
Chemical Hydrogen Storage in Ionic Liquid Media

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Larry G. Sneddon (Penn), Tom Baker (Los Alamos) PIs,
Chang Yoon (student), Martin Bluhm, (postdoctoral) and Vincent Pons (postdoctoral)
Department of Chemistry, University of Pennsylvania, Philadelphia PA 19104-6323
Phone: 215-898-8632; Fax: 215-573-6743; email: lsneddon@sas.upenn.edu

Program Scope and Objectives

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. 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 are required. 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 reactions of molecular chemical hydrides. The goal of this project is to use the unique advantages of ionic liquid solvents⁵ to develop new ways of inducing amineborane dehydrogenations at lower temperatures and to elucidate the important controlling factors in these reactions.

Recent Progress

Our initial work has now shown that ionic liquids provide advantageous media for ammonia borane dehydrogenation in which both the extent and rate of dehydrogenation are significantly increased.

Comparisons of ammonia borane dehydrogenation reactions in the solid-state versus in 1-butyl-3-methyl-imidazolium chloride (bmimCl) solvent are summarized in Fig. 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 250 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 conclusion of each reaction, 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 evolved hydrogen was then quantitatively measured in calibrated volumes using a Toepler pump.

As seen in Fig. 1a, for the reactions carried out in the solid-state at 85°C, there was negligible hydrogen production after 3 h, but after 17 h, 0.9 equivalents of H_2 were 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 equivalents were 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 equivalents of H₂.

In contrast to the results of the solid-state reactions, when ammonia borane dehydrogenation was carried out in bmimCl, no induction period was observed (Fig. 1b). Thus, separate samples heated for only 1 h at 85°, 90° and 95°C evolved 0.5, 0.8 and 1.1 equivalents of H₂, while samples heated at the same temperatures for 3 h produced 0.95, 1.2 and 1.5 equivalents. Heating for 22 h gave a total of 1.2, 1.4 and 1.6 equivalents of H₂, respectively, which are values significantly greater than the 0.9 equivalents ultimately obtained in the solid-state reactions.

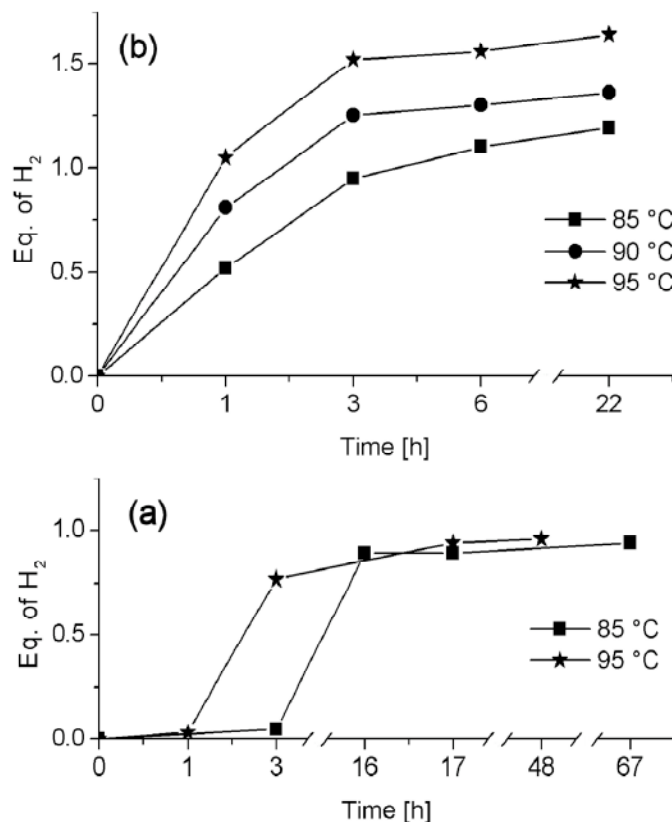


Figure 1. Summary of H₂ release at different temperatures from: (a) solid ammonia borane, and (b) from equal weight mixtures of bmimCl and ammonia borane.

The ¹¹B NMR spectra obtained from pyridine (dried) extracts of the residues of the 85 °C solid-state and IL reactions are compared in Fig. 2. Consistent with the observed absence of H₂ loss, the spectrum (Fig. 2a) of the residue of the 1 h solid-state reaction showed only unreacted ammonia borane (−22.4 ppm) 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 (Figs. 2b and 2d) were quite similar showing multiple resonances.

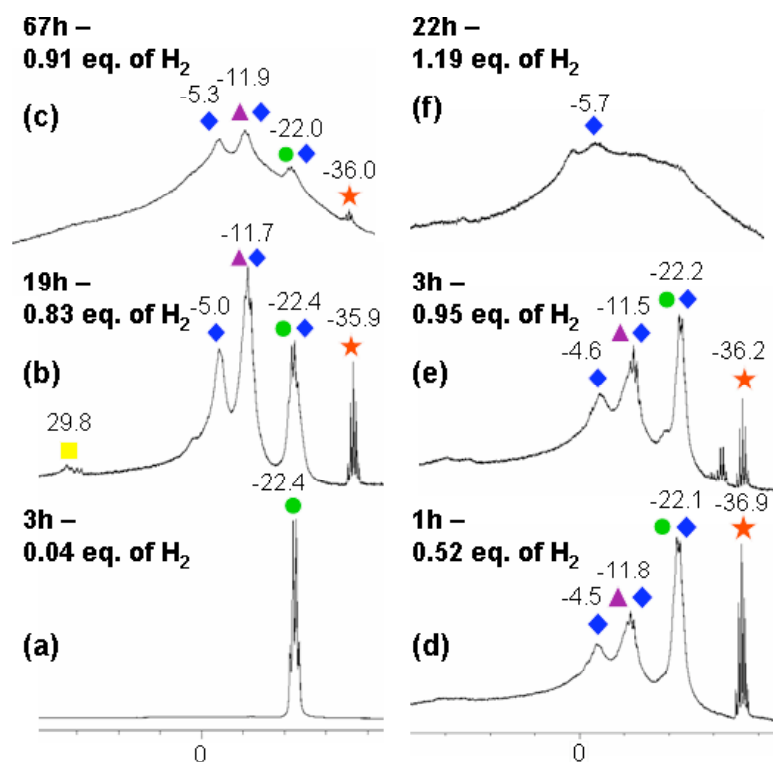


Figure 2. ^{11}B NMR spectra (128 MHz) of the residues (dissolved in pyridine) of ammonia borane dehydrogenation: (left) in the solid-state, and (right) in bmimCl. ● ammonia borane, ★ BH_4^- , ▲ BH_2^+ , ◆ polyaminoborane, ■ B=N. (The signals near -11 ppm may also include a resonance from pyridine- BH_3).

The role of bmimCl in enhancing both the rate and extent of ammonia borane dehydrogenation has yet to be proven, but it is significant that the “diammonate of diborane”⁶ $[(\text{NH}_3)_2\text{BH}_2^+]\text{BH}_4^-$ has also been reported⁷ to form polyaminoborane upon heating. Because of their ionic compositions, ionic liquids are known⁵ to favor the formation of polar intermediates and transition-states and the observation that there is substantial $[(\text{NH}_3)_2\text{BH}_2^+]\text{BH}_4^-$ produced in the ionic liquid reaction within the first hour suggests that the activating effect of the ionic liquid may be related to its ability to induce the formation of $[(\text{NH}_3)_2\text{BH}_2^+]\text{BH}_4^-$.

Future Plans

We are now further exploring the activating effect of ionic liquids in conjunction with their established ability to stabilize nanoparticle dehydrogenation catalysts to develop new more active chemical hydrogen storage systems.

Preliminary results at Los Alamos have now shown that base metal complexes containing N-heterocyclic carbene (NHC) ligands are uniquely stable under the reducing conditions required for catalyzed dehydrogenation of amine-boranes and related B-N compounds. As heterogeneous catalysts present advantages for this application, we will attempt to prepare metal nanoparticles that are capped with NHC ligands and test these

nanoparticles as amine-borane dehydrogenation catalysts. We will assay a variety of ionic liquids as novel media for both synthesis of the nanoparticles and as solvents for the dehydrogenation reactions. Mechanistic details of promising systems will be probed using substrate isotopic labeling coupled with vibrational spectroscopies and high-field multinuclear NMR in the solid state and solution.

Recent DOE Sponsored Publications (September 1, 2005-present)

M. 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" submitted.

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