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Ammonia Borane Hydrogen Release in Ionic Liquids

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The rate and extent of H_2-release from ammonia borane (AB), a promising, high-capacity hydrogen storage material, was found to be enhanced in ionic-liquid solutions. For example, AB reactions in 1-butyl-3-methylimidazolium chloride (bmimCl) (50:50-wt %) exhibited no induction period and released 1.0 H_2-equiv in 67 min and 2.2 H_2-equiv in 330 min at 85 °C, whereas comparable solid-state AB reactions at 85 °C had a 180 min induction period and required 360 min to release ~0.8 H_2-equiv, with the release of only another ~0.1 H_2-equiv at longer times. Significant rate enhancements for the ionic-liquid mixtures were obtained with only moderate increases in temperature, with, for example, a 50:50-wt % AB/bmimCl mixture releasing 1.0 H_2-equiv in 5 min and 2.2 H_2-equiv in only 20 min at 110 °C. Increasing the AB/bmimCl ratio to 80:20 still gave enhanced H_2-release rates compared to the solid-state, and produced a system that achieved 11.4 materials-weight percent H_2-release. Solid-state and solution ^{11}B NMR studies of AB H_2-release reactions in progress support a mechanistic pathway involving: (1) ionic-liquid promoted conversion of AB into its more reactive ionic diammoniate of diborane (DADB) form, (2) further intermolecular dehydrocoupling reactions between hydridic B—H hydrogens and protonic N—H hydrogens on DADB and/or AB to form neutral polyaminoborane polymers, and (3) polyaminoborane dehydrogenation to unsaturated cross-linked polyborazylene materials.

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.[1,2] Owing to its high hydrogen content, ammonia borane (AB) has been identified as one of the leading candidates for chemical hydrogen storage, potentially releasing 19.6 wt % H_2 according to eq 1.[3]

$$H_3NBH_3 \rightarrow BN + 3H_2 \qquad (1)$$

Partial dehydrogenation of ammonia borane can be thermally induced in the solid-state,[4,5] 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. We report here that ionic liquids provide advantageous media for ammonia borane dehydrogenation in which both the extent and rate of hydrogen release are significantly increased. We also present solid-state and in situ ^{11}B NMR studies of reactions in progress that provide insight into the intermediates and mechanistic steps involved in ionic-liquid promoted AB H_2-release.

Experimental Section

Materials. All manipulations were carried out using standard high-vacuum or inert-atmosphere techniques as described by Shriver.[6] 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.[7] The 1-butyl-3-methylimidazolium iodide (bmimI) was synthesized sonochemically from 1-iodobutane and 1-methyl-imidazole according to literature methods.[8] All ionic liquids, including 1-butyl-2,3-dimethylimidazolium chloride (bmmimCl) (EMD), 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF$_4$), 1-butyl-3-methylimidazolium chloride (bmimCl), 1-butyl-3-methylimidazolium triflate (bmimOTf), 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF$_6$), 1-ethyl-2,3-dimethylimidazolium ethylsulfate (emmimEtSO$_4$), 1-ethyl-2,3-dimethylimidazolium triflate (emmimOTf), 1,3-dimethylimidazolium

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methylsulfate (mmimMeSO_4), and 1-propyl-2,3-dimethylimidazolium triflide (pmmimTf_3C) (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.

Physical Measurements. The Toepler pump system used for hydrogen measurements was similar to that described by Shriver[6] and is illustrated in Supporting Information, Figure 1S. The released gases from the reaction vessel were first passed through a liquid nitrogen trap before continuing on to the Toepler pump (700 mL). The released H_2 was then pumped into a series of calibrated volumes with the final pressure of the collected H_2 gas measured (±0.5 mm) with the aid of a U-tube manometer. After the H_2 measurement was completed, the in-line liquid nitrogen trap was warmed to room temperature, and the amount of any volatiles that had been trapped was then also measured using the Toepler pump.

The automated gas buret was based on a design reported by Zheng et al.,[9] but employed all glass connections with a cold trap (−78 °C) inserted between the reaction flask and buret to allow trapping of any volatiles that might have been produced during the reaction.

While bmimCl is a liquid at 85 °C, it is a solid at room temperature; therefore, solid-state ^{11}B NMR analyses (at Pacific Northwest National Laboratories: 240 MHz machine spun at 10 kHz) were used to monitor the products of reactions carried out in bmimCl. All solid-state ^{11}B chemical shifts were measured relative to external $NaBH_4$ (−41 ppm) and then referenced to $BF_3 \cdot O(C_2H_5)_2$ (0.0 ppm). The solution ^{11}B NMR (128.4 MHz Bruker DMX-400) studies in the room temperature ionic-liquid bmimOTf were carried out by heating reaction mixtures composed of 50 mg of AB (1.6 mmol) or 50 mg of DADB (0.8 mmol) and 450 mg of ionic liquid at 85 °C in a sealed NMR tube, with the tube periodically removed from the heating bath to collect ^{11}B NMR spectra of the reaction mixture (recorded at 25 °C). All solid-state and solution ^{11}B NMR chemical shifts are referenced to external $BF_3 \cdot O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift.

Procedures for AB H_2-release reactions. For the experiments where the released H_2 was measured with the Toepler pump, the AB (250 mg, 8.1 mmol) was loaded under N_2 into ~100 mL single neck round-bottom flasks with the ionic liquid (250 mg) given in Supporting Information, Tables 1S-2S. The flasks were then evacuated, sealed, and placed in a hot oil bath preheated to the desired temperature. The flasks were opened at the indicated times, and the released H_2 was quantified using the Toepler pump system. Post reaction, the flasks were evacuated for 30 min through the cold trap to remove any volatile products from the reaction residue. The product residues and volatiles in the cold trap were extracted with dry glyme or pyridine and analyzed by ^{11}B NMR.

For reactions using the automated gas buret, 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 buret 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 s intervals depending on the speed of the reaction. The product residues were extracted with dry glyme or pyridine and analyzed by ^{11}B NMR.

Results and Discussion

Utilization of waste heat from a PEM fuel cell can provide for AB H_2-release reaction temperatures near 85 °C.[5] However, at 85 °C, H_2-release from solid-state AB has been shown to exhibit an induction period of up to 3 h. After hydrogen release begins, only the release of ~0.9 equiv of H_2 can be achieved, rather than the 3 equiv predicted by eq 1, even with prolonged heating at 85 °C.[4,5] As a result, a number of approaches are now being explored to induce efficient AB H_2-release, including, for example, activation by transition metal catalysts,[10−25] acid catalysts,[26] base catalysts,[27] and nano and meso-porous scaffolds.[28−30]

We have previously communicated[4] results showing that AB H_2-release is activated in ionic liquids. Ionic liquids are generally defined as salts that are relatively low viscosity liquids at temperatures below 100 °C.[31−34] 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. These salts have a number of unique properties that make them attractive substitutes for traditional organic solvents in hydrogen

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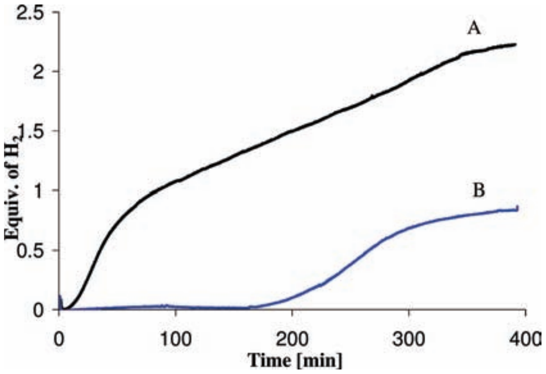

Figure 1. H_2-release measurements (gas buret) at 85 °C of: (A) 50-wt % AB (150 mg) in bmimCl (150 mg) and (B) solid-state AB (150 mg).

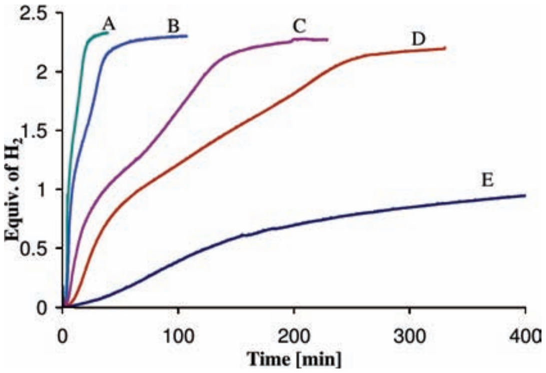

Figure 2. H_2-release measurements (gas buret) of 50-wt % AB (150 mg) in bmimCl (150 mg) at (A) 110 °C, (B) 105 °C, (C) 95 °C, (D) 85 °C, and (E) 75 °C.

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.

Our earlier reported[4] AB H_2-release measurements were periodic values obtained using a Toepler pump, but the new studies reported herein use an automated gas buret[9] that 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 buret, 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 1. For the solid-state AB reaction, there was negligible hydrogen production after 180 min, and only 0.81 equiv of H_2 after 360 min. Other samples heated for longer times (67 h) showed that a total of only 0.9 H_2-equiv 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 buret. 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.

The AB/bmimCl H_2-release plot in Figure 1 also clearly shows that release appears to occur in at least two steps with the release rate for the second H_2-equiv being significantly slower than for the first equivalent. Dramatic increases (Figure 2) in the rate of H_2-release of the 50:50-wt % AB/bmimCl mixture for both the 1st and 2nd H_2-equiv were observed as the temperature was increased with the release of 1.0 H_2-equiv in 37 min and 2.2 H_2-equiv in 161 min at 95 °C, 1.0 H_2-equiv in 9 min and 2.2 H_2-equiv in 45 min at 105 °C, and 1.0 H_2-equiv in 5 min and 2.2 H_2-equiv in 20 min at 110 °C . The 75 °C reaction did not reach 2 H_2-equiv.

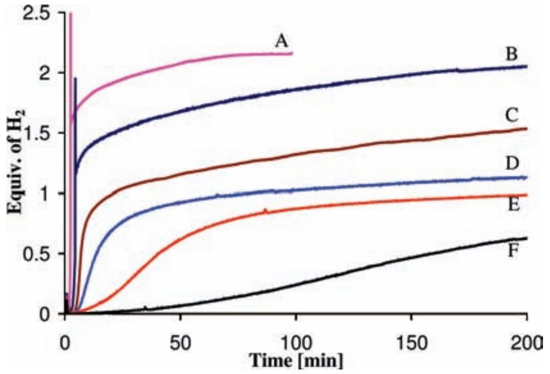

Figure 3. H_2-release measurements (gas buret) of AB (150 mg) in 20.2-wt % bmimCl (38 mg): (A) 120 °C, (B) 110 °C, (C) 105 °C, (D) 95 °C, (E) 85 °C, and (F) 75 °C (The early spike in the data is caused by the initial delay of the buret to respond to H_2-release).

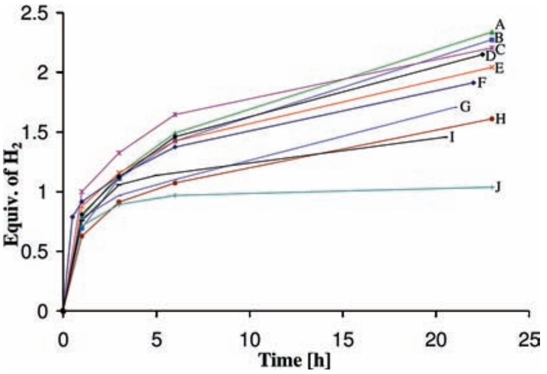

Figure 4. H_2-release measurements (Toepler pump) of the reaction of 50-wt % AB (250 mg) at 85 °C in 250 mg of (A) bmmimCl, (B) bmimCl, (C) emmimEtSO$_4$, (D) bmimBF$_4$, (E) mmimMeSO$_4$, (F) bmimOTf, (G) emmimOTf, (H) bmimI, (I) bmimPF$_6$, and (J) pmmimTf$_3$C.

The U.S. Department of Energy (DOE) has set a 2015 gravimetric total-system target for H_2-storage of 9.0 total-system-wt %.[35,36] The release of 2.2 H_2-equiv from a 50:50 AB/bmimCl mixture corresponds to a release of 7.2 mat-wt % H_2 [mat-wt % H_2 = H_2-wt/(AB+bmimCl-wts)]. 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, it was found that significantly enhanced H_2-release rates compared to the solid-state could still be obtained when employing as little as 20.2-wt % bmimCl. Thus, 2.0 H_2-equiv were released from 80:20 AB/bmimCl solutions in only 52 and 157 min at 120 and 110 °C, respectively, with both solutions then ultimately giving 2.2 H_2-equiv at longer times. The final release observed for these mixtures corresponds to an 11.4 mat-wt % H_2-release.

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(36) Dillich, S. *2009 DOE Hydrogen Program & Vehicle Technologies Program*; http://www.hydrogen.energy.gov/pdfs/review09/st_0_dillich.pdf. DOE has recently lowered the 2015 gravimetric total system target to only 5.5 total system weight %.

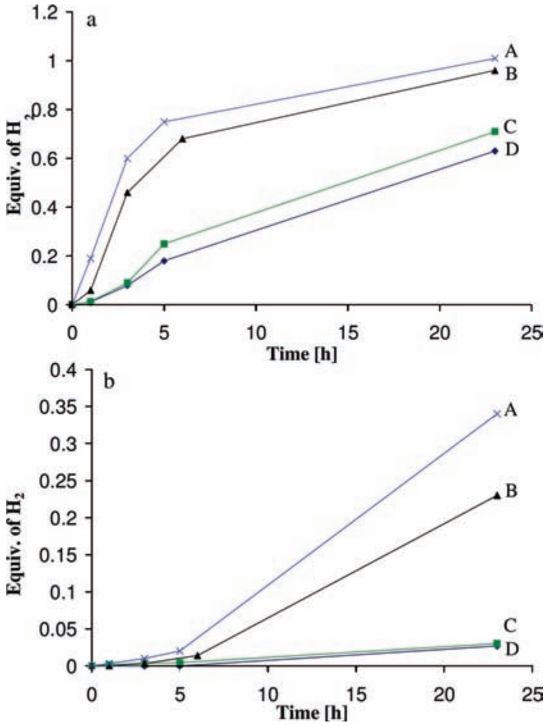

Figure 5. H_2-release measurements (Toepler pump) of the reaction of 50-wt % AB (250 mg) in 250 mg of (A) emmimEtSO$_4$, (B) mmimMeSO$_4$, (C) bmmimCl, and (D) bmimCl at (a) 65 °C and (b) 45 °C.

The 85 °C H_2-release data (Toepler pump measurements) in Supporting Information, Table 1S and Figure 4, show that AB H_2-release is activated in a variety of 50:50-wt % AB/ionic-liquid mixtures, but that these mixtures exhibit a range of H_2-release extents and rates. The biggest differences were observed for the release of the second equivalent. The bmimCl, bmmimCl, bmimBF$_4$, mmimMeSO$_4$, and emmimEtSO$_4$ mixtures all yielded over 2 H_2-equiv at reasonably comparable rates, while the other mixtures showed greatly decreased release rates beyond the first equivalent. For the pmmimTf$_3$C mixture, H_2-release stopped, as was observed for the AB solid-state reactions at 85 °C, after only ~0.9 H_2-equiv. As shown in Supporting Information, Table 2S and Figure 5, the H_2-release rates were significantly decreased upon lowering the temperature with the mmimMeSO$_4$ and emmimEtSO$_4$ mixtures being the most active. At 45 °C, bmimCl and bmmimCl showed little activity.

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. Once H_2-release began, the mixture foamed. As the H_2-release neared the loss of ~1 H_2-equiv, the foam began to convert to a white solid. The entire AB/bmimCl mixture ultimately became solid as the reaction reached over 2 H_2-equiv. Similar behavior was seen for the other 50:50-wt % AB/ionic-liquid mixtures, but with some differences in their liquid ranges. On the other hand, the 80:20-wt % AB/bmimCl mixtures formed a moist paste at room temperature. Upon initial heating, this paste melted, foam again formed, but then rapidly solidified after the onset of H_2-release. Solid formation was likewise observed in H_2-release reactions of 50:50-wt % AB/tetraglyme systems (discussed later) to produce a final two-phase liquid/solid mixture.

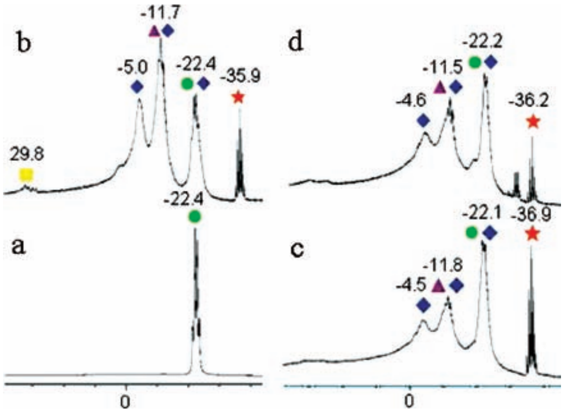

Figure 6. Solution ^{11}B NMR (128.4 MHz) spectra of the residues (extracted in pyridine) of the 85 °C reaction of (**Left**) solid-state AB (250 mg) after H_2-release of (a) 0.04 equiv and (b) 0.83 equiv (**Right**) 50-wt % AB (250 mg) in bmimCl (250 mg) after H_2-release of (c) 0.52 equiv and (d) 0.95 equiv AB (green circles), DADB (brown stars, BH_4^-, magenta triangles BH_2^+), PAB (blue diamonds) , B=N (yellow squares).

The ^{11}B NMR spectra of the pyridine soluble products produced at different stages in the AB solid-state and AB/bmimCl reactions are compared in Figure 6. Consistent with the observed absence of H_2-loss, the spectrum (Figure 6a) of the residue of the 1 h solid-state AB reaction showed only unreacted AB (quartet, −22.3 ppm[37]), whereas the spectrum (Figure 6c) of the 1 h AB/bmimCl mixture clearly showed mutiple resonances indicating a significant reaction that was consistent with its measured 0.52 equiv of H_2-release. As shown in Figures 6b and 6d, 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 H_2-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 H_2-loss, $[(NH_3)_2BH_2]^+BH_4^-$, (DADB) (−13.3 (overlapped) and −37.6 ppm)[7,37] and branched-chain polyaminoborane polymers (PAB) (−7, −13.3, and −25.1 ppm).[4] As dehydrogenation progressed past 1 equiv, only a small amount of material was pyridine soluble; therefore, solid-state NMR was also used to analyze these materials. 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 7) 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,[38−40] indicating that AB dehydrogenation ultimately produced B=N unsaturated products. NMR studies of the dehydrogenated products of AB H_2-release promoted by solid-state thermal reactions[5,41] have likewise shown the formation of B=N unsaturated final products after the release of more than 2 H_2-equiv.

In situ ^{11}B NMR studies (Figure 8) of AB H_2-release at 85 °C in a solution of the room temperature ionic liquid

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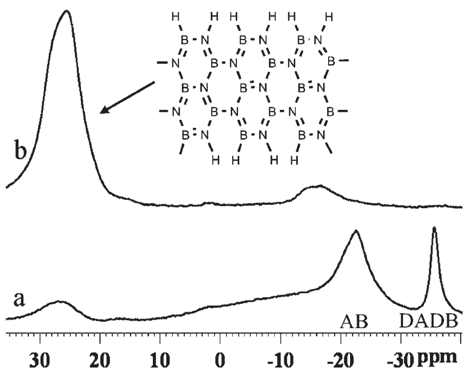

Figure 7. Solid-state ^{11}B NMR (240 MHz) spectra recorded at 25 °C of the reaction of 50-wt % AB (150 mg) in bmimCl (150 mg) at 110 °C after the release of: (a) 1 equiv and (b) 2 equiv.

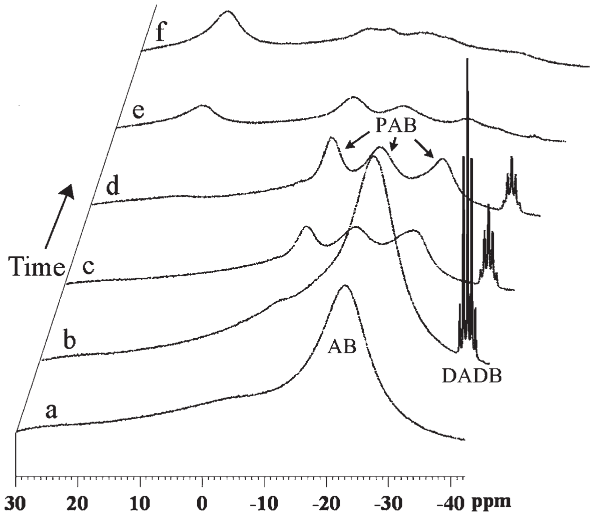

Figure 8. Solution ^{11}B NMR (128.4 MHz) spectra recorded at 25 °C of the reaction of 10-wt % AB (50 mg) in bmimOTf (450 mg) at 85 °C after the release of (a) 0.0 equiv (0 min), (b) 0.1 equiv (10 min), (c) 0.5 equiv (30 min), (d) 0.9 equiv (60 min), (e) 1.5 equiv (180 min), and (f) 2.0 equiv (360 min). (The broad DADB resonance at −13 ppm is obscured by the AB and PAB resonances).

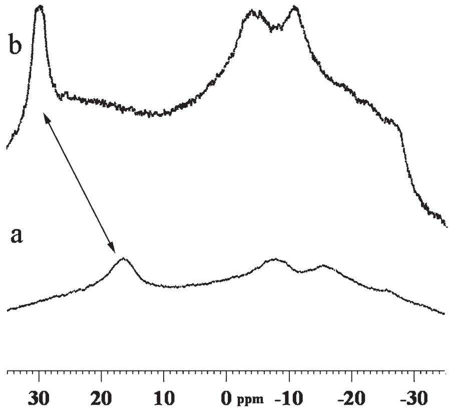

Figure 9. Solution ^{11}B NMR (128.4 MHz) spectra of the reaction of 10-wt % AB (50 mg) in bmimOTf (450 mg) at 85 °C for 6 h: (a) NMR probe at 27 °C and (b) NMR probe at 100 °C.

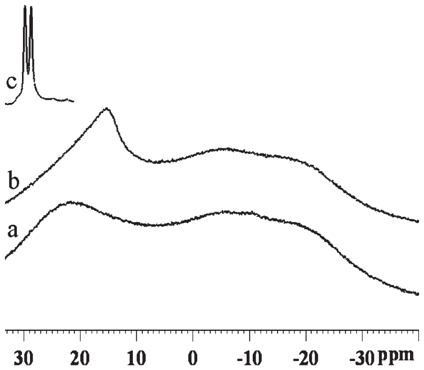

Figure 10. Solution ^{11}B NMR (128.4 MHz) spectra recorded at 25 °C of 10-wt % borazine (50 mg) in bmimI (450 mg) after (a) initial mixing at 25 °C, (b) 19 h at 85 °C, and (c) the toluene extraction after heating.

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 8c) 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 8d) 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 8e) 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 8f) 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 7), 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 H_2-release from AB/mmimMeSO$_4$ and AB/bmimI reactions, showed the growth of a 16 ppm resonance after the release of 2 H_2-equiv. The 16 ppm resonance in these ionic liquid reactions is thus shifted almost 14 ppm upfield relative to that normally found for polyborazylene[38−40] 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.

Given both their polar compositions and planar aromatic like structures and properties, a variety of reversible ionic-liquid interactions would be possible for borazine and polyborazylene, including the formation of ionic-liquid hydrogen-bonded and/or clathrated[43−48] species. Such interactions

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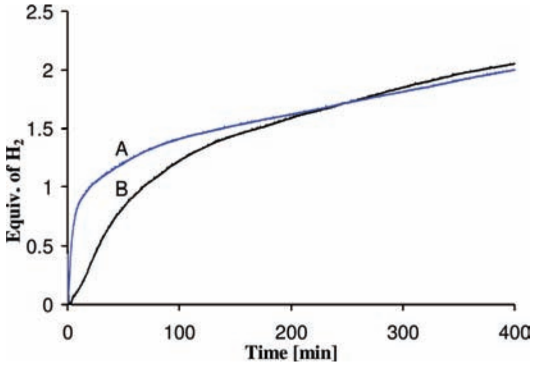

Figure 11. H_2-release measurements (gas buret) of bmimOTf (450 mg) and 10-wt % (50 mg) of (A) DADB and (B) AB.

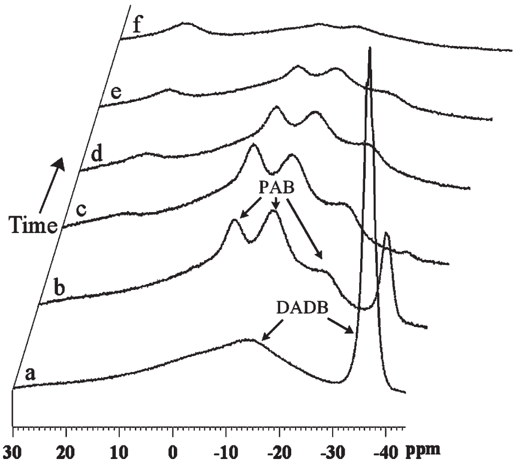

Figure 12. Solution ^{11}B NMR (128.4 MHz) spectra recorded at 25 °C of the reaction of 10-wt % DADB (50 mg) in bmimOTf (450 mg) at 85 °C after the release of (a) 0.0 equiv (0 min), (b) 0.9 equiv (10 min), (c) 1.1 equiv (30 min), (d) 1.3 equiv (60 min), (e) 1.6 equiv (180 min), and (f) 1.9 equiv (360 min).

would be expected to decrease as the temperature is increased and, as shown in the ^{11}B NMR spectra in Figure 9, 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 10a), but this resonance then shifted to 16 ppm after the solution was heated at 85 °C (Figure 10b). That this interaction was reversible was demonstrated by the fact that borazine could then be recovered from the bmimI solution by extraction with toluene (Figure 10c). These results are thus all consistent with a significant reversible interaction between borazine and the ionic liquids. Such interactions may play a key role in retarding the loss of borazine, a likely fuel cell catalyst poison, during AB H_2-release.

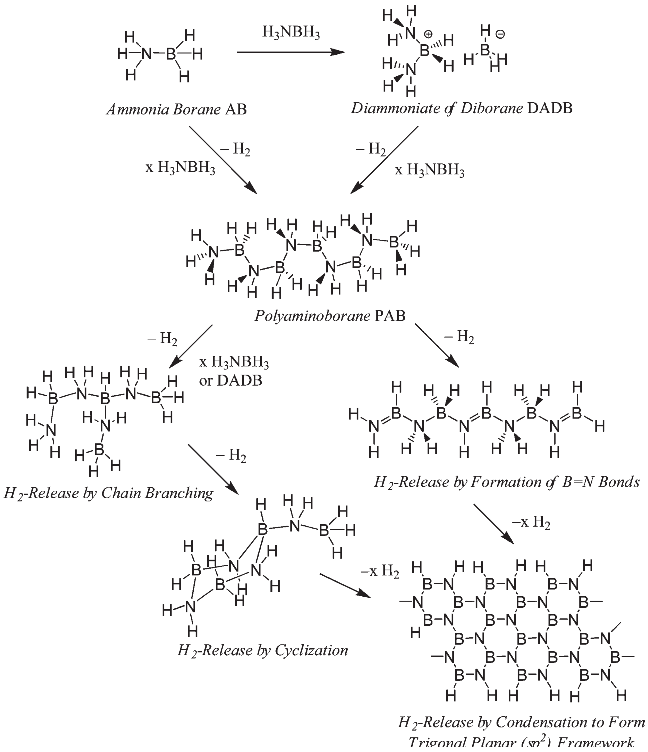

Figure 13. Possible pathway for ionic-liquid promoted H_2-release from AB.

The fact that DADB is a precursor to the formation of the polyaminoboranes, rather than just a side reaction, was demonstrated by H_2-release and ^{11}B NMR studies of DADB reactivity in ionic liquids. These studies showed that the 85 °C reaction of a pre-synthesized[7,37] pure sample of DADB dissolved in bmimOTf (10-wt % DADB) yielded the same type of polyaminoborane products, but with faster H_2-release rates, as those found in the AB/bmimOTf reactions.

$$0.5[(NH_3)_2BH_2^+][BH_4^-] \rightarrow BN+3H_2 \qquad (2)$$

The theoretical DADB H_2-release reaction in terms of AB equiv is given by eq 2. The H_2-release rates for separate 10-wt % DADB and AB samples in bmimOTf are compared in Figure 11, where the faster rate of the DADB reaction is clearly apparent. While AB/bmimOTf required 96 min to release 1.0 H_2-equiv and 274 min for 1.5 H_2-equiv, the DADB required only 28 min for 1.0 H_2-equiv and 94 min for 1.5 H_2-equiv. At 400 min, the DADB/bmimOTf reaction had already released 2.09 H_2-equiv, while the AB/bmimCl reaction was still at 1.76 H_2-equiv. These results are consistent with the observation that DADB H_2-release is also faster than that of AB in solid-state reactions.[41]

As can be seen in the NMR studies in Figure 12, the initial ^{11}B NMR spectrum obtained from a 10-wt % DADB/bmimOTF sample showed only the broad resonances expected for the DADB $(NH_3)_2BH_2^+$ (−13.3 ppm) and BH_4^- (−37.6 ppm) components. However, after heating for only 10 min at 85 °C, most of the DADB had been converted to PAB. At 30 min, 0.9 H_2-equiv had been released and the ^{11}B NMR spectrum at this point (Figure 12c) showed that the DADB had been completely consumed. As the reaction proceeded beyond the release of 1 H_2-equiv, a new resonance grew in that was also at the 16 ppm shift observed in the AB/bmimOTf reactions (Figure 12d−f).

The combined solid-state and solution ^{11}B NMR studies of AB/ionic-liquid and DADB/ionic-liquid H_2-release reactions

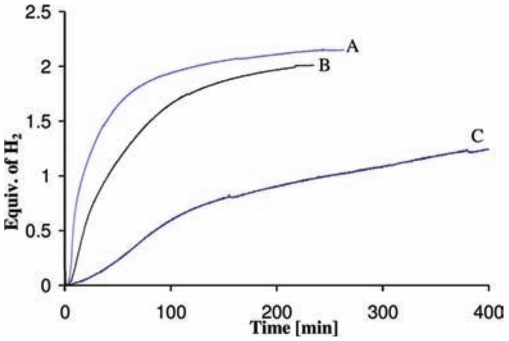

Figure 14. H_2-release measurements (gas buret) of 50-wt % AB (150 mg) in tetraglyme (150 mg) at (A) 95 °C, (B) 85 °C, and (C) 75 °C.

in progress support a AB dehydrogenation pathway in ionic liquids (Figure 13) involving the following: (1) ionic-liquid promoted conversion of AB into its more reactive ionic DADB form, (2) further intermolecular dehydrocoupling reactions between hydridic B−H hydrogens and protonic N−H hydrogens on DADB and/or AB to form polyaminoborane polymers, and (3) polyaminoborane dehydrogenation to unsaturated cross-linked polyborazylene materials. The initial formation of DADB has also been proposed as a key step in thermally induced AB H_2-release reactions in the solid state[41,49] 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.

The AB H_2-release observed in the ionic-liquid solvents was also compared with that obtained for the conventional polar organic solvent, tetraglyme. The H_2-release data for a 50:50 wt % ratio AB/tetraglyme mixture showed that both the extent and rate of H_2-release were comparable to that of the AB/bmimCl reactions (Figure 14). However, the ^{11}B NMR spectra of the AB/tetraglyme reactions showed that, unlike in the ionic liquids, there was little evidence of PAB formation, with the major product being instead borazine (30.1 ppm)[42] along with smaller amounts of BH_4^- (−36.8 ppm)[42] and μ-aminodiborane (−27.5 ppm)[42] (Figure 15). Thus, ionic-liquid solvents are favored for AB H_2-release since they suppress or retard the formation of these undesired products.

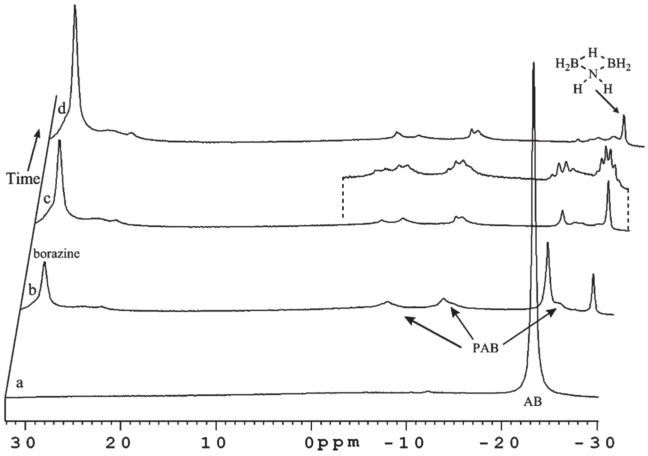

Figure 15. Solution $^{11}B\{^1H\}$ NMR (128 MHz) spectra recorded at 80 °C of the reaction of 10-wt % AB (50 mg) in tetraglyme (450 mg) at 85 °C after (a) 1.1 equiv (60 min), (b) 1.7 equiv (180 min), and (c) 1.9 equiv (360 min). Inset shows ^1H coupled spectra.

In conclusion, their low solvent volatility, 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 continue to make AB/ionic-liquid based systems attractive candidates for chemical hydrogen storage applications.

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Supporting Information Available: Diagram of the Toepler pump apparatus used for some H_2-release measurements; tables of Toepler pump H_2-release data for AB/ionic liquid reactions at different temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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