel. $^{11}$B NMR (Figure 7.5) analysis of the supernatant CS$_2$ layer confirmed the formation of BBr$_3$. The BBr$_3$ was vacuum distilled from the reaction mixture and then reacted with triethylamine to form its Et$_3$N-BBr$_3$ complex to allow a gravimetric determination. The observed formation of 228 mg of the Et$_3$N-BBr$_3$ adduct corresponded to the conversion of ~40% of the boron in the SF1 sample to BBr$_3$.

Analysis by $^{11}$B NMR of the viscous yellow oil layer showed one singlet resonance at -9.4 ppm (Figure 7.6) suggesting the formation of hexabromocyclotriborazane, (H$_2$NBB$_2$)$_3$. This oil, which also contained large amounts of AlBr$_3$, was insoluble in ethereal or chlorinated solvents. Attempts to reduce the B-Br species in this oil by addition of tin hydrides or alanes were unsuccessful, most likely due to the presence of this AlBr$_3$. 
When SF2 was reacted with the HBr/AlBr3/CS2 mixture, only traces of BBr3 were found in the CS2 layer. Thus, the superacidic HBr/AlBr3/CS2 system was not useful for digesting more dehydrogenated spent-fuels.

While this project was in progress, an encouraging report by Mertens et al appeared\textsuperscript{116} claiming that AB spent-fuel digestion was achieved by superacidic HCl/AlCl3/toluene to produce BCl3 in yields up to 60%. However, we were unsuccessful in reproducing the results reported in the Mertens publication. We explored a number of reactions conditions, but in no case was BCl3 formation observed in the reactions of superacidic HCl/AlCl3 with either SF1 or SF2.

### 7.3.2 Reduction of Digested Products

#### 7.3.2.1 Reduction of TFA-digestate with Alane

Treatment of the TFA-digested products of SF1 or SF2 with excess dimethylethylamine-alane at room temperature in toluene resulted in the complete consumption of the digestate material to yield a reduced product having a quartet resonance at -9.6 ppm in its $^{11}$B NMR spectrum (\textbf{Figure~7.7}). Both the shift and multiplicity of this resonance are consistent with the formation of the Me$_2$EtN-BH$_3$ adduct (e.g. Me$_3$N-BH$_3$, -9 ppm; Et$_3$N-BH$_3$, -13 ppm).\textsuperscript{108} The TFA-digestate was not reduced when treated with either silicon or tin hydrides.

The Me$_2$EtN-BH$_3$ adduct was volatile, but with a vapor pressure similar to that of the toluene solvent making separation difficult. Since ammonia borane is only poorly soluble in toluene, anhydrous ammonia was bubbled through the solution in an attempt to induce AB precipitation. However, no displacement of the more-basic dimethylethylamine was found.
7.3.2.2 Reduction of BBr$_3$ to AB

The successful generation of BBr$_3$ in the reactions of the SF1 spent fuel with the superacidic AlBr$_3$/HBr/CS$_2$ system prompted our investigations of efficient methods for the reduction of BX$_3$ boron halides. It has previously been shown that boron-halides can be readily reduced by tin and/or silicon hydrides,\textsuperscript{117,118,119} but the direct reduction of BX$_3$ liberates the pyrophoric gas diborane (B$_2$H$_6$). Such a dangerous material would be difficult to handle safely on larger scales and its production must be eliminated for any industrial scale process to be viable. As outlined in Figure 7.2, our strategy to avoid diborane formation was to first form a L-BBr$_3$ complex via the reaction of the Lewis-acidic BX$_3$ with a Lewis base (L) and then reduce this adduct with tin and/or silicon hydrides to form L-BH$_3$. In the final step, displacement of the Lewis base by ammonia could then generate ammonia borane. In the optimum process, adduct formation, reduction and displacement reactions would all be carried out in the same reaction vessel.

Our initial process used diethylaniline as the coordinating base. As shown in Figure 7.8, diethylaniline readily reacted with BBr$_3$ to form the DEA-BBr$_3$ adduct. Subsequent reduction of the B-Br bonds by Bu$_3$SnH or Et$_3$SiH produced the BH$_3$-coordinated diethylaniline. Displacement of the diethylaniline from this adduct by ammonia to produce NH$_3$BH$_3$ was then achieved by reaction with liquid anhydrous ammonia to give an 84% yield of ammonia borane. Although good yields of AB from BBr$_3$ were obtained in this process, several problems were encountered: (1) unwanted side reactions occurred to produce brominated anilines making recovery of the DEA base difficult, and (2) following reduction with Et$_3$SiH, it was not possible to completely separate the aniline borane from Et$_3$SiBr. Therefore, the subsequent displacement reaction with ammonia produced silazane side products that were difficult to separate.

We subsequently developed and optimized an improved process for the reduction step that used dialkylsulfide bases for adduct formation. This process both avoided the previous side reactions and enabled efficient separations of all products and reactants. As summarized in Figure 7.9, the key steps in the process involved the initial formation of a R$_2$S-BX$_3$ complex, followed by silane or stannane reduction to R$_2$S-BH$_3$ and then finally R$_2$S displacement with ammonia to generate ammonia borane.

**Figure 7.7** $^{11}$B NMR analysis of the reduction of the TFA-digestate with dimethylethylamine-alane.
Figure 7.8 $^{11}$B NMR analysis of the diethylaniline-based synthesis of ammonia borane from BBr$_3$ via coordination/reduction/displacement reactions.

Figure 7.9 Summary of the dialkylsulfide-based coordination/reduction/displacement process for the synthesis of ammonia borane from BBr$_3$.

BBr$_3$ formed stable complexes with a wide variety of dialkylsulfides, including dimethyl-, diethyl-, dibutyl-, dihexyl-, diisopropyl-, diisobutyl-sulfides and tetrahydrothiophene.
The complexes were all soluble in a range of organic solvents. The wide range of volatilities exhibited by these adducts, which depended upon the size of the alkyl chain, allowed versatile fine-tuning and control of the separation procedures/conditions needed for efficient product isolation.

In each case, reduction of the RS$_2$-BBR$_3$ adducts with triethylsilane (TES) yielded a single compound that exhibited a quartet resonance near -23 ppm in its $^{11}$B NMR spectrum that is characteristic of R$_2$S-BH$_3$ complexes. Reactions with R = n-alkyl (dimethyl, dibutyl, etc.) required >12 h and 55 °C for complete reduction, but the disisopropyl-derivative was complete in only 3-4 h. Because of its low-volatility, which enabled efficient isolation of the (C$_6$H$_{13}$)$_2$S-BH$_3$ adduct, the dihexylsulfide was employed in the optimized process illustrated in Figure 7.10. Thus, following the initial formation of (C$_6$H$_{13}$)$_2$S-BBBR$_3$, the addition of excess (3.85 equivalents) of Et$_3$SiH gave complete conversion to (C$_6$H$_{13}$)$_2$S-BH$_3$. The Et$_3$SiBr and any remaining TES were then vacuum distilled from the reaction mixture and separated by trapping at -25 °C and -78 °C, respectively. Because of its low volatility, the (C$_6$H$_{13}$)$_2$S-BH$_3$ adduct remained in the reaction flask.

**Figure 7.10** Reaction summary and product separation scheme for the silane-reduction of (C$_6$H$_{13}$)$_2$S-BBBr$_3$.

Quantitative displacement by ammonia of the dihexylsulfide from (C$_6$H$_{13}$)$_2$S-BH$_3$ to produce ammonia borane was then achieved by stirring the complex in liquid ammonia at -78 °C for 10 min. Since dihexylsulfide is not volatile at room temperature, it could not be distilled from the (C$_6$H$_{13}$)$_2$S/ammonia-borane mixture. Instead, pure ammonia borane in 96% isolated yield was obtained by hexanes extraction of (C$_6$H$_{13}$)$_2$S from this mixture.

The dialkylsulfide-based process was further improved by using stannane reducing agents. These methods gave higher yields, lower temperature reactions, faster times, and allowed complete isolation of all reactants and products. Thus, tributyltin hydride (TBTH) was more active than TES with reactions carried out at 0 °C complete in minutes. These reactions also required only 3 TBTH equivalents and no solvent, thus simplifying product isolation. Since both TBTH and tributyltin bromide are involatile at room temperature, the volatile (C$_2$H$_5$)$_2$S base was employed in the optimized reaction shown in **figure 7.10** so that the (C$_2$H$_5$)$_2$S-BH$_3$ adduct
would be sufficiently volatile that it could be distilled from the reaction flask and trapped at -78 °C.

**Figure 7.11** Reaction summary and separation method for the tin hydride reduction of \((\text{C}_2\text{H}_5)_2\text{S}-\text{BBr}_3\).

Displacement of the diethylsulfide from the \((\text{C}_2\text{H}_5)_2\text{S}-\text{BH}_3\) complex was achieved by stirring the complex in liquid ammonia at -78 °C for 10 min. Pure ammonia borane was then obtained in quantitative yields following the vacuum removal of the excess ammonia and liberated diethylsulfide.

**7.4 Conclusions**

While our boron-halide reduction studies clearly demonstrated that a dialkylsulfide-based coordination/reduction/displacement process gave quantitative conversions of BBr₃ to ammonia borane with efficient and safe product separations, the fact that AB spent-fuels cannot as yet be digested in good yields to BX₃ halides has led to our No-Go decision on this overall AB-regeneration strategy.
Section 8. Publications and Presentations

Publications

Presentations
22. L. G. Sneddon “Amineborane Based Chemical Hydrogen Storage” DOE Tech Team Meeting, Detroit, Michigan, March 2009.


Section 9. References
