

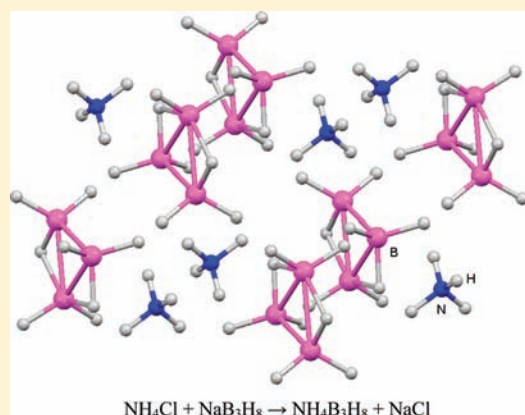
Ammonium Octahydrotriborate ($\text{NH}_4\text{B}_3\text{H}_8$): New Synthesis, Structure, and Hydrolytic Hydrogen Release

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Supporting Information

ABSTRACT: A metathesis reaction between unsolvated NaB_3H_8 and NH_4Cl provides a simple and high-yield synthesis of $\text{NH}_4\text{B}_3\text{H}_8$. Structure determination through X-ray single crystal diffraction analysis reveals weak $\text{N}-\text{H}^{\delta+} \cdots \text{H}^{\delta-}-\text{B}$ interaction in $\text{NH}_4\text{B}_3\text{H}_8$ and strong $\text{N}-\text{H}^{\delta+}-\text{H}^{\delta-}-\text{B}$ interaction in $\text{NH}_4\text{B}_3\text{H}_8 \cdot 18\text{-crown-6} \cdot \text{THF}$ adduct. Pyrolysis of $\text{NH}_4\text{B}_3\text{H}_8$ leads to the formation of hydrogen gas with appreciable amounts of other volatile boranes below 160 °C. Hydrolysis experiments show that upon addition of catalysts, $\text{NH}_4\text{B}_3\text{H}_8$ releases up to 7.5 materials wt % hydrogen.



INTRODUCTION

The safe and efficient hydrogen storage is a major barrier to the use of hydrogen as a transportation fuel. Intensive efforts in recent years have been focused on boron hydrides such as metal borohydrides ($\text{Mg}(\text{BH}_4)_2$,¹ NaBH_4)² and amine boranes ($\text{NH}_3\text{B}_3\text{H}_7$,³ NH_3BH_3)⁴ for hydrogen storage because of their high hydrogen contents. Various catalysts have been investigated to improve hydrogen release from these materials through either thermal decomposition or hydrolysis. However, none of these materials under investigation meets the multiple targets set forth by the U.S. Department of Energy (DOE).

The great variety and distinct properties of boron compounds prompt us to search for a compound that could satisfy the requirements for hydrogen storage. To obtain a high hydrogen capacity, it is essential to find a suitable combination of light-weight cation and H-rich B_mH_n anion. High number of m in B_mH_n leads to a lower hydrogen content and also greater stability of the boron cluster.⁵ Ammonium octahydrotriborate, $\text{NH}_4\text{B}_3\text{H}_8$, has a high hydrogen content of 20.5 wt %. Unfortunately, the first synthesis reported 40 years ago involves pentaborane, B_5H_9 , which is highly volatile and inflames violently upon contact with air.^{6a,b} There are two pentaborane-free patents, but the procedures are complicated and require intermediate compounds and large amounts of solvents.^{6c,d} Probably because of the lack of suitable syntheses, there have been little explorations of its reactivities and properties in 40 years. Here we report (1) a simple and efficient synthesis of this compound; (2) a

crystallographic study of the structure; (3) thermal decomposition; and (4) interesting hydrogen release properties through hydrolysis.

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out on a high-vacuum line or in a glovebox filled with high purity nitrogen. Solvents were dried over sodium/benzophenone and freshly distilled prior to use. Ammonia (Matheson) was distilled from sodium immediately prior to use. NMR spectra were obtained on a Bruker Avance DPX 250 NMR. ¹¹B NMR spectra were obtained at 80.3 MHz and externally referenced to $\text{BF}_3 \cdot \text{OEt}_2$ in C_6D_6 at 0.00 ppm. ¹H NMR spectra were obtained at 250.1 MHz and referenced to $\text{THF}-d_8$. Unsolvated NaB_3H_8 was prepared following the procedure recently developed in our lab.⁷ NH_4Cl (Aldrich) was recrystallized from methanol. Mass spectra of the gas released from the hydrolysis and thermal decomposition were collected through a Balzer's Quadstar 422 Quadrupole mass spectrometer.

Synthesis of $\text{NH}_4\text{B}_3\text{H}_8$. The prepared unsolvated NaB_3H_8 (634 mg, 10 mmol) reacted with NH_4Cl (535 mg, 10 mmol) in liquid ammonia at -78 °C. After 30 min stirring using a magnetic bar, ammonia was removed and the flask was warmed to room temperature. The desired $\text{NH}_4\text{B}_3\text{H}_8$ was extracted using dry tetrahydrofuran (THF) followed by pumping off THF right away, leaving a white powder, $\text{NH}_4\text{B}_3\text{H}_8$ (555

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Table 1. Crystallographic Information

empirical formula	H ₁₂ B ₃ N	C ₁₆ H ₄₄ B ₃ NO ₇
formula weight	58.54	394.95
crystal system	orthorhombic	monoclinic
space group	Cmcm	Pc
Z	4	4
a, Å	7.1530(14)	16.407(3)
b, Å	8.2648(17)	11.215(2)
c, Å	8.3895(17)	13.841(3)
α, deg	90	90
β, deg	90	107.76(3)
γ, deg	90	90
T, K	150	150
V, Å ³	495.97(17)	2425.4(9)
D _{calcd} (g·cm ⁻³)	0.784	1.082
μ (mm ⁻¹)	0.038	0.079
λ, Å	0.71073	0.71073
no. refls collected	1617	8313
no. unique refls	251 (R _{int} = 0.0245)	4286 (R _{int} = 0.0258)
R1 [I > 2σ(I)] ^a	0.0370	0.0420
wR2(all data) ^b	0.1153	0.1043
^a R1 = Σ F _o - F _c /Σ F _o . ^b wR2 = [Σw(F _o ² - F _c ²) ² /Σw(F _o ²) ²] ^{1/2}		

mg, yield 95%). ¹¹B NMR: (THF-*d*₈) δ -29.9 ppm, ¹H NMR (THF-*d*₈): NH₄⁺, δ 6.8 ppm; B₃H₈⁻, δ 0.2 ppm.

X-ray Crystallography. X-ray quality crystals of the NH₄B₃H₈·18-crown-6·THF adduct were grown from 1:1 (molar ratio) mixtures of NH₄B₃H₈ and 18-crown-6 in THF. NH₄B₃H₈ single crystals were grown from anhydrous CH₃CN. **Caution!** At room temperature, signs of decomposition (bubbles) were observed after a few days for both the NH₄B₃H₈/18-crown-6/THF and NH₄B₃H₈/CH₃CN mixtures.

X-ray single crystal diffraction data were collected on a Nonius Kappa CCD diffractometer which employs graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Because of the sensitivity of the compound, single crystals were picked up from the mother solution in a nitrogen filled glovebox and stored in Fomblin oil until data collection. A single crystal coated with Fomblin oil was mounted on the tip of a glass fiber. Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined by employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using the DENZO-SMN package.⁸ Absorption correction for the structure was accounted for by using SCALEPACK.⁸ The structure was solved (Table 1) by direct method using the SHELXTL-97 (full-matrix least-squares refinements) structure solution package.⁹ All nonhydrogen atoms were located and refined anisotropically. Hydrogen atoms on boron and nitrogen atoms were located and refined isotropically, and other hydrogen atom positions were calculated by assuming standard geometries.

Thermal Decomposition Studies. Thermal stability of NH₄B₃H₈ was studied using a Mettler Toledo high-pressure differential scanning calorimeter (DSC27HP) in an argon glovebox with a ramp rate of 5 °C/min. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 7 analyzer. Powder was loaded onto a quartz crucible and heated to 400 °C at a heating rate of 5 °C/min under an Ar flow of 40 cm³/min. The gaseous decomposition products were semiquantified through a calibrated vacuum line. After freezing out the gaseous products at -196 °C, hydrogen content was determined; after removing hydrogen and then raising the temperature to -78 °C, diborane was quantified; the residual product, pentaborane and borazine, were analyzed after diborane was removed and temperature was raised to ~25 °C.¹⁰

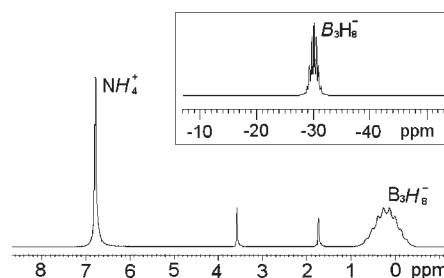


Figure 1. ¹H NMR spectrum of NH₄B₃H₈ recorded in THF-*d*₈ at room temperature. Inset is the ¹¹B NMR spectrum.

Hydrolytic H₂ Release Measurements. In a two-neck flask connected to a vacuum line, 1 mmol NH₄B₃H₈ was mixed with 0.04 mmol CoCl₂. After evacuating all the gases via dynamic vacuum, the flask was sealed and 18 mmol water was injected. After the reaction completion, the flask was opened to a vacuum line, and the evolved gas passed through a liquid nitrogen trap to isolate any non-hydrogen products, including water. The hydrogen was then quantitatively measured using a Toepler pump. About 8.80 mmol H₂ was obtained through the reaction.

For catalyst screening, a gas buret was set up to measure the amount of H₂ gas and to determine the rates of H₂ release.^{3a} Pt/C (10 wt % Pt), Ru/Al₂O₃ (5 wt % Ru), RuCl₃, CoCl₂, NiCl₂, and FeCl₃ were all tested as received. For the catalyst loading, 1 mol % (with reference to NH₄B₃H₈) of noble metal (Pt or Ru) was loaded, while 4 mol % of transition metal (Co, Ni or Fe) was employed.

RESULTS AND DISCUSSIONS

A simple and efficient method has now been developed to synthesize NH₄B₃H₈ via a metathesis reaction between unsolvated NaB₃H₈ and NH₄Cl in liquid ammonia (eq 1).



This reaction proceeds rapidly, and the desired product can be efficiently extracted using THF after removing the liquid ammonia. Furthermore, the yield is ~95%, higher than 79.5% reported for the previous methods.⁶ The unsolvated NaB₃H₈ was prepared via a route recently developed in our lab,⁷ which eliminates the use of dangerous starting materials such as B₂H₆ and BF₃¹¹ and enables a high yield. Therefore, a large-scale and simple synthesis of NH₄B₃H₈ is now possible.

The metathesis reaction has also been explored in several other solvents, and it was found that the solvent had an influence on the course of the reaction. In addition to NH₄B₃H₈, NH₃B₃H₇ and other boron compounds were also observed for the reaction in THF and DME, with the latter resulting in more NH₃B₃H₇.

The successful synthesis in liquid ammonia is corroborated by the NMR spectrum (Figure 1). After extracting NH₄B₃H₈ using THF and then pumping off the THF immediately via dynamic vacuum, pure desired product was obtained. NH₄B₃H₈ exhibits a ¹¹B NMR resonance at -29.9 ppm, which is assigned to B₃H₈⁻.⁷ The ¹H NMR spectrum of NH₄B₃H₈ reveals the existence of both NH₄⁺ (6.8 ppm) and B₃H₈⁻ (0.2 ppm).

The structures of NH₄B₃H₈ and NH₄B₃H₈·18-crown-6·THF adduct were determined through single crystal X-ray diffraction analysis. Selected bond distances and angles are given in Tables 2 and 3, respectively. Figure 2 shows a separate ion pair structure of NH₄B₃H₈, with the shortest N-H^{δ+}...H^{δ-}-B distance being 2.37(3) Å, very close to the sum of van der Waals

Table 2. Selected Bond Distances and Angles of $\text{H}_{12}\text{B}_3\text{N}^a$

N(1)–H(5)	0.85(3)
N(1)–H(6)	0.79(4)
B(1)–B(2)	1.779(2)
B(1)–B(2) [#]	1.779(2)
B(1)–H(4)	1.475(18)
B(1)–H(1)	1.079(17)
B(2)–B(2) [#]	1.813(3)
B(2)–H(3)	1.096(13)
B(2)–H(4)	1.137(17)
H(5)–N(1)–H(6)	113(2)
B(2)–B(1)–B(2) [#]	61.27(11)
B(2)–B(1)–H(4)	39.5(7)
B(2) [#] –B(1)–H(4)	100.8(7)
B(2)–B(1)–H(1)	117.3(7)
B(2) [#] –B(1)–H(1)	117.3(7)
H(4)–B(1)–H(1)	100.4(4)
B(1)–B(2)–B(2) [#]	59.37(5)
B(1)–B(2)–H(3)	121.5(6)
B(2) [#] –B(2)–H(3)	108.5(7)
B(1)–B(2)–H(4)	55.7(9)
B(2) [#] –B(2)–H(4)	115.0(9)
H(3)–B(2)–H(4)	104.2(8)

^a Symmetry transformations used to generate equivalent atoms. [#] = $x, y, -z + 3/2$.

Table 3. Selected Bond Distances and Angles of $\text{C}_{16}\text{H}_{44}\text{B}_3\text{NO}_7$

N(1)–H(2)	0.82(5)
N(1)–H(1)	0.92(4)
N(1)–H(3)	0.87(4)
N(1)–H(4)	0.99(6)
B(1)–B(3)	1.758(6)
B(1)–B(2)	1.796(7)
B(2)–B(3)	1.762(6)
B(1)–H(9)	1.14(4)
B(1)–H(15)	1.27(5)
B(2)–H(11)	1.10(4)
B(2)–H(12)	1.08(5)
B(3)–H(16)	1.41(4)
H(2)–N(1)–H(3)	111(4)
H(1)–N(1)–H(3)	108(3)
H(2)–N(1)–H(4)	111(4)
H(1)–N(1)–H(4)	110(4)
B(3)–B(1)–B(2)	59.4(3)
B(1)–B(3)–B(2)	61.3(3)
B(3)–B(2)–B(1)	59.2(2)
B(3)–B(1)–H(9)	121.4(18)
B(3)–B(1)–H(10)	126(2)
B(2)–B(1)–H(15)	115(2)
B(1)–B(3)–H(16)	102.0(17)
B(2)–B(3)–H(16)	40.6(17)
B(1)–B(3)–H(15)	45.1(19)
B(1)–B(3)–H(14)	115.2(18)

radii between two hydrogen atoms, 2.4 Å. All other N–H^{δ+}...H^{δ-}–B distances are more than 2.47 Å. This seems unusual

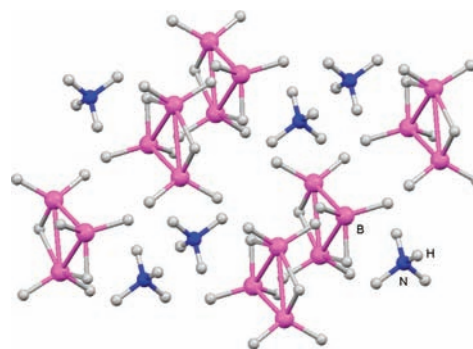


Figure 2. Crystal structure of $\text{NH}_4\text{B}_3\text{H}_8$. B, pink; H, light gray; N, blue.

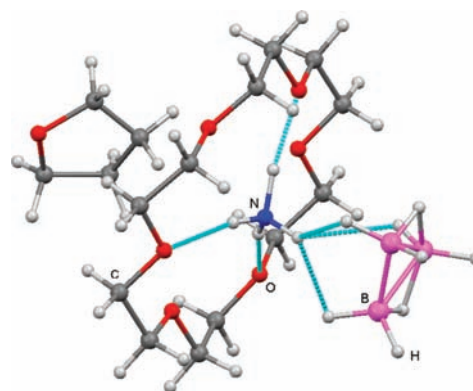


Figure 3. Fragment of the $\text{NH}_4\text{B}_3\text{H}_8 \cdot 18\text{-crown-6} \cdot \text{THF}$ adduct. B, pink; H, light gray; N, blue; O, red; C, gray.

since B–N compounds tend to have close N–H^{δ+}...H^{δ-}–B contacts,^{12a} as observed in $\text{NH}_3\text{B}_3\text{H}_7$ ^{3a} and NH_3BH_3 .^{12b} This structure differs from the reported metal octahydrotriborates, where B_3H_8 can coordinate with a metal center such as for $\text{Cr}(\text{B}_3\text{H}_8)_2$,^{11c} $(\text{CO})_4\text{Mn}(\text{B}_3\text{H}_8)$,¹³ $\text{Mg}(\text{B}_3\text{H}_8)_2(\text{Et}_2\text{O})_2$,¹⁴ and $\text{Ru}(\text{B}_3\text{H}_8)(\text{PPh}_3)\{\kappa^3\text{-HB}(\text{pz})_3\}$.¹⁵

The molecular structure of $\text{NH}_4\text{B}_3\text{H}_8 \cdot 18\text{-crown-6} \cdot \text{THF}$ adduct is illustrated in Figure 3. Ammonium cation has been reported to connect to crown ether by three N–H...O hydrogen bonds between the hydrogen atoms of the ammonium and the oxygen atoms of the crown ether.¹⁶ We likewise found similar interaction present in $\text{NH}_4\text{B}_3\text{H}_8 \cdot 18\text{-crown-6} \cdot \text{THF}$ adduct. There is another independent fragment in the asymmetric unit, very similar to the one shown in Figure 3. The THF molecule is packed into the structure with no interactions with other moieties. The average N–O distance is 2.94 Å, longer than the standard N–O hydrogen bond length (2.87 Å).¹⁷ The hydrogen atom on nitrogen that is not involved in bonding to an oxygen atom interacts with three terminal hydrogen atoms on the boron triangle, with the closest N–H^{δ+}...H^{δ-}–B distance of 1.92(5) Å being shorter than 2.13(3) Å present in $\text{NH}_3\text{B}_3\text{H}_7$ determined by X-ray diffraction analysis,^{3a} significantly less than the sum of van der Waals radii between two hydrogen atoms, 2.4 Å.

$\text{NH}_4\text{B}_3\text{H}_8$ in pure and solid form is stable at room temperature with no detectable signs of decomposition within one month. On the contrary, the adduct decomposes slowly at room temperature with the evolution of hydrogen gas. The poor stability of the adduct is likely due to the stronger N–H^{δ+}...H^{δ-}–B interactions.

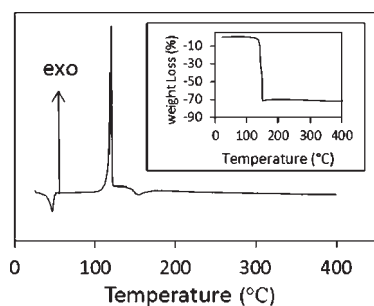
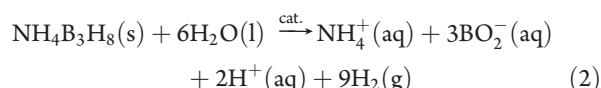


Figure 4. DSC and TGA curves of $\text{NH}_4\text{B}_3\text{H}_8$ ($5^\circ\text{C}/\text{min}$).

NH_4BH_4 , an analogue of $\text{NH}_4\text{B}_3\text{H}_8$, decomposes at -78°C in THF.¹⁸ This is in stark contrast to the slow degradation of $\text{NH}_4\text{B}_3\text{H}_8$ in THF at ambient conditions. Since both compounds contain the same cation, the difference is likely due to the weaker hydridic H^- of B_3H_8 compared to that of BH_4^- . This is consistent with the findings that for boron hydrides the higher number of boron atoms in the structure, the less hydridic the hydrogen is.¹⁹

$\text{NH}_4\text{B}_3\text{H}_8$ has a high hydrogen content, 20.5 wt %. Unfortunately, thermal decomposition analysis shows that this compound gives off 10 wt % hydrogen below 160°C , but with appreciable amounts of diborane, pentaborane, and borazine (Supporting Information). DSC and TGA results (Figure 4) collectively indicate that melting and decomposition take place simultaneously at 120°C , with a substantial weight loss at this temperature. The presence of the boranes results in a $\sim 70\%$ final weight loss. It has been reported that NH_3BH_3 gives off the first equivalent H_2 below 120°C and further releases hydrogen at higher temperature but with a small fraction of borazine.²⁰ Compared with NH_3BH_3 , $\text{NH}_4\text{B}_3\text{H}_8$ produces less hydrogen and more undesired volatile compounds below 160°C . Thus, $\text{NH}_4\text{B}_3\text{H}_8$ is probably not a suitable candidate for hydrogen storage through thermal decomposition.

Hydrolytic studies, however, have demonstrated that $\text{NH}_4\text{B}_3\text{H}_8$ has advantages over NaBH_4 ² and NH_3BH_3 ,^{4c,d} the most studied chemical hydrides for hydrogen storage via hydrolysis. At room temperature, $\text{NH}_4\text{B}_3\text{H}_8$ is more soluble in water (>45 wt % through visual observation) than NH_3BH_3 (26 wt %²¹) and NaBH_4 (35 wt %²²). The lower solubility significantly limits the theoretical hydrogen density of the respective system to 5.1 wt % for NH_3BH_3 and 7.5 wt % for NaBH_4 . Quantitative measurements of H_2 released via hydrolysis using a Toepler pump and gas buret showed that upon adding catalysts, 1 mmol $\text{NH}_4\text{B}_3\text{H}_8$ releases a near theoretical value of 8.80 mmol H_2 . Based on eq 2, therefore, this system has a high theoretical hydrogen weight density [$\text{wt \%} = \text{H}_2/(\text{NH}_4\text{B}_3\text{H}_8 + \text{H}_2\text{O})$] of 10.8 wt %.



In addition, unlike NaBH_4 , which is stable only in strong alkaline solutions,² an aqueous $\text{NH}_4\text{B}_3\text{H}_8$ solution is reasonably stable as shown by ^{11}B NMR studies (Figure 5). At 28°C , for the same molar concentration, that is, 2 M, ^{11}B NMR studies show that more than 50% of NaBH_4 decomposed over a day, while less than 10% of $\text{NH}_4\text{B}_3\text{H}_8$ decomposed over a week.

Hydrolytic studies have shown that upon adding catalysts $\text{NH}_4\text{B}_3\text{H}_8$ rapidly releases pure H_2 (Figure 6). For an aqueous

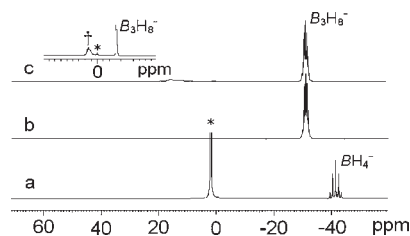


Figure 5. ^{11}B NMR spectra of 2 M aqueous solutions taken after (a) 1 day for NaBH_4 ; (b and c) 1 day and 7 days for $\text{NH}_4\text{B}_3\text{H}_8$. Inset is an expanded spectrum of c. *, $\text{B}_5\text{O}_6(\text{OH})_4^-$; †, $\text{B}_3\text{O}_3(\text{OH})_4^-$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$.

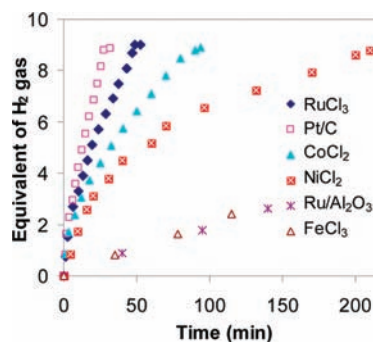


Figure 6. Hydrogen evolution at room temperature from an aqueous $\text{NH}_4\text{B}_3\text{H}_8$ solution (molar ratio of $\text{NH}_4\text{B}_3\text{H}_8:\text{H}_2\text{O}$ being 1:18) containing 10 wt % Pt/C (1 mol % Pt); 5 wt % Ru/ Al_2O_3 (1 mol % Ru), RuCl_3 (1 mol % Ru), CoCl_2 (4 mol % Co), NiCl_2 (4 mol % Ni), and FeCl_3 (4 mol % Fe). Molar ratios are referenced to $\text{NH}_4\text{B}_3\text{H}_8$.

solution with a 1:18 molar ratio of $\text{NH}_4\text{B}_3\text{H}_8$ to H_2O , which represents a material density of 4.6 wt % H, the commercially available 10 wt % Pt/C catalyst (1 mol % Pt) shows the best catalytic activity, with complete hydrolysis in less than 30 min. RuCl_3 also displayed excellent catalytic activity, and this is likely associated with the in situ formation of $\text{Ru}(0)$ as indicated by the formation of a black powder, which was also observed during hydrolysis of both NaBH_4 ² and NH_3BH_3 .^{4c} However, 5 wt % $\text{Ru}/\text{Al}_2\text{O}_3$ (1 mol % Ru) is much less active. The difference is probably associated with the degree of the dispersed catalytic sites. Lower-cost transition metal catalysts were also explored in our study, and fairly good catalytic activity was observed for CoCl_2 . With 4 mol % loading of CoCl_2 , full hydrolysis was complete in about 100 min. A black powder appeared instantly when CoCl_2 was brought into contact with an aqueous $\text{NH}_4\text{B}_3\text{H}_8$ solution, suggesting the formation of cobalt boride (Supporting Information) as found during the hydrolysis of NaBH_4 .² NiCl_2 is less effective and the full hydrolysis required ~ 200 min.

The " BO_2^- " product shown in eq 2 is only a hypothetical formulation, with the actual borate products of these reactions depending upon the final solution concentration and pH.^{3a} The ^{11}B NMR spectrum (Figure 7) of the catalyzed hydrolysis solution of $\text{NH}_4\text{B}_3\text{H}_8$ and H_2O (1:18 ratio) reveals one broad peak centered at 16 ppm which is likely associated with $\text{B}_3\text{O}_3(\text{OH})_4^-$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$, along with another sharp peak situated at around 0 ppm that is also due to $\text{B}_5\text{O}_6(\text{OH})_4^-$.²³ Similar products were also formed during the hydrolysis of $\text{NH}_3\text{B}_3\text{H}_7$.^{3a}

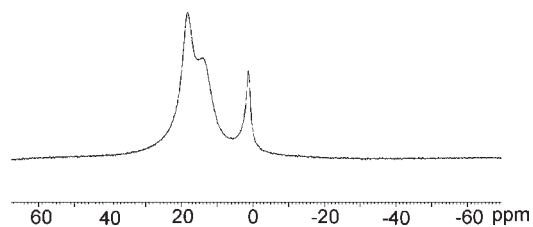


Figure 7. ^{11}B NMR spectrum of the catalyzed hydrolysis solution ($\text{NH}_4\text{B}_3\text{H}_8$: H_2O being 1: 18).

When an aqueous solution with 1:10 molar ratio of $\text{NH}_4\text{B}_3\text{H}_8$ to H_2O was subject to hydrolysis catalyzed by 4 mol % of CoCl_2 , full hydrolysis was achieved in ~ 200 min, which corresponds to a production of 7.5 wt % H_2 . The U.S. DOE recently modified the vehicular hydrogen storage targets to 4.5 wt % by 2010, 5.5 wt % by 2015, and 7.5 wt % for the ultimate.²⁴ $\text{NH}_4\text{B}_3\text{H}_8$ thus could be a potential candidate to meet the 2010 target.

Calculations of the standard heat of hydrolysis from the standard enthalpies of formation indicate that H_2 release from $\text{NH}_4\text{B}_3\text{H}_8$ is much less exothermic (5.43 kcal/mol H_2 , Supporting Information) than from either NaBH_4 (14.9 kcal/mol H_2), NH_3BH_3 (12.7 kcal/mol H_2), or $\text{NH}_3\text{B}_3\text{H}_7$ (18.9 kcal/mol H_2).^{3a} The less exothermic nature favors $\text{NH}_4\text{B}_3\text{H}_8$ over the other candidates from the standpoint of heat management and system design.

As in the cases of NaBH_4 , NH_3BH_3 , and $\text{NH}_3\text{B}_3\text{H}_7$, the formation of borates may affect the performance of the catalysts if the borate precipitates cover the active sites. It should be noted that the removal and transportability of the borates depend on the starting materials and reaction conditions,²⁵ and thus can be improved accordingly. Regeneration of these compounds from the borates has been challenging, but progress has been made in the regeneration of spent fuel back into NH_3BH_3 .²⁶ The final utility of $\text{NH}_4\text{B}_3\text{H}_8$ as a chemical hydrogen storage material will also hinge on the development of an efficient “off-board” regeneration of $\text{NH}_4\text{B}_3\text{H}_8$.

■ ASSOCIATED CONTENT

S Supporting Information. Structural information, calculation of the heat of the hydrolysis, mass spectra of gas from hydrolysis and thermal decomposition. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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