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

Chang Won Yoon and Larry G. Sneddon*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

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Because of their high hydrogen densities, boron based compounds, including especially sodium borohydride (NaBH₄)¹ and ammonia borane (NH₃BH₃),² are now being intensely investigated as chemical hydrogen storage materials that can release hydrogen by hydrolytic processes (eqs 1–2).

NaBH₄(s) + 2H₂O(l) → Na⁺(aq) + BO₂⁻(aq) + 4H₂(g) (1)

NH₃BH₃(s) + 2H₂O(l) → NH₄⁺(aq) + BO₂⁻(aq) + 3H₂(g) (2)

The high hydrogen release capacity that could potentially be achieved by ammonia triborane, NH₃B₃H₇ (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, B₄H₁₀, with ethers to initially form LB₃H₇ (L = tetrahydrofuran or tetrahydropyran) adducts (plus B₂H₆) that, following displacement of the ethers by reaction with anhydrous ammonia, then produced NH₃B₃H₇. Unfortunately, tetraborane is a volatile unstable compound that is explosive in anhydrous ammonia, then produced NH₃B₃H₇. 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 I₂ oxidation of Me₂N⁺B₁H₈⁻ in noncoordinating solvents (e.g., CH₂Cl₂) yielded the B₂H₆-dimer, B₂H₁₄. We have now found that iodine oxidation (with slow warming from −70 to 20 °C) of the air stable Bu₄N⁺B₃H₆⁻ salt in glyme (1,2-dimethoxyethane) (eq 4) allows the efficient preparation of solutions of the (glyme)B₃H₇ adduct. Direct treatment (eq 5) of these (glyme)B₃H₇ solutions with anhydrous ammonia then yields pure NH₃B₃H₇ as a colorless crystalline solid in >80% yields (based on Bu₄N⁺B₃H₆⁻). Since the Bu₄N⁺B₃H₆⁻ salt can itself be readily prepared by iodine oxidation of BH₄⁻, the large-scale, safe synthesis of NH₃B₃H₇ is now possible.

Bu₄N⁺B₃H₆⁻ + 0.5I₂ + glyme → (glyme)B₃H₇ + Bu₄NI + 0.5H₂ (4)

(glyme)B₃H₇ + NH₃ → NH₃B₃H₇ + glyme (5)

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

Figure 2. Metal-catalyzed hydrogen release from aqueous (~0.45 wt %) ammonia triborane solutions containing (●) RhCl₃ (6.9 mol %); (■) 5 wt %-Rh/Al₂O₃ (7.0 mol %-Rh); (◇) [Rh(COD)(Cl)]₂ (7.2 mol %); (▲) 5 wt %-Rh/Al₂O₃ (1.4 mol %-Rh); (◇) no catalyst.

1 is significantly more soluble in water than NH₃BH₃ (26 wt %), with NH₃B₃H₇ solutions of at least 33 wt % being attained. Also, unlike aqueous NaBH₄, which is stable only in strongly alkaline solutions,¹b,c aqueous NH₃B₃H₇ solutions are quite stable at pH 7.5 in air as evidenced by ¹H 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 H₂ was evolved over ~1 h.

More rapid hydrogen release was achieved using metals to catalyze the hydrolysis reaction. Hydrogen release from NaBH₄ and NH₃BH₃ has previously been attained by metal-catalyzed hydrolysis, with Ru-catalysts¹ for NaBH₄ and Pt-catalysts² for NH₃BH₃ 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. [Rh(COD)(μ-Cl)]₂ (COD = 1,5-cyclooctadiene), and RhCl₃ (Figure 2). With high catalyst loadings of RhCl₃, ~7 equiv of hydrogen were released in only 1.5 min at room temperature. Although they are unchanged upon initially dissolving in water,
both the [Rh(COD)(μ-Cl)]$_2$ and RhCl$_3$ 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 $\sim$9 mg ($\sim$0.16 mol) of solid ammonia triborane to a 2 mL aqueous borate-buffered (pH maintained between 7.2 and 8.0) solution containing 1.3 mg (0.012 mmol Rh) of 5 wt-% Rh/Al$_2$O$_3$ 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/Al$_2$O$_3$ (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 NaBH$_4$ hydrolysis ($\sim$9 to 18 kcal/mol, depending on the catalyst$^1$).

Calculations of the standard heats of eqs 1–3 using standard enthalpies of formation,$^7$ indicate that hydrogen release from NH$_3$BH$_3$H$_2$ is slightly more exothermic (15.8 kcal/mol-H$_2$) than that from either NaBH$_4$ (14.9 kcal/mol-H$_2$) or NH$_3$BH$_3$ (12.7 kcal/mol-H$_2$), but is much less than the hydrolytic reactions of metal hydrides (e.g., LiAlH$_4$, $\sim$30 kcal/mol-H$_2$).$^8$

As illustrated in Figure 5, the hydrogen release reaction of a 22.7 wt-% sample of aqueous ammonia triborane containing 0.30 g of H$_2$O, 0.10 g of NH$_3$BH$_3$H$_2$ (1.8 mmol), and 0.04 g of 5 wt-% Rh/Al$_2$O$_3$ (0.02 mmol of Rh) produced 0.027 g (13.5 mmol, 7.5 equiv) of H$_2$ (measured by gas buret) over 3 h at 21 °C. This result corresponds to a production of 6.1 wt-% H$_2$ based on materials [wt % = H$_2$-wt/(NH$_3$BH$_3$H$_2$ + H$_2$O + Rh/Al$_2$O$_3$-wts)] and suggests that the DOE 2007 total-system target$^9$ of 4.5 wt-% for hydrogen release from a chemical hydrogen storage system might be attainable with this system. Under these concentrated conditions, $^{13}$B NMR studies show that the hydrolysis reaction yields condensed polyborates, which upon addition of water form mixtures of B(OH)$_3$/B(OH)$_4$.$^9$ 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 NH$_3$BH$_3$H$_2$ and the hydrogen release studies. This material is available free of charge via the Internet at http://pubs.acs.org.

References