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Article

Preparation of Ammonia Borane in High Yield and Purity, Methanolysis, and Regeneration

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Ammonia borane (AB) is emerging as a promising solid hydrogen carrier, particularly for power generation in portable devices that employ proton-exchange membrane fuel cells. A preparative-scale synthesis of AB from sodium borohydride and ammonium salts in high yields (≥95%) and very high purity (≥98%) has been described. The first systematic study of a transitional metal-catalyzed alcoholysis of AB, comparison of the methanolysis to the hydrolysis of AB, and regeneration of AB from ammonium tetramethoxyborate also has been described.

Introduction

Ammonia borane (AB) is an excellent source of hydrogen (19.4 wt %) for fuel cell applications,[1] and despite its cost,[2] is currently being actively pursued.[3] AB is a nontoxic, environmentally benign, and stable material that can be safely transported without hydrogen loss, which dictates the success of any chemical for hydrogen storage. AB is also equally important for synthetic organic chemistry applications.[4] The literature synthesis of ammonia borane involves the reaction of lithium[5] or sodium borohydride (SBH)[6] and ammonium salts, such as ammonium chloride, sulfate, or carbonate. The low-temperature (−75 °C) isolation of AB is tedious as reported.[7] A synthetic procedure from diborane and ammonia in hexane has also been reported.[8] An efficient and economical synthesis and recycling of AB is critical for the realization of its full potential.

Herein, we report an optimal procedure for the preparative-scale synthesis of AB in high yields and purity from sodium borohydride and ammonium salts.[9] The first systematic study of the transition metal-catalyzed methanolysis of AB, the isolation and characterization of the resulting borate salt, and the recovery of AB has been described. A comparison of the transition metal-catalyzed methanolysis and hydrolysis

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[9] Parts of this work were presented during (a) the inaugural Purdue University Energy Center Hydrogen Initiative Symposium, April 5, 2006, and (b) during the symposium entitled, "Role of Catalysts in Hydrogen Production" sponsored by the FUEL Division of the ACS during the 232nd ACS National Meeting, San Francisco, CA, September 11, 2006. (c) For preliminary reports, see: Ramachandran, P. V. *Prepr. Symp—ACS, Div. Fuel Chem.* **2006**, *51* (2), 515.

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of AB has been made. We have recognized and quantified the liberation of ammonia during the transition metal-catalyzed hydrolysis. The borate products from the hydrolysis and the methanolysis of AB have been characterized by X-ray crystallography.

Experimental Section

General Information. Unless otherwise noted, all manipulations were carried out under an inert atmosphere in flame-dried glassware, cooled under nitrogen.[10] The ^{11}B NMR spectra were recorded using a Varian Gemini-300 spectrometer (64 MHz) with a Nalorac quad probe and were referenced to $BF_3{\cdot}OEt_2$ (0.0 ppm) as an external standard. Tetrahydrofuran (THF) and methanol were purchased from Mallinckrodt chemicals. Dry THF was prepared by distillation over sodium benzophenone ketyl. Dry dioxane, sodium borohydride (SBH), and all of the ammonium salts were purchased from commercial sources and were used as received.

Large-Scale Preparation of Ammonia Borane using Sodium Borohydride and Ammonium Sulfate in THF. ***Caution:*** *A significant amount of hydrogen is generated during the synthesis of AB, which is a potential fire hazard. It is recommended that the reaction be carried out in a well-ventilated hood and that the reaction vessel outlet be led directly into the hood exhaust.*

Sodium borohydride (37.83 g, 1.0 mol) and powdered ammonium sulfate (132.14 g, 1.0 mol) were added to a 10 L three-neck round-bottom flask with indentation fitted with an overhead stirrer, a stopper, and a condenser fitted with a connecting tube. The connecting tube was vented via an oil bubbler to the hood exhaust. THF (6 L) was transferred into the flask, and the contents were vigorously stirred at 40 °C. The reaction was monitored by ^{11}B NMR spectroscopy. Upon completion (~2 h), the reaction mixture was cooled to room temperature (RT) and filtered. The filtrate was concentrated under vacuum to obtain ammonia borane (29.3 g, 96%) in >98% chemical purity, as determined by ^{11}B NMR spectroscopy (64 MHz, −22.1 ppm (q)) and hydride analysis.[10b]

The solvent was recovered and reused for the preparation of subsequent batches of ammonia borane without further purification.

Large-Scale Preparation of Ammonia Borane using Sodium Borohydride and Ammonium Formate in Dioxane. ***Caution:*** *A significant amount of hydrogen is generated during the synthesis of AB, which is a potential fire hazard. It is recommended that the reaction be carried out in a well-ventilated hood and that the reaction vessel outlet be led directly to the hood exhaust.*

Sodium borohydride (379 g, 10 mol) and ammonium formate (945 g, 15 mol) were added under a nitrogen atmosphere to a 20 L three-neck round-bottom flask with indentation fitted with an overhead stirrer, a stopper, and a condenser fitted with a connecting tube. The connecting tube was vented via an oil bubbler to the hood exhaust. Anhydrous dioxane (10 L) was transferred into the flask and the contents were vigorously stirred at 40 °C for ~2 h (^{11}B NMR), until the reaction was complete. *Vigorous stirring was found to be crucial for the rate of the reaction since a similar scale reaction using a round-bottom flask without indentation required 12 h for completion*. The reaction mixture was then cooled to RT and filtered through a Celite bed; the solid residue was washed with dioxane, and the combined filtrates were concentrated to obtain 294 g (95%) of AB in >98% purity. Elemental analysis: theoretical B 35.03, H 19.59, N 45.38; found B 35.13, H 19.21, N 45.01%.

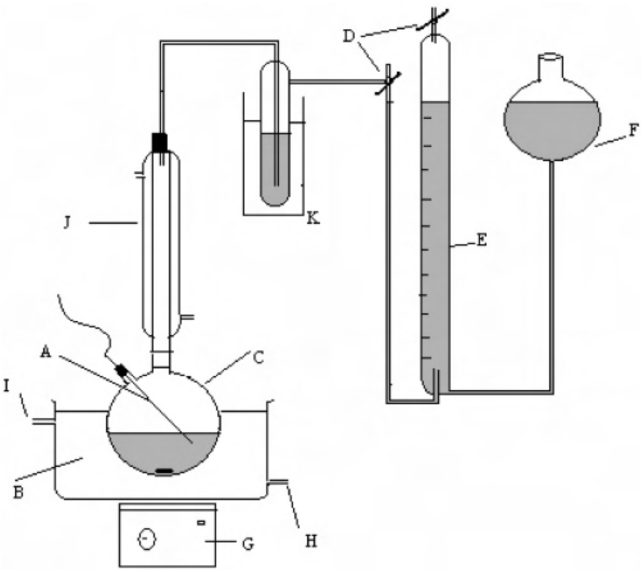

Figure 1. Experimental setup for hydrogen measurement: (A) thermocouple, (B) constant temperature water bath, (C) round-bottom flask, (D) stop cock, (E) gas burette, (F) leveling flask, (G) stirrer, (H) constant temp water inlet, (I) water outlet, (J) reflux condenser, and (K) water trap.

Table 1. Synthesis of AB from SBH and Ammonium Salts in THF[a]

		reaction conditions		
entry	ammonium salt	temp (°C)	time (h)	isolated yield (%)
1	NH_4Cl	25	24	45
2	NH_4Cl	40	11	40
3	$(NH_4)_2CO_3$	25	4	80
4	$(NH_4)_2CO_3$	40	3	85
5	NH_4OAc	25	4	75
6	NH_4OAc	40	10	81
7	NH_4F	25	3	85
8	NH_4F	40	15	78
9	$(NH_4)_2SO_4$	25	5	93
10	$(NH_4)_2SO_4$	40	2	96
11	NH_4NO_3[b]	25	3	83
12	NH_4NO_3	40	5	76
13	NH_4HCO_2	25	5	93
14	NH_4HCO_2	40	2	95
15	$(NH_4)_2SO_4$[c]	40	5	94 (0.3)
16	$(NH_4)_2SO_4$[d]	40	12	90 (1.8)
17	$(NH_4)_2SO_4$[e]	40	20	88 (3)

[a] Yields in parentheses show percent impurities determined from the ^{11}B NMR spectrum. The reaction concentration in THF is 0.165 M $NaBH_4$. [b] ***Caution:*** *The reaction of ammonium nitrate with the sodium borohydride is potentially explosive.* [c] The reaction concentration in THF is 0.2 M $NaBH_4$. [d] The reaction concentration in THF is 0.4 M $NaBH_4$. [e] The reaction concentration in THF is 0.6 M $NaBH_4$.

The product was stable indefinitely in the solid state but underwent slow decomposition in THF and dioxane solutions, precipitating a white solid. Similar behavior is reported in diethyl ether by Shore and Parry.[5,7]

Hydrolysis of AB. Quantification of Liberated Ammonia. An aqueous solution of ammonia borane (12 mL, 25 wt %) was placed in a 2-neck round-bottom flask fitted with septum inlet and a reflux condenser fitted with a connecting tube. The connecting tube was attached to an analytical gas burette filled with $CuSO_4$ solution via

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(10) (a) Procedures for handling air- and moisture-sensitive compounds has been described in Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Synthesis via Boranes*; Aldrich: Milwaukee, WI, 2000; Vol. 1, Chapter 9. (b) For the hydride analysis procedure (estimation of hydrogen after hydrolysis or alcoholysis), see ref 10a, pp 241−245.

Table 2. Synthesis of AB: Solvent Effect[a]

entry	solvents	ammonium salts	time (h)	yield (%) (purity, %)[b]
1	EtOAc	$(NH_4)_2SO_4$	8	70 (76)
2	EtOAc	NH_4HCO_2	9.5	61 (80)
3	CH_2Cl_2	$(NH_4)_2SO_4$	12	52 (58)
4	CH_2Cl_2	NH_4HCO_2	15	45 (46)
5	DMF	$(NH_4)_2SO_4$	7	56 (60)
6	DMF	NH_4HCO_2	8	62 (60)
7	diglyme	$(NH_4)_2SO_4$	4	70 (81)
8	diglyme	NH_4HCO_2	4	76 (78)
9	CCl_4	$(NH_4)_2SO_4$	10	39 (42)
10	CCl_4	NH_4HCO_2	13	48 (46)
11	toluene	$(NH_4)_2SO_4$	5	40 (51)
12	toluene	NH_4HCO_2	7	46 (48)
13	dioxane	$(NH_4)_2SO_4$	10	82 (77)
14	dioxane	NH_4HCO_2	2	95 (98)
15	THF	$(NH_4)_2SO_4$	20	72 (75)
16	THF	NH_4HCO_2	25	76 (80)

[a] The reactions were conducted in 1 M concentrations of the appropriate solvents at 40 °C. [b] On the basis of ^{11}B NMR spectroscopy.

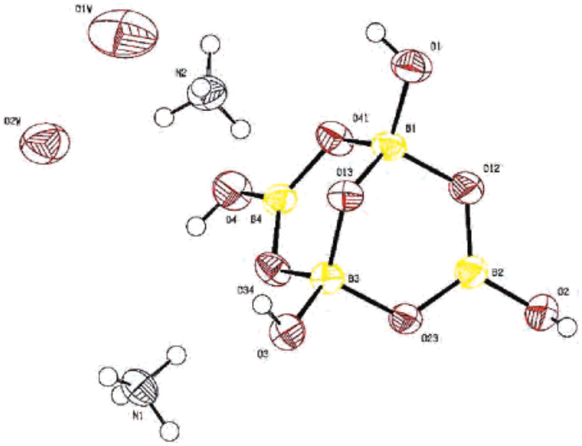

Figure 2. ORTEP diagram of $\{[(NH)_4]_2[B_4O_5(OH)_4]\cdot 1.4H_2O\}$at 50% probability.

Table 3. Hydrolysis of AB in the Presence of Transition Metal Catalyst

entry	catalyst	catalyst (mol %)	reaction time ($t_{1/2}$, min)
1	$RuCl_3$	0.5	<1
2	$RuCl_3$	0.2	2
3	$RuCl_3$	0.1	3
4	$RuCl_3$	0.05	10
5	$CoCl_2$	3	3
6	$CoCl_2$	5	2
7	Pd/C	1	12
8	$PdCl_2$	5	12

Table 4. Quantity of NH_3 Liberated during the Hydrolysis of AB

entry	AB solution (wt %)	catalyst		addition time (min)	NH_3 liberated (%)
		MX_n	mol %		
1	25	$RuCl_3$	0.06	45	7
2	20	$RuCl_3$	0.06	45	6
3	15	$RuCl_3$	0.06	45	4
4	15	$RuCl_3$	0.06	15	4.4
5	15	$RuCl_3$	0.2	45	3
6	15	$RuCl_3$	0.2	15	6
7	10	$RuCl_3$	0.06	45	1
8	6	$RuCl_3$	0.06	15	<1
9	6	$RuCl_3$	0.06	45	~0
10	20	$NiCl_2$	0.6	45	6

a bubbler containing water (100 mL) (Figure 1). A solution of $RuCl_3$ (12 mg, 0.06 mol %) in water (0.3 mL) was added dropwise via syringe, over a period of 45 min. The temperature of the reaction was maintained at 25 °C with a constant temperature bath. Upon completion of the reaction, when hydrogen evolution ceased (~3 h), the aqueous solution of ammonia from the trap was titrated against standard 0.1 N aq HCl. The amount of NH_3 was estimated to be 7%. The quantity of ammonia liberated depended on the concentration of AB solution (see Results and Discussion).

Methanolysis of AB and Isolation of Ammonium Tetramethoxyborate. Ammonia borane (0.66 g, 0.0213 mol) was placed in a two-neck round-bottom flask fitted with septum inlet and a reflux condenser fitted with connecting tube. The connecting tube was attached to an analytical gas burette filled with $CuSO_4$ solution via a gas bubbler containing 100 mL of water to trap any methanol vapor or sublimed borate. A solution of $RuCl_3$ (0.04 g, 1 mol %) in methanol (4 mL) was syringed, all at once, into the reaction flask. The hydrogen generated was measured using analytical gas burette. The temperature of the reaction was maintained at 25 °C using a constant temperature bath. The ^{11}B NMR spectrum (δ 8.7 ppm) revealed the formation of ammonium tetramethoxyborate. A small amount of borate crystals sublimed during the reaction and condensed on the inner wall of the condenser. The wet solid residue was subjected to vacuum (20 Torr) at RT for 5 min to remove the excess methanol, and the crude borate was transferred to a sublimation apparatus under nitrogen and sublimed at 55 °C (oil bath temperature). Yield: 3.1 g (87%). X-ray crystallography revealed the structure of the borate as $[NH_4B(OMe)_4]_5\cdot 2MeOH$.

The aqueous solution from the trap was titrated against standard 0.1 N aq HCl. The amount of borate salt sublimed during the reaction was estimated to be 1% (see Results and Discussion).

General Procedure for the Kinetic Study of the Methanolysis of AB. The transition metal catalyst was placed in a two-neck round-bottom flask fitted with septum inlet and a reflux condenser fitted with a connecting tube. The connecting tube was attached to an analytical gas burette filled with a $CuSO_4$ solution via a gas bubbler containing 100 mL water to trap any methanol vapor or sublimed borate. A solution of AB (1.45 mL, 2 M) was syringed, all at once, into the reaction flask. The hydrogen generated was measured using an analytical gas burette. The temperature of the reaction was maintained at 25 °C using a constant temperature bath. The time was recorded for every 5 mL of the hydrogen liberated. The volume of the hydrogen was plotted against time.

Regeneration of Ammonia Borane from Ammonium Tetramethoxyborate. A suspension of ammonium tetramethoxyborate (0.211 g, 0.0013 mol) and ammonium chloride (0.150 g, 0.0027 mol) in THF (3.5 mL) was cooled to 0 °C under a nitrogen atmosphere. To this, under stirring, a suspension of lithium aluminum hydride (0.08 g, 0.0016 mol) in THF (3.5 mL) was added, dropwise, over a period of 1 h at the same temperature. The reaction mixture was allowed to warm to RT, and the stirring was continued. The reaction was monitored by ^{11}B NMR spectroscopy. After completion of the reaction (~3 h), THF was removed under vacuum; the solid residue was stirred in diethyl ether (70 mL) at 0 °C for 1.5 h and filtered under nitrogen, and the filtrate was concentrated under vacuum to obtain ammonia borane. Yield: 0.025 g (65%) in 98% purity (hydride analysis and ^{11}B NMR spectroscopy). ^{11}B NMR (64 MHz, THF): δ −22.1 (q).

Regeneration of Ammonia Borane using Sealed Stainless Steel Reaction Vessel. A suspension of lithium aluminum hydride (0.16 g, 0.0041 mol) in THF (15 mL) was cooled to −78 °C and was added, under nitrogen, to a stainless steel reaction vessel (Parr reactor) containing a mixture of ammonium tetramethoxyborate (0.422 g, 0.00268 mol) and ammonium chloride (0.3 g, 0.0055 mol),

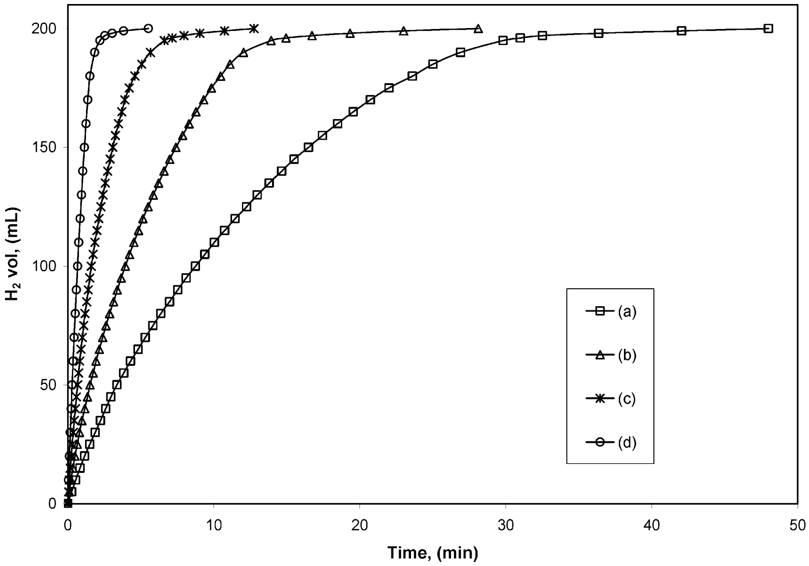

Figure 3. Hydrogen generation by methanolysis of NH_3BH_3 (2.9 mmol) at 25 °C. Plot of volume of H_2 vs reaction time using (a) 0.0625, (b) 0.125, (c) 0.25, and (d) 0.5 mol % $RuCl_3$.

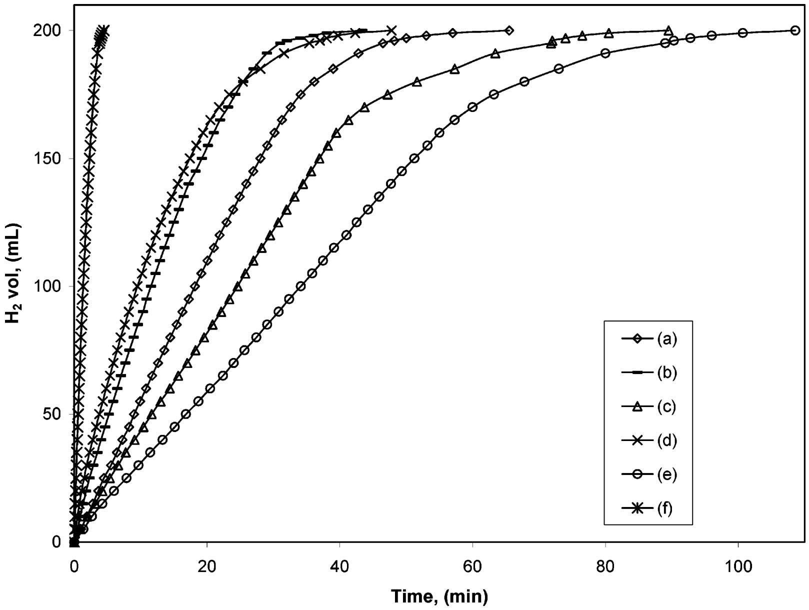

Figure 4. Hydrogen generation by methanolysis of NH_3BH_3 (2.9 mmol) at 25 °C. Plot of volume of H_2 vs reaction time with (a) 2 mol % $NiCl_2$, (b) 2 mol % $CoCl_2$, (c) 2 mol % Pd/C, (d) 2 mol % Raney Ni, (e) 2 mol % $PdCl_2$, and (f) $RhCl_3$.

and the reaction vessel was sealed immediately. The contents were stirred at ambient pressure at RT. The reaction was monitored by removing aliquots and examining them by ^{11}B NMR spectroscopy. After completion of the reaction (~8 h), THF was removed under vacuum, and the solid residue was stirred in diethyl ether (100 mL) at 0 °C for 1.5 h and was filtered under nitrogen, and the filtrate was concentrated under vacuum to obtain 0.065 g (81%) of ammonia borane in 98% purity. ^{11}B NMR (64 MHz, THF): δ −22.1 (q).

Results and Discussion

Our repeated attempts to prepare AB from lithium borohydride and ammonium chloride in diethyl ether as reported[7] resulted in ~30% yields. Hence, we examined the preparation from sodium borohydride (SBH) using various ammonium salts, initially, in THF, with the aid of ^{11}B NMR spectroscopy to determine the optimal conditions. The results are summarized in Table 1. Although we obtained excellent yields (96%) in THF at 40 °C with ammonium sulfate or ammonium formate (Scheme 1), a low concentration of the reaction medium with respect to SBH ($\leq$0.165 M) is crucial for the purity and yield of the product. Higher concentrations resulted in longer reaction times and trace amounts of impurities. It was observed that 0.3−3% of impurities were formed at 0.2−0.6 M concentrations, and the reaction time also increased to 5−20 h. The ^{11}B NMR spectrum showed the impurities as a triplet at −11 ppm (suggesting a tetracoordinated $[>BH_2]^-$ species) and a broad peak at −8 ppm. A 2−8% decrease in the yield of AB was also noted. It is

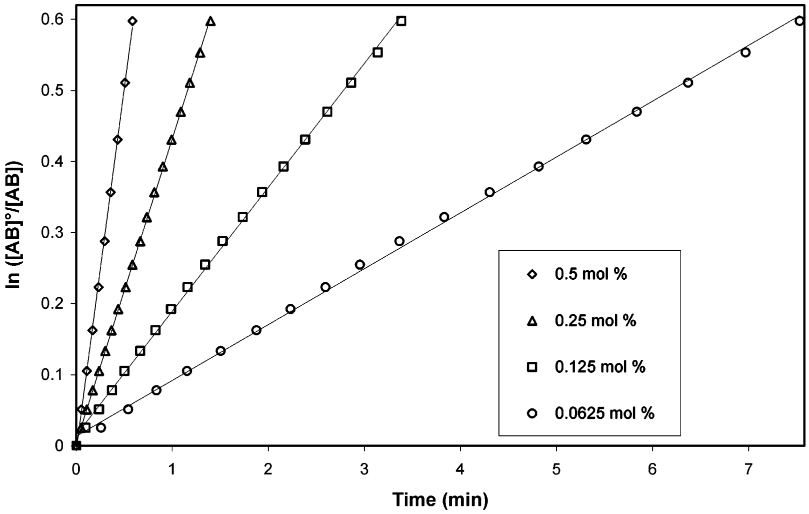

Figure 5. Methanolysis of AB (first order in [AB]). A plot of concentrations of $RuCl_3$ vs time.

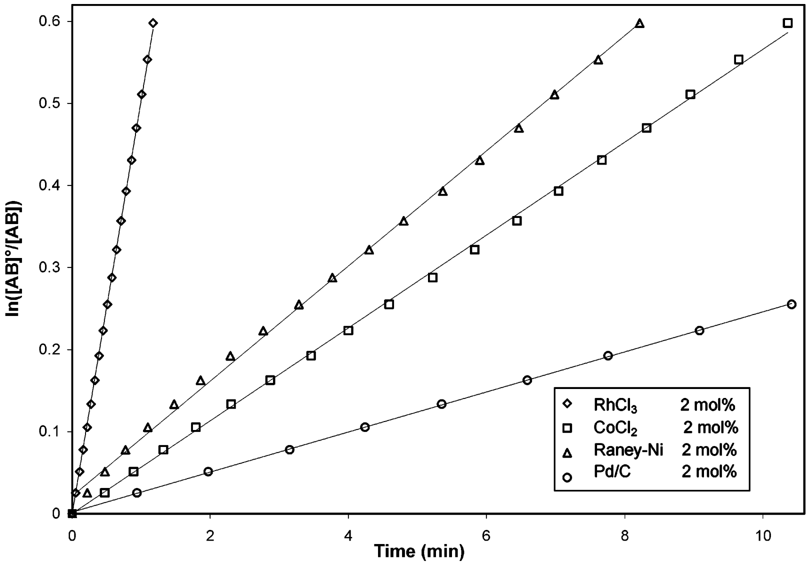

Figure 6. Methanolysis of AB (first order in [AB]) using 2 mol % $RhCl_3$, $CoCl_2$, Raney Ni, and and Pd/C.

noteworthy that the previous report for the preparation of AB from SBH and $(NH_4)_2CO_3$ required 24 h for completion, as well as purification of AB by sublimation.[6]

Scheme 1. Synthesis of Ammonia Borane from SBH and Ammonium Sulfate in THF.

$$2NaBH_4 + (NH_4)_2SO_4 \xrightarrow[40\ °C,\ 2\ h]{THF} \underset{96\%}{2NH_3{-}BH_3} + Na_2SO_4 + 2H_2$$

The low concentration of the reaction medium was a concern for scaling up the process. Hence, the effect of solvents on the reaction was examined, restricting ourselves to ammonium sulfate and formate (Table 2). The best yields and purities of AB was obtained at 40 °C in dioxane (1 M) using ammonium formate (Scheme 2). Under these optimized conditions, we carried out the preparation of AB in 10 mol scale! The solvent was recovered, distilled, and reused in subsequent AB preparation without loss of yield or purity.

Scheme 2. Synthesis of Ammonia Borane from SBH and Ammonium Formate in Dioxane.

$$NaBH_4 + HCO_2NH_4 \xrightarrow[40\ °C,\ 2\ h]{Dioxane} \underset{95\%}{NH_3BH_3} + NaHCO_2 + H_2$$

While the hydrolysis[11,12] and alcoholysis[13,14] of borohydrides and other metal hydrides have been examined over

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[11] For the hydrolysis of borohydrides see (a) Brown, H. C.; Brown, C. A. *J. Am. Chem. Soc.* **1962**, *84*, 1493. (b) Ptichkin, B. B. *Plast. Massy* **1987**, *2*, 63. (c) Korobov, I. I.; Mozgina, M. G. *Zh. Neorg. Khim.* **1992**, *37*, 1465. (d) Amendola, S. C.; Sharp-Goldman, S. L.; Janjua, M. S.; Spencer, N. C.; Kelly, M. T.; Petillo, P. J.; Binder, M. *Int. J. Hydrogen Energy* **2000**, *25*, 969. (e) Kojima, Y.; Suzuki, K.; Fukumoto, K.; Sasaki, M.; Yamamoto, T.; Kawai, Y.; Hayashi, H. *Int. J. Hydrogen Energy* **2002**, *27*, 1029. (f) Jeong, S. U.; Kim, R. K.; Cho, E. A.; Kim, H. J.; Nam, S. W.; Oh, I. H.; Hong, S. H.; Kim, S. H. *J. Power Sources* **2005**, *144*, 129.

[12] For hydrolysis of other metal hydrides, see: (a) Kong, V. C. Y.; Foulkes, F. R.; Kirk, D. W.; Hinatsu, J. T. *Int. J. Hydrogen Energy* **1999**, *24* (7), 665. (b) Laurent, J. Y.; Gaillard, F.; Capron, P.; Locatelli, D. Fr. Patent FR 2893606, 2007.

[13] For alcoholysis of borohydride, see: (a) Ramachandran, P. V.; Hazra, D; Raju, B. C.; Reddy M., V.; Bhattacharyya, A. U.S. Pat. Appl. 2005255024, 2005. (b) Davis, R. E.; Gottbrath, J. A. *J. Am. Chem. Soc.* **1962**, *84*, 895.

[14] For methanolysis of other metal hydrides, see: Morita, Y.; Suzuki, M. Jpn. Patent JP 2003206101, 2003.

the past several decades for hydrogen generation, a similar reaction of alcoholysis of AB has not been studied sufficiently. Unlike borane−THF or borane−dimethyl sulfide, amine boranes do not react violently with water.[15] AB, with a solubility of 23% in methanol,[1a] does not liberate hydrogen readily. A Pd and Raney Ni-catalyzed methanolic cleavage of borane−amine complexes has been reported.[16]

Scheme 3. Transition Metal-Catalyzed Hydrolysis of AB.

$$NH_3BH_3 + 4H_2O \xrightarrow[RT]{\text{TM catalyst}} NH_4B(OH)_4 \rightleftharpoons NH_4B_3O_3(OH)_4 \rightleftharpoons NH_4B_4O_5(OH)_4 \rightleftharpoons [NH_4]_2B_5O_6(OH)_4 + 3H_2$$

Initially, we examined the hydrolysis of AB (Scheme 3).[17] While AB is stable in water,[17a] we observed the liberation of 3 equiv of hydrogen in the presence of transition metal catalysts (Table 3). We also observed the liberation of ammonia at higher concentrations, as was determined by a change in color of the cupric sulfate solution at the point of contact in the analytical gas burette. To quantify the liberated ammonia, the generated hydrogen was passed through water at RT (Figure 1), which was then titrated against standard 0.1 N HCl. The quantity of ammonia liberated depends on the mol % and the rate of addition of the catalyst (Table 4). For example, it was observed that 15 wt % AB solution produced 6% NH_3, when 0.2 mol % $RuCl_3$ was added within 15 min, and 3% NH_3, when added, slowly, in 45 min. At low catalyst concentrations, the mode of addition did not show a significant effect on the quantity of NH_3 liberated. Thus, the same 15 wt % AB solution produced 4.4% NH_3, when 0.06 mol % $RuCl_3$ was added within 15 min, and 4% NH_3, when added within 45 min. We varied the AB and catalyst concentrations and found no liberation of NH_3, detectable by titration, with 6 wt % AB and 0.06 wt % catalyst under slow addition mode. However, we did not carry out ammonia detection using electrochemical sensors. Ammonia liberated during AB hydrolysis can be detrimental to fuel cells, which should be either curtailed or efficiently trapped.

Depending on the concentrations of AB, the ^{11}B NMR resonance of the hydrolysis reaction mixture varied between 8−16 ppm because of an equilibrium of different borate species (Scheme 3). At higher concentrations, the borate salt crystallized from the reaction solution, which showed a singlet (in H_2O) at δ 12 ppm. The structure of the crystallized salt was determined as ammonium tetraborate $\{[(NH)_4]_2[B_4O_5(OH)_4]\cdot 1.41H_2O\}$ by X-ray crystallography (Figure 2). It should be noted that the structure of borate anions are pH dependent and that such polyborate anions are formed at higher pH.[19]

Table 5. First-Order Rate Constants for the Transition Metal-Catalyzed Methanolysis of AB[a]

entry	catalyst	catalyst (mol %)	slope (min^{-1})	correlation coefficient (r^2)	rate constant (k) ($m^3\ kg^{-1}\ s^{-1}$)
1	$RuCl_3$	0.0312	0.026	0.9986	0.21×10^{-3}
2	$RuCl_3$	0.0625	0.079	0.9988	1.27×10^{-3}
3	$RuCl_3$	0.125	0.174	0.9989	5.67×10^{-3}
4	$RuCl_3$	0.250	0.428	0.9998	28.1×10^{-3}
5	$RuCl_3$	0.5	1.019	0.9993	131×10^{-3}
6	$RhCl_3$	2	0.504	0.9996	1.62×10^{-3}
7	$CoCl_2$	2	0.056	0.9992	0.18×10^{-3}
8	Pd/C	2	0.026	0.9971	0.07×10^{-3}
9	Raney Ni	2	0.070	0.9982	0.27×10^{-3}

[a] The concentration of AB in methanol was 2 M.

We then carried out the alcoholysis of AB with a series of aliphatic alcohols (see Supporting Information) and determined that methanol provides the best result. The screening of several transition metal catalysts for the methanolysis of AB (Table 5, 6) indicated that $RuCl_3$ is the catalyst of choice. It was observed that 1 mol % $RuCl_3$ liberated 3 equiv of hydrogen in ~1 min. A plot of the volume of hydrogen liberated versus the reaction time at various mol % of $RuCl_3$ and other transition metal catalysts at ambient conditions are presented in Figures 3 and 4.

The methanolysis of AB, under our experimental conditions, in the presence of $RuCl_3$, $RhCl_3$, $CoCl_2$, Pd/C, and Raney Ni was found to be first order in [AB]. However, it showed zero-order kinetics in the presence of $NiCl_2$ and $PdCl_2$. The plot of $\ln([AB]°/[AB])$ against time for the first-order reaction is shown in the Figures 5 and 6. The values of the first-order rate constant (Table 5) were determined from the slopes of the straight lines (integrated rate law for the first-order reaction, $\ln([AB]°/[AB]) = (m_{cat}k/V)t$, where V is reaction volume and m_{cat} is catalyst mass). The slopes for the zero-order reactions were obtained from the plot of $[AB]° - [AB]$ as a function of time (Figure 7). The rate constants (k) were calculated (Table 6) using the integrated rate law for the zero-order reaction ($[AB]° - [AB]) = (m_{cat}kt)/V$.

Scheme 4. $RuCl_3$-Catalyzed Methanolysis of AB.

$$5NH_3BH_3 + 22MeOH \xrightarrow[\text{RT, 1 min}]{1\%\ RuCl_3} [NH_4B(OMe)_4]_5\cdot 2MeOH + 15H_2$$

We then focused on the isolation, characterization, and recycling of the intermediate ammonium tetramethoxyborate[18] formed during the reaction. Because of the solubility of the borate salt in methanol, we treated AB with stoichiometric amounts of methanol in the presence of 1 mol % $RuCl_3$ and observed that <3 equiv of hydrogen was generated. A 15% excess is necessary for complete methanolysis (gravimetric density 3.4 wt % hydrogen) (Scheme 4). During the reaction, the crystals of the borate salt condensed on the inner wall of the condenser. Upon completion of the

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(15) AB has 26% solubility in water. A 10% water solution of ammonia borane loses 1.8% hydrogen over 4 days, 4.8% over a month, and 45% over 18 months, see ref 1a.

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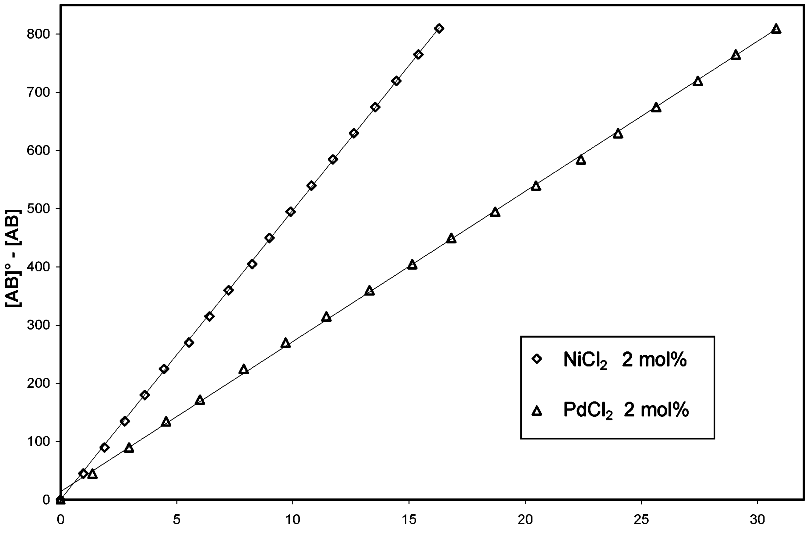

Figure 7. Methanolysis of AB (zero order in [AB]) using 2 mol % $NiCl_2$ and $PdCl_2$.

Table 6. Zero-Order Rate Constants for the Transition Metal-Catalyzed Methanolysis of AB[a]

entry	catalyst	catalyst (mol %)	slope (mol m^3 min^{-1})	correlation coefficient (r^2)	rate constant (k) (mol kg^{-1} s^{-1})
1	$NiCl_2$	2	49.72	0.9999	160×10^{-3}
2	$PdCl_2$	2	25.79	0.9996	60×10^{-3}

[a] The concentration of AB in methanol was 2 M.

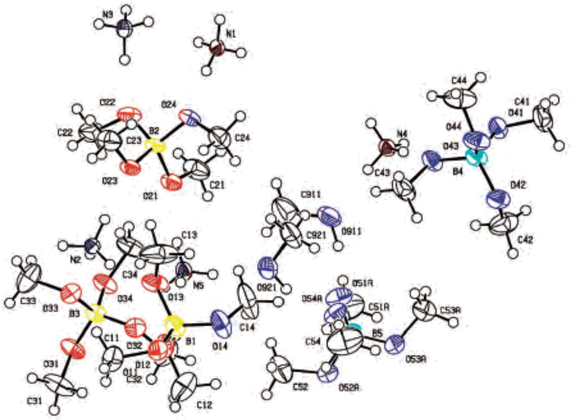

Figure 8. ORTEP diagram of $[NH_4B(OMe)_4\ ]_5{\cdot}2MeOH$ at 50% probability.

Table 7. Crystallographic Data of $\{[(NH)_4]_2[B_4O_5(OH)_4]{\cdot}1.41H_2O\}$ and $[NH_4B(OMe)_4]_5{\cdot}2MeOH$

chemical formula	$H_4B_4O_9{\cdot}1.41(H_2O){\cdot}2(H_4N)$	$C_{22}H_{88}B_5N_5O_{22}$
a	7.1997(8) Å	22.4122(9) Å
b	10.6039(10) Å	12.0086(3) Å
c	7.2604(8) Å	18,8850 (5) Å
V	548.15(10) $Å^3$	5082.7 (3) $Å^3$
Z	2	4
fw	252.75	829.02
space group	$P2_1$ (No. 4)	$Pca2_1$ (No. 29)
T	260 K	150 K
λ	0.71073 Å	Mo Kα 0.71073 Å
D_{obsd}	1.531 g cm^{-3}	1.083 g cm^{-3}
R (F_0)	0.064	0.051
R_w (F_0^2)	0.169	0.102

methanolysis (^{11}B NMR, 8.7 ppm), the crude borate was subjected to vacuum (20 Torr) at room temperature for a short period of time. Extensive drying results in the loss of the borate caused by sublimation. Careful sublimation (~50−54 °C) of the solid borate provided 87% yield of an orthorhombic crystalline material, $[NH_4B(OMe)_4]_5{\cdot}2MeOH$ (Figure 8). A unit cell contains four of the asymmetric pentamer units of ammonium borate with two methanol molecules of crystallization. The presence of sublimed borate salt in the water trap was confirmed by the ^{11}B NMR, which was quantified by titration (~1%). The ^{11}B NMR spectrum of the titrated solution showed singlet at peak at 19 ppm for the boric acid. Unlike the hydrolysis, we believe that methanolysis does not liberate NH_3. This can be probably be explained by the structure of the methanolysis product, which was confirmed by X-ray crystallography to be $[NH_4B(OMe)_4]_5{\cdot}2MeOH$ (Table 7). While the B/N ratio is 1:1 in the ammonium tetramethoxyborate from the methanolysis, it is 2:1 in the ammonium tetraborate from hydrolysis. In fact, this should account for a loss of 50 wt % of NH_3. However, we observed only 1−7% of ammonia liberation, depending on the concentrations. This may be accounted by the formation of other ammonium borate species, such as $NH_4B(OH)_4$, $NH_4[B_5O_6(OH)_4]$, and $NH_4[B_3O_3(OH)_4]$ in solution.[19b]

The recycling of the tetramethoxyborate was then undertaken to achieve an efficient recyclable hydrogen generation system from AB. In our initial attempts to reduce $NH_4B(OMe)_4$ directly to AB using metal hydrides, we obtained poor (~10%) yields with $LiAlH_4$ and sodium borohydride This is the result of the loss of ammonia from the borate salt in the presence of LAH. Upon further examination, we observed that the addition of NH_4Cl as a source of ammonia was necessary to improve the yield. Thus, the treatment of the recovered ammonium tetramethoxyborate with $LiAlH_4$ and NH_4Cl in THF for 3 h at RT and atmospheric pressure yielded 65% of AB. We improved the yield further to 81% by carrying out the reaction in a sealed reactor for 8 h (Scheme 5). The purity of AB as determined by elemental analysis and hydrogen estimation is >98%. Thus, we have

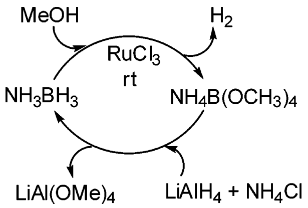

Figure 9. Ammonia−borane hydrogen cycle.

achieved the first successful hydrogen generation cycle involving ammonia borane (Figure 9).

Scheme 5. Regeneration of AB from Ammonium Tetramethoxyborate.

$$NH_4B(OMe)_4 + NH_4Cl + LiAlH_4 \xrightarrow[\substack{0\,^\circ C\text{ to RT}\\ 3-8\text{ h}}]{THF} NH_3BH_3 + Al(OMe)_3 + MeOH + H_2 + LiCl + NH_3$$

Conclusion

In summary, we have reported a 10 mol scale synthesis of ammonia borane from sodium borohydride and ammonium formate in dioxane (1 M) in near quantitative yield and purity.[20] This synthesis should aid in the progress of fuel-cell research involving AB. We have also reported the transition metal-catalyzed hydrolysis and methanolysis of AB and the isolation and characterization of crystalline ammonium borates from both of these reactions. The concentration-dependent ammonia liberation during the hydrolysis can be detrimental for fuel cell applications and has been quantified. The ammonia liberation demands low concentration AB solutions for hydrogen generation via hydrolysis, which decreases the wt % of hydrogen to ∼1%. While the recycling of AB from hydrolysis product is a multistep process (borate → $B(OH)_3$ → $B(OMe)_3$ → $NaBH_4$ → NH_3BH_3), an efficient one-pot regeneration of ammonia borane from the methanolysis intermediate, ammonium tetramethoxyborate, has been achieved.

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Supporting Information Available: Experimental details, spectral data, and X-ray crystallographic data of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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