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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).

$$NaBH_4(s) + 2H_2O(l) \rightarrow Na^+(aq) + BO_2^-(aq) + 4H_2(g) \tag{1}$$

$$NH_3BH_3(s) + 2H_2O(l) \rightarrow NH_4^+(aq) + BO_2^-(aq) + 3H_2(g) \tag{2}$$

The high hydrogen release capacity that could potentially be achieved by ammonia triborane, $NH_3B_3H_7$, (**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.

$$NH_3B_3H_7(s) + 6H_2O(l) \rightarrow NH_4^+(aq) + 3BO_2^-(aq) + 2H^+(aq) + 8H_2(g) \tag{3}$$

Ammonia triborane was first synthesized by Kodama[3] 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 $NH_3B_3H_7$. 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.

Binder[4] previously reported that I_2 oxidation of $Me_4N^+B_3H_8^-$ 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 $Bu_4N^+B_3H_8^-$ 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 $NH_3B_3H_7$ as a colorless crystalline solid in >80% yields (based on $Bu_4N^+B_3H_8^-$). Since the $Bu_4N^+B_3H_8^-$ salt can itself be readily prepared[5] by iodine oxidation of BH_4^-, the large-scale, safe synthesis of $NH_3B_3H_7$ is now possible.

$$Bu_4N^+B_3H_8^- + 0.5I_2 + \text{glyme} \rightarrow (\text{glyme})B_3H_7 + Bu_4NI + 0.5H_2 \tag{4}$$

$$(\text{glyme})B_3H_7 + NH_3 \rightarrow NH_3B_3H_7 + \text{glyme} \tag{5}$$

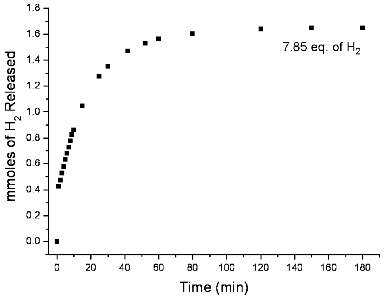

Figure 1. Acid-induced hydrogen release from ammonia triborane.

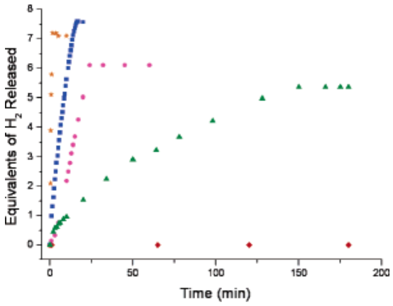

Figure 2. Metal-catalyzed hydrogen release from aqueous (∼0.45 wt %) ammonia triborane solutions containing (★) $RhCl_3$ (6.9 mol %); (■) 5 wt %-Rh/Al_2O_3 (7.0 mol %-Rh); (●) $[Rh(COD)(Cl)]_2$ (7.2 mol %); (▲) 5 wt %-Rh/Al_2O_3 (1.4 mol %-Rh); (◆) no catalyst.

1 is significantly more soluble in water than NH_3BH_3 (26 wt %[2d]), with $NH_3B_3H_7$ solutions of at least 33 wt % being attained. Also, unlike aqueous $NaBH_4$, which is stable only in strongly alkaline solutions,[1b,c] aqueous $NH_3B_3H_7$ 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-catalysts[1] for $NaBH_4$ and Pt-catalysts[2] 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, $[Rh(COD)(\mu\text{-}Cl)]_2$ (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,

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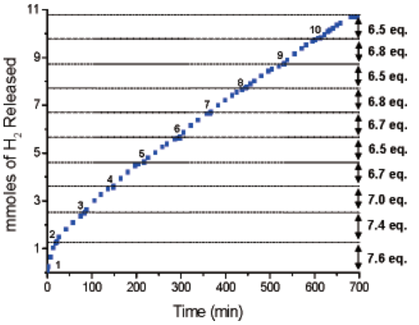

Figure 3. Hydrogen evolution following repeated additions of ammonia triborane to an aqueous solution containing 5 wt %-Rh/Al_2O_3.

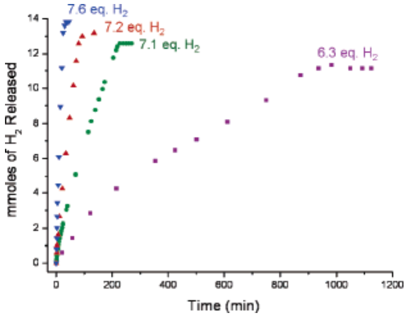

Figure 4. Hydrogen release at different temperatures (▼, 50; ▲, 35; ●, 20; ■, 0 °C) versus time for 4.9 wt % aqueous solutions of ammonia triborane catalyzed by 5 wt %-Rh/Al_2O_3 (1.1 mol %-Rh).

both the $[Rh(COD)(\mu\text{-}Cl)]_2$ 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 ∼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/Al_2O_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_2O_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 (∼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 $NH_3B_3H_7$ is slightly more exothermic (15.8 kcal/mol-H_2) than that from either $NaBH_4$ (14.9 kcal/mol-H_2) or NH_3BH_3 (12.7 kcal/mol-H_2), but is much less than the hydrolytic reactions of metal hydrides (e.g., $LiAlH_4$, ∼30 kcal/mol-H_2).[8]

As illustrated in Figure 5, the hydrolysis reaction of a 22.7 wt % sample of aqueous ammonia triborane containing 0.30 g of H_2O, 0.10 g of $NH_3B_3H_7$ (1.8 mmol), and 0.04 g of 5 wt %-Rh/Al_2O_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/($NH_3B_3H_7$ + H_2O + Rh/Al_2O_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, ^{11}B NMR studies show that the hydrolysis reaction yields condensed polyborates, which upon addition of water form mixtures of $B(OH)_3/B(OH)_4^-$.[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.

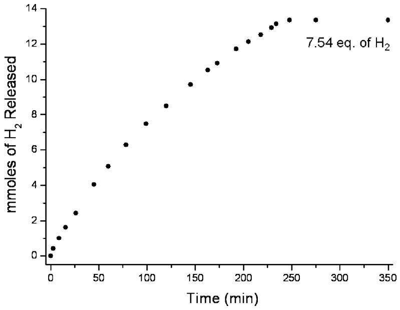

Figure 5. Rhodium (5 wt %-Rh/Al_2O_3, 1.0 mol %-Rh) catalyzed H_2 release from a 22.7-wt % aqueous solution of ammonia triborane (1.8 mmol) yielding 6.1 wt % H_2 [wt % = H_2-wt/($NH_3B_3H_7$ + H_2O + Rh/Al_2O_3-wts)].

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Supporting Information Available: Experimental procedures for the synthesis of $NH_3B_3H_7$ and the hydrogen release studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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