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

Table of Contents

1. Executive Summary	1
2. Overview	7
3. Ammonia Borane Hydrogen Release in Ionic Liquids	9
Summary	9
3.1 Introduction	9
3.2 Experimental Section	9
3.2.1 Materials	10
3.2.2 Physical Measurements	10
3.2.2.1 H₂-Release Measured with a Toepler Pump	10
3.2.2.2 H₂-Release Measured with an Automated Gas Burette	10
3.2.2.3 Procedures for ¹¹B NMR Studies of Reaction Products	11
3.3 Results and Discussion	12
3.3.1 Why Use Ionic Liquids?	12
3.3.2 Procedures for AB H₂-release reactions	13
3.3.3 Solid-State vs. Ionic Liquid H₂-Release	14
3.3.4 ¹¹B NMR Characterization of Reaction Products and Pathways	17
3.3.4.1 ¹¹B NMR of Pyridine Extracts from Reaction Products	17
3.3.4.2 Solid-State ¹¹B NMR Studies	19
3.3.4.3 <i>In Situ</i> ¹¹B NMR Studies in Ionic Liquids	19
3.3.5 Why do Ionic Liquids Accelerate AB H₂-release? What is the Role of DADB?	22
3.3.6 H₂-Release Reactions in Tetraglyme	24
3.4 Conclusions	25
4. Base Promoted Ammonia Borane Hydrogen Release	26
Summary	26
4.1 Introduction	26
4.2 Experimental Section	26
4.2.1 Materials	26
4.2.2 Physical Measurements	27
4.2.3 Procedures for AB H₂-Release Reactions	27
4.2.4 Computational Methods	28
4.3 Results and Discussion	28
4.3.1 Ammonia Borane H₂-Release Reactions Promoted by Lithium Amide and Lithium Hydride	28
4.3.2 Ammonia Borane H₂-Release Reactions Promoted by Proton Sponge	31
4.3.2.1 H₂-Release from AB/PS Solid-State Reactions	31
4.3.2.2 H₂-Release from AB/PS Solution Reactions	33
4.3.2.2.1 Initial Reactions Measured with the Toepler Pump	33
4.3.2.2.2 H₂-Release Reactions Measured with the	34

Automated Gas Burette	
4.3.3 ^{11}B NMR Studies of Reaction Pathways and Intermediates	35
4.3.3.1 Solid-State ^{11}B NMR Studies	35
4.3.3.2 <i>In Situ</i> ^{11}B NMR Studies of Reaction Progress in Ionic Liquids	37
4.3.4 Proton Sponge Reduces Foaming During AB Thermolysis	38
4.3.5 H_2 -Release in Other Ionic Liquids and Tetraglyme	38
4.3.6 Why Does Proton Sponge Induce H_2 -Release from AB?	39
4.4 Conclusions	42
5. Metal-Catalyzed Ammonia Borane H_2-Release in Ionic Liquids	43
Summary	43
5.1 Introduction	43
5.2 Experimental Section	43
5.2.1 Materials	43
5.2.2 Physical Measurements	44
5.2.3 Procedures for AB H_2 -Release Reactions	44
5.2.3.1 H_2 -Release Measured with a Toepler Pump	44
5.2.3.2 H_2 -Release Measured with an Automated Gas Burette	45
5.3 Results and Discussion	45
5.4 Conclusions	51
6. Synthesis and Hydrolytic H_2-Release from Ammonia Triborane	52
Summary	52
6.1 Introduction	52
6.2 Experimental Section	52
6.2.1 Materials	52
6.2.2 Physical Measurements	53
6.2.3 Preparation of $\text{NH}_3\text{B}_3\text{H}_7$ (1) from $\text{Bu}_4\text{N}^+\text{B}_3\text{H}_8^-$	53
6.2.4 General Procedures for Hydrolytic H_2 -Release Measurements from Aqueous $\text{NH}_3\text{B}_3\text{H}_7$ Solutions	53
6.2.4.1 Stability of Solid and Aqueous Ammonia Triborane	54
6.2.4.2 Hydrolysis of 1 with HCl	54
6.2.4.3 Hydrolysis of 1 with Metal Catalysts	54
6.2.4.3.1 Extended Catalyst Lifetime Studies of $[\text{Rh}(\text{COD})(\mu\text{-Cl})]_2$ (22.7 and 7.9 mol%) in the absence of buffer solutions	54
6.2.4.3.2 Extended Catalyst Lifetime Studies of 5-wt% Rh/ Al_2O_3 (7 mol% Rh) in the presence of buffer solutions	54
6.2.4.3.3 Hydrolysis of 1 with Rh/ Al_2O_3 at Different Temperatures	55
6.2.4.4 Hydrolysis of a Concentrated Aqueous $\text{NH}_3\text{B}_3\text{H}_7$ Solution	55
6.3 Results and Discussion	55

6.3.1 Synthesis	55
6.3.2 Hydrolytic Hydrogen Release	56
6.4 Conclusions	62
7. Regeneration of Spent Ammonia Borane Hydrogen Fuels	63
Summary	63
7.1 Introduction	63
7.2 Experimental Section	64
7.2.1 Materials	64
7.2.2 Physical Methods	64
7.2.3 Synthesis of Spent Fuel at 85 °C (SF1)	64
7.2.4 Synthesis of Spent Fuel at 120 °C (SF2)	64
7.2.5 Acid Digestions of Spent Fuels	65
7.2.5.1 Digestion of Spent Fuels with Oxyacids	65
7.2.5.1.1 Digestion of Spent Fuel with Trifluoroacetic Acid (TFA)	65
7.2.5.1.2 Digestion of Spent Fuels with Other Oxyacids	65
7.2.5.2 Digestion of Spent Fuels with Haloacids	65
7.2.5.2.1 Digestion Reactions with Anhydrous HCl	65
7.2.5.2.2 Digestion Reactions with Superacidic HCl in Ionic Liquids	66
7.2.5.2.3 Digestion Reactions with Superacidic AlBr ₃ /HBr/CS ₂	66
7.2.5.2.4 Digestion Reactions with Superacidic AlCl ₃ /HCl/CS ₂	66
7.2.6 Reduction Studies of Digestates of Spent Fuels	67
7.2.6.1 Reduction of TFA-Digestated Spent Fuels	67
7.2.6.2 Complexation of BX ₃ , Reduction of B-X and Base-Displacement to Reform AB	67
7.2.6.2.1 Triethylamine (TEA) BX ₃ Complexation and B-X Reduction by Tributyltin Hydride (TBTH)	67
7.2.6.2.2 N,N-Diethylaniline (DEA) BBr ₃ Complexation, B-Br Reduction with Triethylsilane (TES) and DEA Displacement to Produce Ammonia Borane	67
7.2.6.2.3 Complexation of BBr ₃ with Dialkylsulfides and Reduction of Adducts	68
7.2.6.2.3.1 Synthesis of AB from BBr ₃ -Adducts with Triethylsilane (TES)	68
7.2.6.2.3.2 Synthesis of AB from BBr ₃ -Adducts with Tributyltin Hydride (TBTH)	68
7.3 Results and Discussion	69
7.3.1 Digestion of Ammonia Borane Spent Fuels with Strong Acids	69
7.3.1.1 Digestion of Spent AB Fuel with Oxyacids	69
7.3.1.2 Digestion of AB Spent Fuels with Haloacids	70

7.3.2 Reduction of Digested Products	72
7.3.2.1 Reduction of TFA-digestate with Alane	72
7.3.2.2 Reduction of BBr ₃ to AB	73
7.4 Conclusions	76
8. Publication and Presentations	77
9. References	80

List of Figures and Tables

Section 1	1
Figure 1.1 Summary of H ₂ -release results from 50:50 wt% ammonia-borane/ionic-liquid mixtures at 85 °C.	2
Figure 1.2 H ₂ -release measurements of: (left) 50-wt% AB in bmimCl showing the significant increase in H ₂ -release with increased temperature, and (right) 20-wt% AB in bmimCl at different temperatures showing both their fast rates and higher materials wt-%.	2
Figure 1.3 Proposed mechanistic pathways and intermediates for ionic-liquid activated ammonia borane H ₂ -release.	3
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.	3
Figure 1.5 H ₂ -release measurements of the reactions of 50-wt% AB in bmimCl at 65 °C with 5-mol% catalysts.	4
Figure 1.6 (left) H ₂ -release following repeated AT additions to an aqueous solution containing 5-wt% Rh/Al ₂ O ₃ . (right) Rhodium (5-wt% Rh/Al ₂ O ₃ , 1.0-mol% Rh) catalyzed H ₂ -release from a 22.7-wt% aqueous AT solution yielding 6.1-wt% H ₂ [wt% = H ₂ -wt/(NH ₃ B ₃ H ₇ +H ₂ O+Rh/Al ₂ O ₃ -wts)].	5
Figure 1.7 Overview of Penn approach to AB regeneration	6
Section 2	7
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.	7
Section 3	9
Figure 3.1 Toepler pump system used for H ₂ -release measurements.	10
Figure 3.2 Automated gas burette used for H ₂ -release measurements.	11
Figure 3.3 Structures of ionic liquids used in these studies.	13
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).	14
Figure 3.5 H ₂ -release measurements (gas burette) of 50-wt% AB (150 mg) in bmimCl (150 mg) at various temperatures.	15
Figure 3.6 H ₂ -release measurements (gas burette) of AB (150 mg) in 20.2-wt% bmimCl (38 mg) at various temperatures.	16
Figure 3.7 H ₂ -release measurements (Toepler pump) of the reaction of 50-wt% AB (250 mg) at 85 °C in 250 mg of various ionic liquids.	16

Figure 3.8 H ₂ -release measurements (Toepler pump) of the reaction of 50-wt% AB (250 mg) in 250 mg of various ionic liquids at (a) 65 °C and (b) 45 °C.	17
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 H ₂ -release of: (a) 0.04 equiv. and (b) 0.83 equiv. (Right) 50-wt% AB (250 mg) in bmimCl (250 mg) after H ₂ -release of: (c) 0.52 equiv. and (d) 0.95 equiv.	18
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.	19
Figure 3.11 Solution ¹¹ B 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).	20
Figure 3.12 Crystallographically determined structure of 1,3-dimethylimidazolium hexafluorophosphate with 0.5 mol benzene included as a clathrate.	20
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 at various temperatures.	21
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 various times.	21
Figure 3.15 H ₂ -release measurements (gas burette) of bmimOTf (450 mg) and 10-wt% (50 mg) of DADB and AB.	22
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.	23
Figure 3.17 Possible pathway for ionic-liquid promoted H ₂ -release from AB.	23
Figure 3.18 H ₂ -release measurements (gas burette) of 50-wt% AB (150 mg) in tetraglyme (150 mg) at various temperatures.	24
Figure 3.19 Solution ¹¹ B{ ¹ 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.	25
Section 4	26
Figure 4.1 H ₂ -release measurements (Toepler pump) of the reaction of pure solid-state AB (250 mg) and with 8 mol% LiNH ₂ and 17 mol% LiH at 85 °C.	29
Figure 4.2 Solution ¹¹ B NMR (128.4 MHz) spectra of the residues (extracted in pyridine) of the 85 °C reaction of AB with bmimCl, LiNH ₂ and LiH.	30
Figure 4.3 H ₂ -release measurements for solid state AB reactions with Proton Sponge at 85 °C using the Toepler pump and gas burette.	31
Figure 4.4 ¹¹ B{ ¹ H} NMR (128.4 MHz) spectra recorded at 25 °C of the glyme extract of the reaction of solid-state AB with and without Proton Sponge.	32
Figure 4.5 Solid-state ¹¹ B NMR (240 MHz) spectra recorded at 25 °C of the reaction of solid-state AB reactions with and without Proton Sponge after 1 equivalent was released.	32
Figure 4.6 H ₂ -release measurements (Toepler pump) of the reaction of AB in bmimCl with Proton Sponge at 85 °C.	33
Figure 4.7 Differential Scanning Calorimetry analyses of the reactions of AB in bmimCl	34

with Proton Sponge at various temperatures.

Figure 4.8 H₂-release measurements (gas burette) of the reaction of AB in bmimCl with Proton Sponge at various temperatures. 35

Figure 4.9 H₂-release measurements (gas burette) of partially dehydrogenated AB where 1 H₂-equivalent was initially released at 85 °C, then bmimCl and bmimCl/Proton Sponge were added to separate samples and heating resumed at 85 °C. 35

Figure 4.10 Solid-state ¹¹B NMR (240 MHz) spectra recorded at 25 °C of the reaction of AB and Proton Sponge in bmimCl at 85 °C. 36

Figure 4.11 DFT optimized geometries (B3LYP/6-31G(d)) and GIAO calculated (B3LYP/6-311G(d)) ¹¹B NMR chemical shifts. 36

Figure 4.12 Solid-state ¹¹B NMR (240 MHz) spectrum recorded at 25 °C of the reaction of AB and Proton Sponge in bmimCl at 85 °C for 23 h. 37

Figure 4.13 Solution ¹¹B NMR (128 MHz) spectra recorded at 25 °C of the reaction of AB in mmimMeSO₄ at 85 °C with and without Proton Sponge. 37

Figure 4.14 Foaming resulting from the reaction of 250 mg AB in 250 mg bmimCl after 1 h at 100 °C with and without Proton Sponge. 38

Figure 4.15 H₂-release measurements (Toepler pump) of the reaction of AB in ionic liquids or tetraglyme with Proton Sponge at 85 °C. 38

Figure 4.16 Solution ¹¹B{¹H} NMR (128 MHz) spectra recorded at 80 °C of the reaction of AB and Proton Sponge in tetraglyme at 85 °C. 39

Figure 4.17 Crystallographically determined structure of [Et₃BNH₂BH₃]⁻ K⁺•18-crown-6 40

Figure 4.18 Possible anionic polymerization pathway for PS-promoted H₂-release from AB. 41

Figure 4.19 DFT (B3LYP/6-31G(d)) optimized geometry and GIAO (B3LYP/6-311G(d)) calculated ¹¹B NMR shifts for [Et₃BNH₂BH₂NH₂BH₃]⁻. 42

Section 5 43

Figure 5.1 Comparisons of the H₂-release activities at different temperatures (Toepler pump measurements) of the reactions of AB (250 mg) in 50-wt% emmimEtSO₄ with and without 2.5-mol% of [Rh(COD)Cl]₂. 46

Table 5.1 Summary of experimental data for uncatalyzed, Rh-catalyzed and Pd-catalyzed hydrogen-release of NH₃BH₃ in 50-wt % ionic liquid at 85, 65 and 45 °C. 45

Figure 5.2 H₂-release measurements on the automated gas burette of the reaction of Me₂NHBH₃ (150 mg) in 50-wt% bmimCl at 65 °C with 2.5-mol% [Rh(COD)Cl]₂. 46

Figure 5.3 DSC analysis of 50-wt% NH₃BH₃ in bmimCl with and without 5 mol% Rh.. 47

Figure 5.4 H₂-release measurements using the automated gas burette of the 65 °C reaction of AB (150 mg) in 50-wt% bmimCl with different mol% Rh. 47

Figure 5.5 H₂-release measurements using the automated gas-burette of the reaction of AB (150 mg) in 90-wt% bmimOTf at 65 °C with 5-mol% catalysts. 48

Figure 5.6 In situ solution ¹¹B NMR spectra of the reaction of 10-wt% AB in bmimOTf at 85 °C: (left) uncatalyzed; (right) with 2.5-mol% [Rh(COD)Cl]₂. 48

Figure 5.7 H₂-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 49

Figure 5.8 H₂-release measurements using the automated gas burette of the reactions of 50-wt% Me₂NHBH₃ in bmimCl at 65 °C with 5-mol% catalysts. 49

Figure 5.9 In situ solution ^{11}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 .	49
Figure 5.10. AB H_2 -release rates at 65 °C measured with the automatic gas burette for the $\text{Pd}(\text{DBA})_2$ catalyst with different ionic-liquids, wt%-AB and catalyst-concentrations.	50
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% $\text{Pd}(\text{DBA})_2$ and (right) 10-wt% AB in bmimOTf with 1 mol% $\text{Pd}(\text{DBA})_2$.	50
Figure 5.12 Solid State ^{11}B NMR spectrum of the reaction of 50-wt% AB in bmimCl at 65°C for 23 h with 5-mol% Rh.	51
Figure 5.13 Solid State ^{11}B NMR of the reaction of 50-wt% AB in bmimCl at 65 °C with 5-mol% of $\text{Pd}(\text{DBA})_2$ after the release of only 0.5, 1.0 and 1.2 H_2 -equivalents.	51
Section 6	52
Figure 6.1 $^{11}\text{B}\{^1\text{H}\}$ NMR spectra for the reaction progression leading to the formation of $\text{NH}_3\text{B}_3\text{H}_7$ 1 .	56
Figure 6.2 ^{11}B NMR spectra of a 20-wt% aqueous solution of 1 at room temperature for several days.	57
Figure 6.3 Hydrogen release from (a) a 0.45-wt% aqueous solution of 1 upon reaction with various amounts of HCl.	57
Figure 6.4 Metal-catalyzed hydrolytic H_2 -release from aqueous (0.45-wt%) solution of 1 .	59
Figure 6.5 Hydrogen evolution following repeated additions (11 cycles) of 1 to a borate buffered solution containing 5-wt% Rh/ Al_2O_3 .	60
Figure 6.6 ^{11}B NMR spectra of aqueous 1 solutions at various concentrations after hydrolysis.	60
Figure 6.7 The effect of catalyst loadings and temperature on H_2 -release rates from a 0.45- wt% aqueous solution of 1 .	61
Section 7	63
Figure 7.1 Possible spent-fuel products of ammonia borane H_2 -release.	63
Table 7.1 Summary of Oxyacid Spent-Fuel Digestion Reactions and Product ^{11}B NMR Shifts	65
Figure 7.2 Overview of Penn approach to AB regeneration	69
Figure 7.3 ^{11}B NMR analysis of the digestion of spent-fuel SF1 with trifluoroacetic acid.	70
Figure 7.4 Summary of the results of the reactions of anhydrous HCl with AB spent-fuels, polyborazylene and boron nitride.	70
Figure 7.5 ^{11}B NMR analysis of the 65 °C digestion of spent-fuel SF1 with superacidic bmimCl/ AlCl_3 /HCl.	71
Figure 7.6 ^{11}B NMR analysis of the digestion of spent-fuel SF1 with superacidic HBr/ AlBr_3 / CS_2 .	72
Figure 7.7 ^{11}B NMR analysis of the reduction of the TFA-digestate with dimethylethylamine-alane.	73
Figure 7.8 ^{11}B NMR analysis of the diethylaniline-based synthesis of ammonia borane from BBr_3 via coordination/reduction/displacement reactions.	74
Figure 7.9 Summary of the dialkylsulfide-based coordination/reduction/displacement process for the synthesis of ammonia borane from BBr_3 .	74

Figure 7.10 Reaction summary and product separation scheme for the silane-reduction of $(\text{C}_6\text{H}_{13})_2\text{S-BBr}_3$. 75

Figure 7.11 Reaction summary and separation method for the tin hydride reduction of $(\text{C}_2\text{H}_5)_2\text{S-BBr}_3$. 76

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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, NH_3BH_3 (AB), 19.6-wt% H_2 , and ammonia triborane $\text{NH}_3\text{B}_3\text{H}_7$ (AT), 17.7-wt% H_2 , were initially identified by the Center as promising, high-capacity chemical hydrogen storage materials with the potential 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 H_2 -release and on new strategies for the regeneration the amineborane spent-fuel materials.

The Penn approach to improving amineborane H_2 -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 H_2 -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 H_2 -Release. While partial AB dehydrogenation has been achieved in the solid-state, milder conditions and more controllable AB H_2 -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 ($< 100\text{ }^\circ\text{C}$), 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 H_2 -release studies in **Figure 1.1**, ionic liquids were demonstrated to have an activating effect on AB H_2 -release that eliminated the induction period observed in the solid-state H_2 -release reactions and increased both the extent and rate of AB H_2 -release.

H_2 -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 H_2 -release were possible with only modest increases in temperature. Thus, at $110\text{ }^\circ\text{C}$, over 2 H_2 -equivalents were released in only ~ 20 min. As can also be seen in **Figure 1.2** (right), significantly enhanced H_2 -release rates compared to the solid-state were still achieved when employing as little as 20.2-wt% bmimCl, thereby resulting in a H_2 -release system with 11.4 materials-wt% H_2 -release.

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.

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_3BNH_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 H_2 -release measurements of the reactions of 50-wt% AB in bmimCl at 65 °C 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 1st 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) $\text{NH}_3\text{B}_3\text{H}_7$ 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/(NH₃B₃H₇+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 hydrolyses for other applications having less stringent weight requirements.

Ammonia Borane Regeneration. The efficient regeneration of ammonia borane from BNH_x 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

Second Step: One-Pot Conversion of BX_3 to AB

Coordination of BX_3

BX Reduction

Base Displacement by NH_3 to Yield AB

Figure 1.7 Overview of Penn approach to AB regeneration.

Spent fuel materials resulting from AB H_2 -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 H_2 -release with superacidic $\text{AlBr}_3/\text{HBr}/\text{CS}_2$ solutions yielded BBr_3 which could be distilled out of the reaction mixtures; however, the digestion of more highly dehydrogenated spent fuels with ~ 2 equivalents of H_2 -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 BBr_3 to ammonia borane with efficient and safe product separations, the fact that AB spent-fuels cannot as yet be digested in good yields to BX_3 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 H_2 -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 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, such as borazine, continue to make AB/ionic-liquid based systems attractive candidates for chemical hydrogen storage applications. These studies have also demonstrated 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 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_3BH_3 (AB), 19.6 wt% H_2 , and ammonia triborane $\text{NH}_3\text{B}_3\text{H}_7$ (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 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^{1,2,3} to promote the rate and extent of H₂-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 H₂-equiv. in 67 min and 2.2 H₂-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 H₂-equiv. at 85 °C, with the release of only another ~0.1 H₂-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 H₂-equiv. in 5 min and 2.2 H₂-equiv. in only 20 min at 110 °C. Increasing the AB/bmimCl ratio to 80:20 still gave enhanced H₂-release rates compared to the solid-state, and produced a system that achieved 11.4 materials-weight percent H₂-release. Solid-state and solution ¹¹B NMR studies of AB H₂-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.^{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% H₂ according to Equation 3.1.⁶

Partial dehydrogenation of ammonia borane can be thermally induced in the solid-state,^{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 *in situ* ¹¹B NMR studies of reactions in progress are also presented that provide insight into the intermediates and mechanistic steps involved in ionic-liquid promoted AB H₂-release.

3.2 Experimental Section

All manipulations were carried out using standard high-vacuum or inert-atmosphere techniques as described by Shriver.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.⁹ The 1-butyl-3-methylimidazolium iodide (bmimI) was synthesized sonochemically from 1-iodobutane and 1-methyl-imidazole according to literature methods.¹⁰ All ionic liquids, including 1-butyl-2,3-dimethylimidazolium chloride (bmmimCl) (EMD), 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄), 1-butyl-3-methylimidazolium chloride (bmimCl), 1-butyl-3-methylimidazolium triflate (bmimOTf), 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆), 1-ethyl-2,3-dimethylimidazolium ethylsulfate (emmimEtSO₄), 1-ethyl-2,3-dimethylimidazolium triflate (emmimOTf), 1,3-dimethylimidazolium methylsulfate (mmimMeSO₄) and 1-propyl-2,3-dimethylimidazolium triflate (pmmimTf₃C) (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 H₂-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 H₂-release worked best for reactions with slow H₂-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 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 were then also measured using the Toepler pump.

Figure 3.1 Toepler pump system used for H₂-release measurements.

3.2.2.2 H₂-Release Measured with an Automated Gas Burette

For reactions with faster rates, an automated gas burette was employed for H₂-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 H₂-release at short time ranges.

Figure 3.2 Automated gas burette used for H₂-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 H₂ stream, along with any additional volatiles, passed through the -78 °C trap and flowed into the bottom of the oil-filled burette. As H₂ 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 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.

3.2.2.3 Procedures for ¹¹B 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 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) and then referenced to BF₃•O(C₂H₅)₂ (0.0 ppm).

The solution ¹¹B 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 ¹¹B NMR spectra of the reaction mixture (recorded at 25 °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.

3.3 Results and Discussion

Utilization of waste heat from a PEM fuel cell can provide for AB H₂-release reaction temperatures near 85 °C.⁷ However, at 85 °C, H₂-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 H₂ 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 H₂-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 H₂-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 homogeneous 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 mmimMeSO₄, are particularly useful for running *in situ* ¹¹B 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.

3.3.2 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 under N₂ 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 H₂ 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

residue. 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 initial¹ 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 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 2nd H_2 -equiv. being significantly slower

than for the 1st equiv. Dramatic increases (**Figure 3.5**) in the rate of H₂-release of the 50:50-wt% AB/bmimCl mixture for both H₂-equivalents were observed as the temperature was increased with the release of 1.0 H₂-equiv. in 37 min and 2.2 H₂-equiv. in 161 min at 95 °C, 1.0 H₂-equiv. in 9 min and 2.2 H₂-equiv. in 45 min at 105 °C, and 1.0 H₂-equiv. in 5 min and 2.2 H₂-equiv. in 20 min at 110 °C. The 75 °C reaction did not reach 2 H₂-equiv.

Figure 3.5 H₂-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 H₂-storage of 9.0 total-system-wt%.³⁷ The release of 2.2 H₂-equiv. from a 50:50 AB/bmimCl mixture corresponds to a release of 7.2 mat-wt% H₂ [mat-wt% H₂ = H₂-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 H₂-release rates compared to the solid-state could still be obtained when employing as little as 20.2-wt% bmimCl. Thus, 2.0 H₂-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 H₂-equiv. at longer times. The final release observed for these mixtures corresponds to an 11.4 mat-wt% H₂-release.

The 85 °C H₂-release data (Toepler pump measurements) in **Figure 3.7** show that AB H₂-release is activated in a variety of 50:50-wt% AB/ionic-liquid mixtures, but that these mixtures exhibit a range of H₂-release extents and rates. The biggest differences were observed for the release of the 2nd equivalent. The bmimCl, bmmimCl, bmimBF₄, mmimMeSO₄ and emmimEtSO₄ (refer to **Figure 3.3** for structures) mixtures all yielded over 2 H₂-equiv. at reasonably comparable rates, while the other mixtures showed greatly decreased release rates beyond the 1st equiv. For the pmmimTf₃C mixture, H₂-release stopped, as was observed for the AB solid-state reactions at 85 °C, after only ~0.9 H₂-equiv. As shown in **Figure 3.8**, the H₂-release rates were significantly decreased upon lowering the temperature with the mmimMeSO₄ and emmimEtSO₄ 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) bmmimCl, (B) bmimCl, (C) emmimEtSO₄, (D) bmimBF₄, (E) mmimMeSO₄, (F) bmimOTf, (G) emmimOTf, (H) bmimI, (I) bmimPF₆ and (J) pmmimTf₃C.

Figure 3.8 H₂-release measurements (Toepler pump) of the reaction of 50-wt% AB (250 mg) in 250 mg of: (A) emmimEtSO₄, (B) mmimMeSO₄, (C) bmmimCl and (D) bmimCl at (a) 65 °C and (b) 45 °C.

3.3.4 ¹¹B 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 H₂-release reaction began, the mixture foamed. As the H₂-release neared the loss of ~1 H₂-equiv., the foam began to convert to a white solid. The entire AB/bmimCl mixture ultimately became solid as the reaction reached over 2 H₂-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 H₂-release. Solid formation was likewise observed in H₂-release reactions of 50:50-wt% AB/tetraglyme systems (discussed later) to produce a final two-phase liquid/solid mixture.

3.3.4.1 ¹¹B NMR of Pyridine Extracts from Reaction Products

The ¹¹B 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 H₂-loss, the spectrum (**Figure 3.9a**) of the residue of the 1 h solid-state AB reaction showed only unreacted AB (quartet, -22.3 ppm³⁸), 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 H₂-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-equiv., 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)^{9,38} 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 ¹¹B 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 $\text{B}=\text{N}$ 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 $\text{B}=\text{N}$ 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/mmimMeSO₄ and AB/bmimI 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 polyborazylene³⁹⁻⁴¹ 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 Solution ¹¹B 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 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 ¹¹B 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.

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 ¹¹B 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.

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 ¹¹B NMR spectrum obtained from a 10-wt% DADB/bmimOTf sample showed only the broad resonances expected for the DADB (NH₃)₂BH₂⁺ (-13.3 ppm) and BH₄⁻ (-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 ¹¹B 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 H₂-release measurements (gas burette) of bmimOTf (450 mg) and 10-wt% (50 mg) of: (A) DADB and (B) AB.

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 H₂-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 H₂-Release Reactions in Tetraglyme

The AB H₂-release observed in the ionic liquid solvents was also compared with that obtained for the conventional polar organic solvent, tetraglyme. The H₂-release data for a 50:50 wt% ratio AB/tetraglyme mixture showed that both the extent and rate of H₂-release were comparable to that of the AB/bmimCl reactions (**Figure 3.18**). However, the ¹¹B 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 BH₄⁻ (-36.8 ppm)⁴² and μ -aminodiborane (-27.5 ppm)⁴² (**Figure 3.19**). Thus, ionic liquid solvents are favored for AB H₂-release since they suppress or retard the formation of these undesired products.

Figure 3.18 H₂-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.

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 ^1H 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}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 H₂-Release

Summary

The addition of small amounts of bases, including LiNH₂, 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 H₂-release from ammonia borane (AB). For example, while H₂-release from pure AB at 85 °C stops after only ~0.9 equivalents, AB reactions with the addition of 8 mol% of LiNH₂ or 17 mol% LiH at 85 °C yielded ~1.5 equivalents of H₂ (corresponding to ~9.5 materials-wt % H₂). Nevertheless, more detailed studies of the LiNH₂/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 LiBH₄ product. On the other hand, the reactions with Proton Sponge were found to promote the rate and extent (to over 2 equivalents) of H₂-release from ammonia borane (AB) in both the solid state and in ionic-liquid and tetraglyme 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 H₂ 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 tetraglyme since they reduced the formation of undesirable products, such as borazine. Solid-state and solution ¹¹B NMR studies of PS-promoted reactions in progress support a reaction pathway involving initial AB deprotonation to form the H₃BNH₂⁻ 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 [Et₃BNH₂BH₃]⁻Li⁺ with AB show evidence of chain-growth providing additional support for a PS-promoted AB anionic dehydropolymerization H₂-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 H₂-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, [(NH₃)₂BH₂]⁺BH₄⁻, (DADB) from AB and that DADB is the key intermediate for H₂-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 tetraglyme and it is shown that these bases enhance H₂-release from AB via a very different mechanistic pathway involving anionic AB dehydropolymerization initiated by the H₃BNH₂⁻ 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 (mmimMeSO₄),

1-butyl-2,3-dimethylimidazolium chloride (bmimCl), and 1-ethyl-2,3-dimethylimidazolium ethylsulfate (edimEtSO₄) 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 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 **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% (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-release^{2,52} 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 H₂-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 H₂ were produced. Even with prolonged heating (67 h) at this temperature no further H₂-release was observed. However, the AB reactions with the addition of 8 mol% of LiNH₂ (18 mg) or 17 mol% LiH (13 mg) at 85 °C led to significant increases in the extent of H₂-release (~1.5 equivalents in both cases at 15 h). In both cases, these values correspond to the release of ~9.5 materials-wt % H₂.

Figure 4.1 H₂-release measurements (Toepler pump) of the reaction of pure solid-state AB (250 mg) and with 8 mol% LiNH₂ and 17 mol% LiH at 85 °C.

Figure 4.2 shows comparisons of the ¹¹B 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 H₂ was released, the spectra appear similar. However, at the later times where more H₂ 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 ppm quintet peaks in the LiNH₂ 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 BH₄⁻ component of the diammoniate of diborane [(NH₃)₂BH₂]⁺BH₄⁻ (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 LiNH₂ and LiH reactions was found to not be from DADB, but instead to arise from an undesirable product, LiBH₄. Unfortunately, since LiBH₄ does not decompose until >350 °C,⁵³ its formation in the AB/lithium-base reactions prevents further AB H₂-release beyond at 85 °C.

Figure 4.2 Solution ^{11}B NMR (128.4 MHz) spectra of the residues (extracted in pyridine) of the 85 °C reaction of: **(Left)** AB (250 mg) with bmimCl (250 mg) at 1h, with LiNH₂ (18 mg) at 2h, and with LiH (13 mg) at 3h. **(Right)** AB (250 mg) with bmimCl (250 mg) at 6h, with LiNH₂ (18 mg) at 15h, and with LiH (13 mg) at 15h.

Our studies of the roles of LiNH₂ and LiH in inducing H₂-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 H₃BNH₂[−] anion, with this anion then inducing anionic dehydropolymerization of AB to produce a growing polyaminoborane polymer (**Equation 4.3**).

Our studies also showed that the undesirable LiBH₄ product could form in these systems via reactions such as shown in **Equations 4.4** and **4.5**.

4.3.2 Ammonia Borane H₂-Release Reactions Promoted by Proton Sponge

In order to avoid the formation of stable alkali-metal borohydrides during base promoted AB H₂-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 (pK_a ~12), non-nucleophilic base, bis(dimethylamino)naphthalene (Proton Sponge, PS),⁵⁴ can also induce AB H₂-release via an anionic dehydropolymerization mechanism with the advantage that the formation of a stable BH₄⁻ salt is avoided.

4.3.2.1 H₂-Release from AB/PS Solid-State Reactions

As shown in **Figure 4.3a**, initial H₂-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 H₂-release. While the reaction with 1.0 mol % PS still showed an induction period with no H₂-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 H₂-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 H₂-equivalents. More detailed H₂-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 H₂-release was increased upon the addition of 5.2 mol% PS.

Figure 4.3 H₂-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 diammoniate of diborane, [(NH₃)₂BH₂]⁺BH₄⁻, (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 H₂-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 ¹¹B 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 sp²

boron-framework of cross-linked polyborazylene structures,³⁹⁻⁴¹ thus indicating that AB dehydrogenation ultimately produces B=N unsaturated products. Consistent with this conclusion, the ^{11}B NMR spectra of the volatile products of the PS/AB reactions collected in the cold trap through which the released H_2 had been passed, also indicated some borazine ($\text{B}_3\text{N}_3\text{H}_6$) 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.

Figure 4.4 $^{11}\text{B}\{^1\text{H}\}$ NMR (128.4 MHz) spectra (insets show ^1H 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)

Figure 4.5 Solid-state ^{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_2 -equivalent was released and (b) AB (150 mg) at 85 °C until 1 H_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 3¹ 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 DADB^{9,38} 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 reported⁵⁵⁻⁵⁸ for the H_3BNH_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 reactions⁷ have likewise shown the formation of similar types of $\text{B}=\text{N}$ 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 mmimMeSO₄ 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 mmimMeSO₄ (**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 mmimMeSO₄ (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 H₂-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 H₂-release, was found to have the unanticipated, but highly beneficial, effect of significantly reducing foaming during AB H₂-release in the bmimCl/PS reactions.

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 H₂-Release in Other Ionic Liquids and Tetraglyme

PS was also found to increase AB H₂-release in both other ionic liquids and tetraglyme, with both the extent and rate of H₂-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 ¹¹B NMR spectra of the tetraglyme/PS reactions also showed evidence for the initial formation of the H₃BNH₂⁻ 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)⁴² along with smaller amounts of BH₄⁻ (-36.8 ppm)⁴² and μ -aminodiborane (-27.5 ppm)⁴² (**Figure 4.16**). Thus, ionic liquid solvents are favored for AB H₂-release since they suppress or reduce the formation of these products.

Figure 4.15 H₂-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.

Figure 4.16 Solution $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz) spectra (insets show ^1H coupled spectra) recorded at 80 °C of the reaction of AB (50 mg) and 5.2 mol% PS (18 mg) in tetraglyme (450 mg) at 85 °C after: (a) 1 h, (b) 3 h, and (c) 6 h.

4.3.6 Why Does Proton Sponge Induce H_2 -Release from AB?

In Section 3,¹ 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 ($[\text{BH}_2(\text{NH}_3)_2]\text{BH}_4^-$), (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.^{7,50} 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.⁵⁴ 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.⁵⁴ The observation of a ^{11}B NMR signal near -21.0 ppm and a ^1H NMR signal at ~ 18.9 ppm, characteristic of AB deprotonation to form the $\text{H}_3\text{BNH}_2^-\text{PSH}^+$ 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 $\text{H}_3\text{BNH}_2^-\text{Li}^+$ salt has previously been prepared *in situ* from AB and n-BuLi at 0 °C.⁵⁶ More recently, ball milling^{55,58,59} and solution reactions^{60,61} of AB with metal hydrides have been used to generate $\text{H}_3\text{BNH}_2^-\text{M}^+$ ($\text{M} = \text{Li}$ and Na) and $(\text{H}_3\text{BNH}_2^-)_2\text{Ca}^{2+}$. We found²⁹ 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_3B -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 $-\text{BH}_3$ (calc -25.3) units in the anion.²⁹

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

The structures of $\text{H}_3\text{BNH}_2^-\text{M}^+$ ($\text{M} = \text{Li}$ and Na) and $(\text{H}_3\text{BNH}_2^-)_2\text{Ca}^{2+}$ have recently been established from the analyses of their high resolution powder diffraction data,^{59,61} and that of $(\text{H}_3\text{BNH}_2^-)_2\text{Ca}^{2+} \cdot 2\text{THF}$ by a single-crystal X-ray determination.⁶⁰ The crystallographic determination of the $[\text{Et}_3\text{BNH}_2\text{BH}_3]^- \text{K}^+ \cdot 18\text{-crown-6}$ complex in **Figure 4.17**,²⁹ confirmed that following AB nitrogen-deprotonation by the triethylborohydride, the Lewis-acidic triethylborane group coordinated at the nitrogen.

Electronic structure calculations on $[\text{H}_2\text{NBH}_3]^- \text{M}^+$ 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 basicity than in AB. This increases the ability of these anions to release 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 AB 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 H_3NBH_3 to produce, as shown in **Figure 4.18**, a growing anionic polyaminoborane polymer. DFT/GIAO calculations of model anionic polymers showed that their ^{11}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 NH_2 hydrogens of a polyaminoborane polymer relative to those on terminal NH_3 units should result in the NH_2 protons being less reactive for dehydrocoupling reactions that could liberate more than one-equivalent of H_2 . Thus, the increased release-rate for the second equivalent of 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 H_2 -elimination reactions with the protons at these NH_2 sites.

Figure 4.18 Possible anionic polymerization pathway for PS-promoted 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 $[\text{Et}_3\text{BNH}_2\text{BH}_3]^- \text{Li}^+$ with AB.²⁹ The higher Lewis acidity of the BH_3 group compared to the Et_3B 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 H₂ during the reaction of equal equivalents of NH₃BH₃ with [Et₃BNH₂BH₃]⁻Li⁺ at 23 °C and an electrospray mass spectrum indicated formation of Et₃BNH₂BH₂NH₂BH₃⁻. the ¹¹B NMR spectra was in good agreement with the calculated ¹¹B NMR shifts for the DFT optimized geometry of the chain growth product Et₃BNH₂BH₂NH₂BH₃⁻ given in **Figure 4.19**. These results provide additional strong support for a PS-induced H₂-release mechanism involving an intermolecular anionic dehydropolymerization pathway initiated by the NH₂BH₃⁻ anion.

Figure 4.19 DFT (B3LYP/6-31G(d)) optimized geometry and GIAO (B3LYP/6-311G(d)) calculated ¹¹B NMR shifts for [Et₃BNH₂BH₂NH₂BH₃]⁻.

4.4 Conclusions

The work described in this section demonstrated base-activation of AB H₂-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 H₃BNH₂⁻ anion. For the bmimCl/PS reactions, significantly increased rates of AB H₂-release, yielding over 2 equivalents of H₂, 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 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 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.^{62,63} 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.¹²⁻²⁷ 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.⁸

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)Cl]₂ (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 H₂-Release Data for uncatalyzed, Rh-catalyzed and Pd-catalyzed NH₃BH₃ reactions in 50-wt % ionic liquid at 85, 65 and 45 °C.

Time [h]	Temp [°C]	H ₂ -Release		
		Uncatalyzed ^a equiv. (mmol)	Rh-catalyzed ^{a,b} equiv. (mmol)	Pd-catalyzed ^c equiv. (mmol)
1	85	1.00 (8.09)	1.28 (10.4)	1.5
3	85	1.32 (10.7)	1.56 (12.6)	1.6
6	85	1.64 (13.3)	1.75 (14.2)	1.6
23	85	2.20 (17.8)	2.10 (17.0)	1.8
1	65	0.19 (1.51)	0.73 (5.94)	1.2
3	65	0.60 (4.87)	1.00 (8.12)	
5	65	0.75 (6.08)	1.07 (8.66)	
23	65	1.01 (8.19)	1.26 (10.2)	
1	45	0.003 (0.028)	0.41 (3.30)	0.2
3	45	0.01 (0.083)	0.57 (4.65)	0.4
5	45	0.02 (0.19)	0.68 (5.50)	0.5
23	45	0.34 (2.77)	0.92 (7.47)	0.7

^a 250 mg NH₃BH₃ (8.1 mmol) and 250 mg emmimEtSO₄; ^b 100 mg [Rh(COD)Cl]₂ (5 mol% Rh);

^c 150 mg NH₃BH₃, 150 mg bmimCl, and 140 mg Pd(DBA)₂.

5.2.3.2 H₂-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 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.

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 H₂-release to form cyclotriborazane, μ-aminodiborane, borazine and insoluble BNH_n oligomers.¹⁴ He also showed that Rh catalyzed Me₂NHBH₃

dehydrogenation in toluene to form the $(\text{Me}_2\text{NBH}_2)_2$ cyclic dimer. Although ionic liquids have been used for a wide variety of metal-catalyzed chemical reactions,⁶⁴ our work⁶² demonstrating that $[\text{Rh}(\text{COD})\text{Cl}]_2$ also catalyzed AB H_2 -release in emmimEtSO₄, 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/emmimEtSO₄ solutions with and without 2.5-mol% of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (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.

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% emmimEtSO₄ with and without 2.5-mol% of $[\text{Rh}(\text{COD})\text{Cl}]_2$.

As shown in **Figure 5.2**, the $[\text{Rh}(\text{COD})\text{Cl}]_2$ complex was also found to be quite active in 50-wt% bmimCl for the catalyzed dehydrocyclization of Me_2NHBH_3 to $(\text{Me}_2\text{NBH}_2)_2$.

Figure 5.2 H_2 -release measurements on the automated gas burette of the reaction of Me_2NHBH_3 (150 mg) in 50-wt% bmimCl at 65 °C with 2.5-mol% $[\text{Rh}(\text{COD})\text{Cl}]_2$.

Differential scanning calorimetric studies carried out at PNNL, demonstrated that the Rh-catalyst significantly lowered the temperature required for H₂-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 H₂-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% NH₃BH₃ in bmimCl with and without 5 mol% Rh.

As presented in **Figure 5.4**, the AB H₂-release rate was found to be dependent on the Rh catalyst concentration, but again, in each case, H₂-release from these concentrated (50-wt%) solutions at 65 °C essentially stopped after the release of only ~1 H₂-equivalent.

Figure 5.4 H₂-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 H₂-release was observed for the metal-catalyzed reactions with more dilute (~10-wt%) AB solutions in emmimEtSO₄. Thus, the release of over 2 H₂-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 H₂-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% bmimOTf at 65 °C with 5-mol% catalysts.

The ¹¹B-NMR spectra of monoglyme extracts of the 50-wt% AB/emmimEtSO₄ 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 H₂. 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 ¹¹B-NMR observations presented in **Figure 5.6** of the reactions of 10-wt% AB in bmimOTf 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 H₂-release in the uncatalyzed and metal-catalyzed reactions in ionic-liquids.

Figure 5.6 In situ solution ¹¹B NMR spectra of the reaction of 10-wt% AB in bmimOTf at 85 °C: (left) uncatalyzed; (right) with 2.5-mol% [Rh(COD)Cl]₂.

The H₂-release measurements summarized in **Figures 5.7** and **5.8**, demonstrated that a number of metals catalyze H₂-release from both AB and Me₂NHBH₃ in the bmimCl ionic-liquid, including Rh, Ni, Pd and Ru based catalysts.

Figure 5.7 H₂-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 H₂-release measurements using the automated gas burette of the reactions of 50-wt% Me₂NHBH₃ in bmimCl at 65 °C with 5-mol% catalysts.

In situ solution ¹¹B NMR studies of the Ni and Ru-catalyzed AB H₂-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 ¹¹B NMR spectra of the progress of the reactions of 10-wt% AB in bmimOTf at 65 °C with: (left) 5-mol% RuCl₃; (right): 5-mol% NiCl₂.

The Pd(DBA)₂ complex proved to have the highest rates for AB H₂-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 H₂-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.

In situ solution ¹¹B NMR studies (**Figure 5.11**) of the Pd(DBA)₂-catalyzed AB H₂-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 H₂-release.

Figure 5.11 In situ solution ¹¹B NMR studies monitoring the progress of H₂-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.

The solid-state ¹¹B NMR spectra (**Figures 5.12 and 5.13**) of the insoluble AB spent-fuel products of the metal-catalyzed H₂-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.³⁹⁻⁴¹ Thus, even though the uncatalyzed and metal-catalyzed AB H₂-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 sp² boron-nitrogen framework with B=N units.

Figure 5.12 Solid State ¹¹B 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 ¹¹B NMR of the reaction of 50-wt% AB in bmimCl at 65 °C with 5-mol% of Pd(DBA)₂ after the release of only 0.5, 1.0 and 1.2 H₂-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 H₂-release in ionic liquid media. A number of transition metals were found to catalyze AB H₂-release in ionic-liquids with the rhodium and palladium metals showing the highest activities. 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 with the metal catalysts having the biggest effect on the release of the 1st H₂-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 H₂-release reactions.

Section 6. Synthesis and Hydrolytic H₂-Release from Ammonia Triborane

Summary

Our studies^{65,66} demonstrated that iodine oxidation of B₃H₈⁻ in glyme solution produced (glyme)B₃H₇. Subsequent displacement of the coordinated glyme by reaction with anhydrous ammonia provided a safe and convenient preparation of ammonia triborane, NH₃B₃H₇ (**1**). Studies of ammonia triborane hydrolytic H₂-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% H₂-release being achieved from a 22.7-wt% aqueous solution of **1** at room temperature in the presence of 5-wt% Rh/Al₂O₃ (1.1 mol% Rh). The rate of H₂-release was controlled by both the catalyst loadings and temperature. While the DOE total-system H₂-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 NH₃BH₃ and NaBH₄ 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% H₂) or thermolysis, **Equation 6.2**, (17.7 materials-wt% H₂) makes it an attractive candidate for chemical hydrogen storage.

Although Kodama first synthesized⁶⁷ NH₃B₃H₇ 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 studies⁶⁸⁻⁷⁴ that predict a symmetric single hydrogen-bridged C_s-symmetric structure, and the early single crystal X-ray determination⁷⁵ 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 NaBH₄ (98%), iodine, 18-crown-6, RhCl₃, [Rh(COD)(μ-Cl)]₂ (COD = 1,5-cyclooctadiene), Pd/Al₂O₃, Pt/C, Pt (nanosize, activated), Pd (submicron), Ru powder, and NiCl₂ and Aldrich or Strem Rh/Al₂O₃, Ru/Al₂O₃, and RuCl₃ 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. Bu₄N⁺B₃H₈⁻ 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 ^1H NMR spectra at 400.1 MHz were obtained on a Bruker DMX-400 spectrometer equipped with appropriate decoupling accessories. ^1H NMR spectra at 500.1 MHz were obtained on a Bruker AM-500 spectrometer. All ^{11}B chemical shifts are referenced to external $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All ^1H chemical shifts were measured relative to internal residual protons from the lock solvents (99.9% CD_2Cl_2 or 99.5% C_6D_6) and are referenced to $(\text{CH}_3)_4\text{Si}$ (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 $\text{NH}_3\text{B}_3\text{H}_7$ (**1**) from $\text{Bu}_4\text{N}^+\text{B}_3\text{H}_8^-$

After a solution of $\text{Bu}_4\text{N}^+\text{B}_3\text{H}_8^-$ (1.0 g, 3.53 mmol) in dry glyme (10.0 mL) was cooled at $-70\text{ }^\circ\text{C}$ 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 $(\text{glyme})\text{B}_3\text{H}_7$. The solution was again cooled at $-70\text{ }^\circ\text{C}$ 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_2Cl_2 as an eluent gave a white crystalline powder, $\text{NH}_3\text{B}_3\text{H}_7$ (0.16 g, 2.83 mmol) in 80% yield. The melting point and spectroscopic data match the literature values for $\text{NH}_3\text{B}_3\text{H}_7$.⁷⁸ $\text{Mp} = \sim 73\text{ }^\circ\text{C}$. ^1H NMR (400.13 MHz, CD_2Cl_2) 3.58 (t, 3, NH_3), 1.62 (br, 7, B_3H_7). ^1H NMR (500.14 MHz, C_6D_6) 2.00 (br, 7, B_3H_7), 1.01 (t, 3, NH_3). ^{11}B NMR (128.4 MHz, CD_2Cl_2) -7.7 (br, s, 2, B_2 and B_3), -32.8 (br, s, 1, B_1). 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 $50\text{ }^\circ\text{C}$ 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 $\text{NH}_3\text{B}_3\text{H}_7$ 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 $\text{NH}_3\text{B}_3\text{H}_7$ 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 $30\text{ }^\circ\text{C}$ and $50\text{ }^\circ\text{C}$, 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_3BH_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_2PO_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_3BH_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 $[\text{Rh}(\text{COD})(\mu\text{-Cl})]_2$ (22.7 and 7.9 mol%) in the absence of buffer solutions

The $[\text{Rh}(\text{COD})(\mu\text{-Cl})]_2$ (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 $[\text{Rh}(\text{COD})(\mu\text{-Cl})]_2$ (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_2O_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 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, and then adjusting the pH of the solution to 7.2. The 5-wt% Rh/ Al_2O_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-wts)] 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 LB₃H₇ (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.

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 B₃H₇-dimer, B₆H₁₄. 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**).

As shown in **Figure 6.1**, upon treatment with iodine at low temperature, the $B_3H_8^-$ anion was oxidized to give a new compound that exhibited broad ^{11}B 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) B_3H_7 , -3.6 ($B_{2,3}$) and -11.1 (B_1) ppm. Treatment of the glyme solution with anhydrous ammonia at -70 °C then afforded **1**. Any unreacted $B_3H_8^-$ 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 $^{11}B\{^1H\}$ NMR spectra for the reaction progression leading to the formation of **1**: (a) $B_3H_8^-$; (b) (glyme) B_3H_7 formed after I_2 oxidation of $B_3H_8^-$ in glyme; (c) **1** formed following ammonia displacement of the coordinated glyme (before purification), and (d) **1** after silica gel filtration.

6.3.2 Hydrolytic Hydrogen Release

As described earlier by **Equation 6.1**, oxidative hydrolysis of **1** could release 8 equivalents of H_2 making such a process potentially competitive with either $NaBH_4$ or NH_3BH_3 based hydrolytic H_2 -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 $NaBH_4$, which is stable only in strongly alkaline solutions,^{80,81} $NH_3B_3H_7$ was reasonably stable in neutral aqueous solutions, as evidenced by the ^{11}B 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 ^{11}B 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 (● $\text{NH}_3\text{B}_3\text{H}_7$; ▼ NH_3BH_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_3BH_3 has previously been demonstrated^{165,82-94} 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.

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^{28,73} 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**).

Hydrogen release from NaBH₄ and NH₃BH₃ has previously been attained by metal-catalyzed hydrolysis, with Ru-catalysts^{80,81} for NaBH₄ and Pt-catalysts⁸² 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)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.^{95,96} 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).⁹⁷

Figure 6.4 Metal-catalyzed hydrolytic H_2 -release from aqueous (0.45-wt%) solution of **1** containing (■) RhCl_3 (6.9 mol%); (●) 5-wt% $\text{Rh}/\text{Al}_2\text{O}_3$ (7.0 mol%-Rh); (▼) RuCl_3 (7.1 mol%) (inset); (▲) $[\text{Rh}(\text{COD})\mu\text{-Cl}]_2$ (7.1 mol%); (★) Ni_3B (35-41 mol%); (◆) 5-wt% Ru supported on ion exchange resins (6.3 mol%); (◄) 5-wt% $\text{Pd}/\text{Al}_2\text{O}_3$ (6.7 mol%); (►) Ru powder (22.6 mol%); (●)† 5-wt% Rh/C (5.3 mol%), NiCl_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% $\text{Ru}/\text{Al}_2\text{O}_3$ (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 $[\text{Rh}(\text{COD})\text{Cl}]_2$, and if more **1** was then added to this solution, then a decrease in the rate of H_2 -release was observed. On the other hand, if a borate buffer was used to maintain the solution pH, then the $\text{Rh}/\text{Al}_2\text{O}_3$ 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% $\text{Rh}/\text{Al}_2\text{O}_3$ showed little change in the hydrogen release rates over 11 cycles.

The " BO_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 ^{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 $\text{B}(\text{OH})_3/\text{B}(\text{OH})_4^-$, along with a weak signal at 12.4 ppm from $\text{B}_3\text{O}_3(\text{OH})_4^-$.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 $\text{B}_3\text{O}_3(\text{OH})_4^-$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$ were dominant.⁹⁸⁻¹⁰⁰ Thus, although the 5-wt% $\text{Rh}/\text{Al}_2\text{O}_3$ 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 NaBH₄^{80,97,101} and NH₃BH₃^{83,85} 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 catalyst^{97,102,103}).

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).^{104,105}

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)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 hydrolyses 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 H_2 -release were successfully digested in a number of strong acid systems to produce, according to ^{11}B 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 H_2 -release with superacidic $AlBr_3/HBr/CS_2$ solutions yielded BBr_3 which could be distilled out of the reaction mixtures; however, the digestion of more highly dehydrogenated spent fuels with ~ 2 equivalents of H_2 -release could not be attained. Boron-halide reduction studies demonstrated that complexes readily formed upon reaction of BBr_3 with dialkylsulfides and that these R_2S-BBr_3 adducts could be quantitatively reduced to R_2S-BH_3 with either tin hydrides or silanes. The dialkylsulfides were then easily displaced from R_2S-BH_3 by ammonia to yield ammonia borane.

7.1 Introduction

The efficient regeneration of ammonia borane from spent fuel BNH_x 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 H_2 -release, a variety of molecular, polymeric and/or solid-state materials with very different chemical reactivities are formed (**Figure 7.1**).

Figure 7.1 Possible spent-fuel products of ammonia borane H_2 -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.⁸

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), BBr_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_2Cl_2 were purchased from Fisher and dried as described elsewhere.¹⁰⁶ Polyborazylene was synthesized via the controlled thermal polymerization of borazine.^{39,40}

7.2.2 Physical Methods

^{11}B NMR at 128.3 MHz and 1H 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 $BF_3 \cdot OEt_2$ (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 $(CH_3)_4Si$ (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 7.1 Summary of Oxyacid Spent-Fuel Digestion Reactions and Product ¹¹B NMR Shifts

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

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 $(\text{B}_3\text{N}_3\text{H}_9\text{Cl}_3)_x$ 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 Supercritical HCl in Ionic Liquids

An acidic $\text{AlCl}_3/\text{BmimCl}$ 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 $\text{AlCl}_3/\text{BmimCl}$ 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-species were found in the cold traps. The ^{11}B NMR analyses of the $\text{AlCl}_3/\text{BmimCl}$ solutions diluted with CH_2Cl_2 showed new peaks at: (a) δ -31.2 (s), 0.2 (s), 0.0 (s). (b) δ 1.3 (s), 0.2 (s), -0.8 (s), -1.3 (s). Attempts to separate the products from the $\text{AlCl}_3/\text{BmimCl}$ solutions by distillation and/or extraction were unsuccessful.

7.2.5.2.3 Digestion Reactions with Supercritical $\text{AlBr}_3/\text{HBr}/\text{CS}_2$ 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 adduct¹⁰⁹ was concentrated in vacuo, yielding 228 mg (0.65 mmol, a 40% yield based on a NH_2BH_2 formula for SF1) and was identified by its characteristic ^{11}B NMR spectrum (128.3 MHz, CDCl_3): δ -6.1 (s). The yellow oil that had separated from the CS_2 layer was analyzed by ^{11}B NMR (128.3 MHz, neat): δ -9.4 (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 Supercritical $\text{AlCl}_3/\text{HCl}/\text{CS}_2$

(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-diethylmethylaniline borane.¹¹⁰ The mixture was fractionated on a high-vacuum line through consecutive 0 °C, -40 °C, and -198 °C traps. Toluene and the new $\text{Et}_2\text{MeNBH}_3$ adduct were retained at -40 °C, but attempts to quantitatively separate these were unsuccessful. ^{11}B NMR (128.3 MHz, CDCl_3): δ -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_2Cl_2 solution of the white solid indicated the formation of the TEA- BCl_3 adduct.¹¹⁰ ^{11}B NMR analysis indicated that the reaction of the solids in a stirred CH_2Cl_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 .¹¹⁰ Attempts to separate the adduct from the tributyltin chloride and residual TBTH were unsuccessful. For TEA- BCl_3 : ^{11}B NMR: δ 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_2Cl_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 .¹¹⁰ For TEA- BBr_3 : ^{11}B NMR: δ -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 .¹¹⁰

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_2Cl_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 .¹¹¹ Ammonia was then bubbled through 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}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 ^1H 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_2Cl_2 with equimolar amounts of a number of dialkylsulfides, including dimethyl, diethyl, dibutyl, dihexyl, diisopropyl and diisobutyl-sulfides and tetrahydrothiophene, resulted in the clean formation of their corresponding sulfide- BBr_3 adducts. The adducts all showed a single ^{11}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}B NMR resonance near -21 ppm. Complete reductions of the $(n\text{-alkyl})_2\text{S-BBr}_3$ adducts with TES at 55°C took 12-15 h, while the TES reductions of the $\text{R}_2\text{S-BBr}_3$ (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_2Cl_2 (~ 8 mL) were vacuum transferred into a 100 mL round-bottom flask equipped with a sidearm, stopcock and stirbar. This 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}B NMR analysis showed complete reduction of the BBr_3 to form the $\text{Hex}_2\text{S-BH}_3$ adduct. The mixture was fractionated on a high-vacuum line through consecutive -25°C , -78°C and -196°C traps. The $\text{Hex}_2\text{S-BH}_3$ 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%) 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 $\text{Et}_2\text{S-BH}_3$ 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%).

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_3BH_3 .

First Step: Acid Digestion of Spent Fuels

Second Step: One-Pot Conversion of BX_3 to AB

Coordination of BX_3

BX Reduction

Base Displacement by NH_3 to Yield AB

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_4X 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

When either SF1 or SF2 was stirred at 65 °C in an $\text{AlCl}_3/\text{bmimCl}$ 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 $(\text{H}_2\text{NBCl}_2)_3$ (3.7 ppm¹¹²), NH_3BCl_3 (3.28¹¹³) and $(\text{HNBCl})_3$ (30.3 ppm¹¹⁴). 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 $\text{HBr}/\text{AlBr}_3/\text{CS}_2$ 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 $\text{Et}_3\text{N}-\text{BBr}_3$ complex to allow a gravimetric determination. The observed formation of 228 mg of the $\text{Et}_3\text{N}-\text{BBr}_3$ adduct corresponded to the conversion of $\sim 40\%$ 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, $(\text{H}_2\text{NBBR}_2)_3$.¹¹⁵ 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 .

Figure 7.6 ^{11}B NMR analysis of the digestion of spent-fuel SF1 with superacidic $\text{HBr}/\text{AlBr}_3/\text{CS}_2$.

When SF2 was reacted with the $\text{HBr}/\text{AlBr}_3/\text{CS}_2$ mixture, only traces of BBr_3 were found in the CS_2 layer. Thus, the superacidic $\text{HBr}/\text{AlBr}_3/\text{CS}_2$ system was not useful for digesting more dehydrogenated spent-fuels.

While this project was in progress, an encouraging report by Mertens et al appeared¹¹⁶ claiming that AB spent-fuel digestion was achieved by superacidic $\text{HCl}/\text{AlCl}_3/\text{toluene}$ to produce BCl_3 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 BCl_3 formation observed in the reactions of superacidic HCl/AlCl_3 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 (**Figure 7.7**). Both the shift and multiplicity of this resonance are consistent with the formation of the $\text{Me}_2\text{EtN}-\text{BH}_3$ adduct (e.g. $\text{Me}_3\text{N}-\text{BH}_3$, -9 ppm; $\text{Et}_3\text{N}-\text{BH}_3$, -13 ppm).¹⁰⁸ The TFA-digestate was not reduced when treated with either silicon or tin hydrides.

The $\text{Me}_2\text{EtN}-\text{BH}_3$ 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.

Figure 7.7 ^{11}B NMR analysis of the reduction of the TFA-digestate with dimethylethylamine-alane.

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 $\text{AlBr}_3/\text{HBr}/\text{CS}_2$ 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,^{117,118,119} but the direct reduction of BX_3 liberates the pyrophoric gas diborane (B_2H_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_3SnH or Et_3SiH produced the BH_3 -coordinated diethylaniline. Displacement of the diethylaniline from this adduct by ammonia to produce NH_3BH_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_3SiH , it was not possible to completely separate the aniline borane from Et_3SiBr . 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 $\text{R}_2\text{S-BX}_3$ complex, followed by silane or stannane reduction to $\text{R}_2\text{S-BH}_3$ and then finally R_2S displacement with ammonia to generate ammonia borane.

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 $\text{RS}_2\text{-BBr}_3$ 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 $\text{R}_2\text{S-BH}_3$ complexes.¹¹⁴ Reactions with $\text{R} = n\text{-alkyl}$ (dimethyl, dibutyl, etc.) required >12 h and 55 °C for complete reduction, but the diisopropyl-derivative was complete in only 3-4 h. Because of its low-volatility, which enabled efficient isolation of the $(\text{C}_6\text{H}_{13})_2\text{S-BH}_3$ adduct, the dihexylsulfide was employed in the optimized process illustrated in **Figure 7.10**. Thus, following the initial formation of $(\text{C}_6\text{H}_{13})_2\text{S-BBr}_3$, the addition of excess (3.85 equivalents) of Et_3SiH gave complete conversion to $(\text{C}_6\text{H}_{13})_2\text{S-BH}_3$. The Et_3SiBr 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 $(\text{C}_6\text{H}_{13})_2\text{S-BH}_3$ adduct remained in the reaction flask.

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

Quantitative displacement by ammonia of the dihexylsulfide from $(\text{C}_6\text{H}_{13})_2\text{S-BH}_3$ 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 $(\text{C}_6\text{H}_{13})_2\text{S}$ /ammonia-borane mixture. Instead, pure ammonia borane in 96% isolated yield was obtained by hexanes extraction of $(\text{C}_6\text{H}_{13})_2\text{S}$ 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 $(\text{C}_2\text{H}_5)_2\text{S}$ base was employed in the optimized reaction shown in **figure 7.10** so that the $(\text{C}_2\text{H}_5)_2\text{S-BH}_3$ 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 (C₂H₅)₂S-BBr₃.

Displacement of the diethylsulfide from the (C₂H₅)₂S-BH₃ 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

1. M. E. Bluhm, M. G. Bradley, R. Butterick III, U. Kusari, and L. G. Sneddon "Amineborane Based Chemical Hydrogen Storage: Enhanced Ammonia Borane Dehydrogenation in Ionic Liquids" *J. Am. Chem. Soc.* **2006**, *128*, 7748-7749.
2. M. E. Bluhm, M. G. Bradley and L. G. Sneddon "Promoted Hydrogen Release from Amineborane" *Prepr. Sym., ACS Div. Fuel Chem.* **2006**, *51*, 571-572.
3. C. W. Yoon and L. G. Sneddon "Ammonia Triborane: A Promising New Candidate for Amineborane-Based Chemical Hydrogen Storage" *J. Am. Chem. Soc.* **2006**, *128*, 13992-2.
4. L. R. Alden, C. P. Griffin and L. G. Sneddon "Metal-Catalyzed Hydrogen Release from Ammonia Borane in Ionic Liquids" *Prepr. Sym., ACS Div. Fuel Chem.* **2008**, *53*, 670-671.
5. D. W. Himmelberger, M. E. Bluhm and L. G. Sneddon "Proton Sponge Induced Release from Ammonia Borane in Ionic Liquids" *Prepr. Sym., ACS Div. Fuel Chem.* **2008**, *53*, 666-667.
6. C. W. Yoon, P. J. Carroll and L. G. Sneddon "Ammonia Triborane: A New Synthesis, Structural Determinations and Hydrolytic Hydrogen-Release Properties" *J. Am. Chem. Soc.* **2009**, *131*, 855-864.
7. D. W. Himmelberger, C. W. Yoon, M. E. Bluhm, P. J. Carroll and L. G. Sneddon "Base Promoted Ammonia Borane Hydrogen Release" *J. Am. Chem. Soc.* **2009**, *131*, 14101-14110.
8. D. W. Himmelberger, L. R. Alden, M. E. Bluhm, P. J. Carroll and L. G. Sneddon "Ammonia Borane Hydrogen Release in Ionic Liquids" *Inorg. Chem.* **2009**, *48*, 9883-9889.
9. E. Berkeley, L. Alden and Larry G. Sneddon "Metal Catalyzed Ammonia Borane Dehydrogenations in Ionic Liquids" manuscript in preparation.

Presentations

1. L. G. Sneddon "Amineborane Based Chemical Hydrogen Storage" Tech Team Meeting, Houston, Texas, February 2006.
2. M. G. Bradley, M. E. Bluhm and L. G. Sneddon "Amineborane-Based Chemical Hydrogen Storage" Boron Americas Meeting, San Juan, Puerto Rico, August 2006.
3. C. W. Yoon and L. G. Sneddon "Ammonia Triborane: A Promising Candidate for Amineborane-Based Chemical Hydrogen Storage" Boron Americas Meeting, San Juan, Puerto Rico, August 2006.
4. M. E. Bluhm, M. G. Bradley, R. E. Butterick, U. Kusari and L. G. Sneddon "Enhanced Ammonia Borane Dehydrogenation in Ionic Liquids" National American Chemical Society Meeting, San Francisco, September 2006.
5. M. E. Bluhm, M. G. Bradley and L. G. Sneddon "Promoted Hydrogen Release from Ammonia Borane" poster at the National American Chemical Society Meeting, San Francisco, September 2006.
6. C. W. Yoon and L. G. Sneddon "Ammonia Triborane: A Promising Candidate for Amineborane-Based Chemical Hydrogen Storage" poster at the National American Chemical Society Meeting, San Francisco, September 2006.

7. M. G. Bradley, M. E. Bluhm and L. G. Sneddon "Chemical Hydrogen Storage: Hydrogen Release for Ammonia Borane in Ionic Liquids" poster (first place poster award) at Green Solvents for Processes Conference, Friedrichshafen, Germany, October 2006.
8. M. E. Bluhm, C. W. Yoon, D. Himmelberger, L. R. Alden, M. G. Bradley and L. G. Sneddon "Amineborane Chemical Hydrogen Storage" invited lecture at The Chinese University of Hong Kong, Hong Kong, November 2006.
9. M. E. Bluhm, C. W. Yoon, D. Himmelberger, L. R. Alden, M. G. Bradley and L. G. Sneddon "Amineborane Chemical Hydrogen Storage" invited lecture at the Korea Advanced Institute of Science and Technology, Daejeon, Korea, November 2006.
10. M. E. Bluhm, C. W. Yoon, D. Himmelberger, L. R. Alden, M. G. Bradley and L. G. Sneddon "Amineborane Chemical Hydrogen Storage" invited lecture at Sogang University, Seoul, Korea, November 2006.
11. L. G. Sneddon, M. E. Bluhm and M. G. Bradley "Amineborane Chemical Hydrogen Storage" invited lecture at the symposium on Hydrogen Storage at the Materials Research Meeting, Boston, November 2006.
12. L. G. Sneddon "Amineborane Based Chemical Hydrogen Storage" DOE Tech Team Meeting, Pasco, Washington, March 2007.
13. L. G. Sneddon, M. E. Bluhm, L. Alden, D. Himmelberger and M. G. Bradley "Amineborane Based Chemical Hydrogen Storage" invited lecture in the Sheldon Shore Award Symposium at the National American Chemical Society Meeting, Chicago, March 2007.
14. L. G. Sneddon "Amineborane Based Chemical Hydrogen Storage" invited lecture at the University of Toronto, May 2007.
15. L. G. Sneddon, M. E. Bluhm, L. Alden, D. Himmelberger and M. G. Bradley "Amineborane Based Chemical Hydrogen Storage" invited lecture at the Symposium on Hydrogen Storage at the Materials Science and Technology Conference, Detroit, September 2007.
16. L. G. Sneddon "Amineborane Based Chemical Hydrogen Storage" DOE Tech Team Meeting, Detroit, Michigan, January 2008.
17. L. R. Alden, M. E. Bluhm, C. P. Griffin, L. G. Sneddon "Improved Hydrogen Release from Ammonia Borane in Ionic Liquids" Materials Research Meeting, San Francisco, March 2008.
18. B. Ewing and L. G. Sneddon "Progress Towards Ammonia Borane Regeneration" Materials Research Meeting, San Francisco, March 2008.
19. Laif Alden, C. P. Griffin, and L. G. Sneddon "Metal Catalyzed Hydrogen Release from Ammonia Borane in Ionic Liquids " National American Chemical Society Meeting, Philadelphia, August 2008.
20. D. Himmelberger, M. Bluhm and L. G. Sneddon "Proton Sponge Induced Hydrogen Release in Ionic Liquids" National American Chemical Society Meeting, Philadelphia, August 2008.
21. L. G. Sneddon "Amineborane Based Chemical hydrogen Storage" invited lecture at the International Meeting on Boron Chemistry Barcelona, Spain, September 2008.
22. L. G. Sneddon "Amineborane Based Chemical Hydrogen Storage" DOE Tech Team Meeting, Detroit, Michigan, March 2009.
23. E. Berkeley, L. Alden, P. Carroll and L. G. Sneddon "Ammonia borane dehydrogenation using metal catalysts in ionic liquids" poster at the National American Chemical Society Meeting, Washington D.C., August 2009.

24. D. Himmelberger, L. Alden, M. Bluhm and L. G. Sneddon "Activated hydrogen release from ammonia borane in ionic liquids" National American Chemical Society Meeting, Washington D.C., August 2009.
25. D. Himmelberger, M. E. Bluhm, L. R. Alden, C. W. Yoon, B. Ewing, E. Berkeley, M. G. Bradley and L. G. Sneddon "Amineborane Chemical Hydrogen Storage" invited lecture at Indiana University, November 2009.
26. D. Himmelberger, M. E. Bluhm, L. R. Alden, C. W. Yoon, B. Ewing, E. Berkeley, M. G. Bradley and L. G. Sneddon "Amineborane Chemical Hydrogen Storage" Riley O. Schaeffer Lecturer at the University of New Mexico, November 2009.
27. E. Berkeley, D. Himmelberger, M. E. Bluhm, L. R. Alden, and L. G. Sneddon "Amineborane Chemical Hydrogen Storage" Boron Americas Meeting, East Lansing, MI, June 2010.

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