Ammonia Triborane: A Promising New Candidate for Amineborane-Based Chemical Hydrogen Storage

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Because of their high hydrogen densities, boron based compounds, including especially sodium borohydride (NaBH_4)¹ and ammonia borane (NH_3BH_3),² are now being intensely investigated as chemical hydrogen storage materials that can release hydrogen by hydrolytic processes (eqs 1–2).

The high hydrogen release capacity that could potentially be achieved by ammonia triborane, $\text{NH}_3\text{B}_3\text{H}_7$, (**1**) oxidative-hydrolysis (eq 3) should likewise make it an attractive candidate for chemical hydrogen storage. But, owing to the lack of a suitable method for its efficient synthesis, there have been no previous explorations of the chemical hydrogen storage properties of this compound. We

report here both a convenient and safe method for the synthesis of ammonia triborane and our initial studies of its hydrolytic hydrogen-release properties that indicate it is a promising new material for chemical hydrogen storage applications.

Ammonia triborane was first synthesized by Kodama³ via the cleavage reaction of tetraborane, B_4H_{10} , with ethers to initially form LB_3H_7 (L = tetrahydrofuran or tetrahydropyran) adducts (plus B_2H_6) that, following displacement of the ethers by reaction with anhydrous ammonia, then produced $\text{NH}_3\text{B}_3\text{H}_7$. Unfortunately, tetraborane is a volatile unstable compound that is explosive in air, and, as a result, any large-scale synthesis based on its use is not feasible.

Binder⁴ previously reported that I_2 oxidation of $\text{Me}_4\text{N}^+\text{B}_3\text{H}_8^-$ in noncoordinating solvents (e.g., CH_2Cl_2) yielded the B_3H_7 -dimer, B_6H_{14} . We have now found that iodine oxidation (with slow warming from -70 to 20 °C) of the air stable $\text{Bu}_4\text{N}^+\text{B}_3\text{H}_8^-$ salt in glyme (1,2-dimethoxyethane) (eq 4) allows the efficient preparation of solutions of the (glyme) B_3H_7 adduct. Direct treatment (eq 5) of these (glyme) B_3H_7 solutions with anhydrous ammonia then yields pure $\text{NH}_3\text{B}_3\text{H}_7$ as a colorless crystalline solid in $>80\%$ yields (based on $\text{Bu}_4\text{N}^+\text{B}_3\text{H}_8^-$). Since the $\text{Bu}_4\text{N}^+\text{B}_3\text{H}_8^-$ salt can itself be readily prepared⁵ by iodine oxidation of BH_4^- , the large-scale, safe synthesis of $\text{NH}_3\text{B}_3\text{H}_7$ is now possible.

Figure 1. Acid-induced hydrogen release from ammonia triborane.

Figure 2. Metal-catalyzed hydrogen release from aqueous (~ 0.45 wt %) ammonia triborane solutions containing (★) RhCl_3 (6.9 mol %); (■) 5 wt % $-\text{Rh}/\text{Al}_2\text{O}_3$ (7.0 mol % $-\text{Rh}$); (●) $[\text{Rh}(\text{COD})(\text{Cl})]_2$ (7.2 mol %); (▲) 5 wt % $-\text{Rh}/\text{Al}_2\text{O}_3$ (1.4 mol % $-\text{Rh}$); (◆) no catalyst.

1 is significantly more soluble in water than NH_3BH_3 (26 wt %^{2d}), with $\text{NH}_3\text{B}_3\text{H}_7$ solutions of at least 33 wt % being attained. Also, unlike aqueous NaBH_4 , which is stable only in strongly alkaline solutions,^{1b,c} aqueous $\text{NH}_3\text{B}_3\text{H}_7$ solutions are quite stable at pH 7.5 in air as evidenced by ^{11}B NMR studies that showed a 25 wt % solution remained unchanged over 4 days.

Efficient hydrogen release from aqueous solutions of **1** was obtained upon the addition of either acids or appropriate metal-catalysts. As shown in Figure 1, quantitative measurements of hydrogen release using a gas buret showed that when an excess of aqueous HCl (1 mL of 12.1 M HCl) was added to 12 mg (0.21 mmol) of **1**, a near theoretical value of 7.85 equiv (1.65 mmol) of H_2 was evolved over ~ 1 h.

More rapid hydrogen release was achieved using metals to catalyze the hydrolysis reaction. Hydrogen release from NaBH_4 and NH_3BH_3 has previously been attained by metal-catalyzed hydrolysis, with Ru-catalysts¹ for NaBH_4 and Pt-catalysts² for NH_3BH_3 exhibiting the highest reactivities. We have now screened a variety of potential catalysts for ammonia triborane hydrolysis and found high activities for the rhodium based systems, Rh(0) supported on alumina, $[\text{Rh}(\text{COD})(\mu\text{-Cl})]_2$ (COD = 1,5-cyclooctadiene), and RhCl_3 (Figure 2). With high catalyst loadings of RhCl_3 , ~ 7 equiv of hydrogen were released in only 1.5 min at room temperature. Although they are unchanged upon initially dissolving in water,

Figure 3. Hydrogen evolution following repeated additions of ammonia triborane to an aqueous solution containing 5 wt % -Rh/Al₂O₃.

Figure 4. Hydrogen release at different temperatures (▼, 50; ▲, 35; ●, 20; ■, 0 °C) versus time for 4.9 wt % aqueous solutions of ammonia triborane catalyzed by 5 wt % -Rh/Al₂O₃ (1.1 mol % -Rh).

both the [Rh(COD)(μ-Cl)]₂ and RhCl₃ appear to undergo reduction upon ammonia triborane addition suggesting that Rh clusters and/or colloids may be the active catalytic species in these systems.⁶

The rhodium catalysts have also been found to have extended lifetimes. Thus, as indicated in Figure 3, hydrogen evolution measurements following periodic additions of ~9 mg (~0.16 mol) of solid ammonia triborane to a 2 mL aqueous borate-buffered (pH maintained between 7.2 and 8.0) solution containing 1.3 mg (0.012 mmol Rh) of 5 wt % -Rh/Al₂O₃ showed little change in the hydrogen release rates over 10 cycles.

An Arrhenius plot of the initial rate data (Figure 4) for hydrogen release from a 5 wt % -Rh/Al₂O₃ (1.1 mol % -Rh) catalyzed reaction of a 4.9 wt % ammonia triborane solution at different temperatures yielded an activation energy of 13.4 kcal/mol, which is in the range found for metal-catalyzed NaBH₄ hydrolysis (~9 to 18 kcal/mol, depending on the catalyst¹).

Calculations of the standard heats of eqs 1–3 using standard enthalpies of formation,⁷ indicate that hydrogen release from NH₃B₃H₇ is slightly more exothermic (15.8 kcal/mol-H₂) than that from either NaBH₄ (14.9 kcal/mol-H₂) or NH₃BH₃ (12.7 kcal/mol-H₂), but is much less than the hydrolytic reactions of metal hydrides (e.g., LiAlH₄, ~30 kcal/mol-H₂).⁸

As illustrated in Figure 5, the hydrolysis reaction of a 22.7 wt % sample of aqueous ammonia triborane containing 0.30 g of H₂O, 0.10 g of NH₃B₃H₇ (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 equiv) of H₂ (measured by gas buret) over 3 h at 21 °C. This result corresponds to a production of 6.1 wt % H₂ based on materials [wt % = H₂-wt/(NH₃B₃H₇ + H₂O + Rh/Al₂O₃-wts)] and suggests that the DOE 2007 total-system target⁹ of 4.5 wt % for hydrogen release from a chemical hydrogen storage system might be attainable with this

Figure 5. Rhodium (5 wt % -Rh/Al₂O₃, 1.0 mol % -Rh) catalyzed H₂ release from a 22.7-wt % aqueous solution of ammonia triborane (1.8 mmol) yielding 6.1 wt % H₂ [wt % = H₂-wt/(NH₃B₃H₇ + H₂O + Rh/Al₂O₃-wts)].

system. Under these concentrated conditions, ¹¹B NMR studies show that the hydrolysis reaction yields condensed polyborates, which upon addition of water form mixtures of B(OH)₃/B(OH)₄⁻.¹⁰ Thus, the real utility of this process as a chemical hydrogen storage system will ultimately depend on the development of new “off-board” methods to regenerate ammonia triborane from these borates.

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Supporting Information Available: Experimental procedures for the synthesis of NH₃B₃H₇ and the hydrogen release studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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