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Amineborane-Based Chemical Hydrogen Storage: Enhanced Ammonia Borane Dehydrogenation in Ionic Liquids

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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. Although many molecular hydride complexes have certain features that might be attractive for chemical hydrogen storage, the high hydrogen capacities needed for transportation applications exclude most compounds. Amineboranes, such as ammonia borane, NH_3BH_3 (19.6 wt % H_2), are thus unique in their potential ability to store and deliver large amounts of molecular hydrogen through dehydrogenation reactions.

Partial dehydrogenation of ammonia borane can be thermally induced in the solid state,[1−4] 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 will need a replacement for the volatile organic solvents that have traditionally been employed for solution-phase ammonia borane hydrides dehydrogenations.[1e,5] 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.

Ionic liquids are salts that are liquid at low temperatures (<100 °C). These salts have unique properties[6] that make them attractive substitutes for organic solvents in hydrogen storage systems, including (1) negligible vapor pressures, (2) stability to elevated temperatures, (3) ability to dissolve a wide range of compounds and gases, (4) weakly coordinating anions and cations that provide an inert reaction medium which can stabilize polar transition states, and (5) recycling with little loss of activity.

Comparisons of ammonia borane dehydrogenations in the solid state versus in 1-butyl-3-methylimidazolium chloride (bmimCl) solvent are summarized in Figure 1. Reactions in the solid state were conducted in sealed, evacuated glass vessels that were heated in a thermostatically controlled oven. The bmimCl/NH_3BH_3 reactions were carried out by adding equal weights of bmimCl (dried) and NH_3BH_3 together in evacuated 100 mL flasks equipped with a vacuum adapter and then immersing the body of the flasks into an oil bath at the desired temperature. At the reaction conclusion, the sealed vessels or flasks were opened to a vacuum line, and the evolved hydrogen passed through a liquid nitrogen trap in order to isolate any volatile non-hydrogen products, such as borazine. The hydrogen was then quantitatively measured in calibrated volumes using a Toepler pump.

As seen in Figure 1a, for the reactions carried out in the solid state at 85 °C, there was negligible hydrogen production after 3 h,[7] but after 17 h, 0.9 equiv of H_2 was produced. Even with prolonged heating (67 h) at this temperature, no further H_2 release was observed. Similar results were observed at 95 °C, but with a shorter initial induction period. Thus, while there was no H_2 evolution after 1 h, 0.8 equiv was obtained after 3 h. Again, as with the 85 °C sample, prolonged heating at 95 °C (48 h) yielded a total of only 0.9 equiv of H_2.

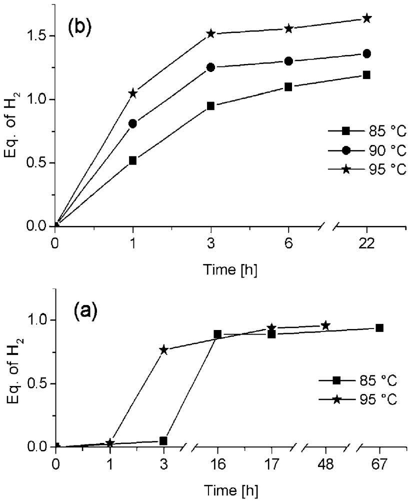

Figure 1. Summary of H_2 release at different temperatures (a) from solid ammonia borane and (b) from equal weight mixtures of bmimCl and ammonia borane.

In contrast to the solid-state reactions, ammonia borane dehydrogenations in bmimCl showed no induction period (Figure 1b) with hydrogen evolution beginning immediately upon placing the sample in the heated oil bath. Separate samples heated for only 1 h at 85, 90, and 95 °C evolved 0.5, 0.8, and 1.1 equiv of H_2, while samples heated at these temperatures for 3 h produced 0.95, 1.2, and 1.5 equiv. Heating for 22 h gave a total of 1.2, 1.4, and 1.6 equiv of H_2, respectively, which are values significantly greater than the 0.9 equiv ultimately obtained in the solid-state reactions. Including the bmimCl weight, the final values correspond to the evolution of 3.9, 4.5, and 5.4 wt % H_2.

The ^{11}B NMR spectra obtained from pyridine (dried) extracts of the residues of the 85 °C solid-state and bmimCl reactions are compared in Figure 2. Consistent with the observed absence of H_2 loss, the spectrum (Figure 2a) of the residue of the 1 h solid-state reaction showed only unreacted ammonia borane (−22.4 ppm[8]), whereas the 1 h bmimCl sample clearly showed significant reaction. The spectra of the residues of the 19 h solid-state and 3 h bmimCl reactions (Figure 2b and d) were quite similar, showing multiple resonances.

Depending on the conditions, several species have been previously observed[1−5,9] upon heating ammonia borane: borazine ($B_3N_3H_6$),[1d,e,2,5,9] cycloborazanes[1e,5] (e.g., $B_3N_3H_{12}$), and polyaminoborane[1−3] $(BH_2NH_2)_n$. Because they could poison a fuel cell, volatile products, such as borazine, are undesirable in hydrogen storage applications, and it is significant that in the bmimCl reactions only traces of borazine were detected. The diammoniate of diborane,[10]

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10.1021/ja062085v CCC: $33.50 © 2006 American Chemical Society

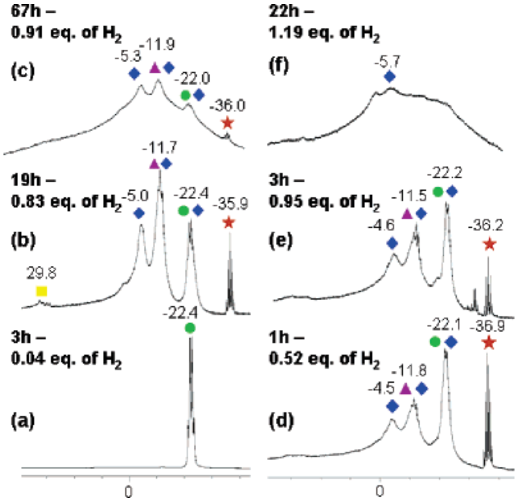

Figure 2. ^{11}B NMR spectra (128 MHz) of the residues (extracted in pyridine) of ammonia borane dehydrogenation: (left) in the solid-state and (right) in bmimCl. Green, ammonia borane; orange, BH_4^-; purple, BH_2^+; blue, polyaminoborane; yellow, B═N. (The signals near −11 ppm may also include a resonance from pyridine−BH_3; the broad humps underlying the weak spectra in c and f arise from the boron background of the NMR probe.)

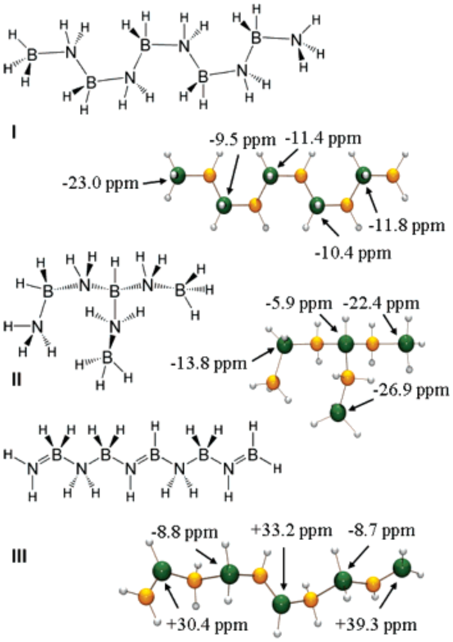

Figure 3. DFT/GIAO calculated ^{11}B NMR chemical shifts for possible structures arising from the dehydropolymerization of ammonia borane.

$[(NH_3)_2BH_2^+]BH_4^-$, has been reported[10d] to have resonances near −38 (BH_4^-) and −14 ppm (BH_2^+), and its presence is consistent with the spectra in b, d, and e of Figure 2. The results (Figure 3) of DFT/GIAO ^{11}B chemical shift calculations (Gaussian03, 6311-G* level) on structures that could result from ammonia borane dehydropolymerization are consistent with the previous assignments[1e] of resonances in the −10 to −13 ppm range to the BH_2 groups of both cycloborazanes and polyaminoborane and allow the assignment of resonances near −5 ppm to N−BH−N borons resulting from chain-branched polymeric structures and those near −25 ppm to polymer-terminating BH_3 groups (overlapping the resonance of the starting ammonia borane).

Dehydrogenation to polyaminoborane or cycloborazanes would release only 1 equiv of hydrogen, but further dehydrogenation should lead to B═N unsaturation. The weak downfield resonances in spectra b and e in Figure 2 agree with the calculated shift ranges (Figure 3, III) for borons in internal B═N or terminal B═NH_2 units, but are somewhat upfield of the value calculated for the terminal N═BH_2 group. In the extended time solid-state reactions, these resonances did not grow, and even after 67 h, appreciable soluble saturated polyaminoborane remained (Figure 2c). These resonances are also not apparent in spectrum 2f, but the more extensive dehydrogenation found at longer times in bmimCl, while resulting in the consumption of the polyaminoborane, produced unsaturated residues that could no longer be extracted (less than ∼20%) into pyridine.

The role of bmimCl in enhancing the rate and extent of ammonia borane dehydrogenation has yet to be proven, but it is significant that $[(NH_3)_2BH_2^+]BH_4^-$ has also been reported to form polyaminoborane upon heating.[11] Ionic liquids are known to favor the formation of polar intermediates and transition states,[6] and the observation that $[(NH_3)_2BH_2^+]BH_4^-$ and/or BH_4^- are produced in the bmimCl reaction within the first hour (Figure 2d) suggests that the activating effect of the ionic liquid may be related to its ability to induce formation of such ionic species. We are now exploring this effect in conjunction with the established ability of ionic liquids to stabilize nanoparticle dehydrogenation catalysts to develop more active chemical hydrogen storage systems.

Acknowledgment. We thank the U.S. Department of Energy Center of Excellence for Chemical Hydrogen Storage and the Division of Basic Energy Sciences for support.

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JA062085V