

Acid Initiation of Ammonia–Borane Dehydrogenation for Hydrogen Storage**

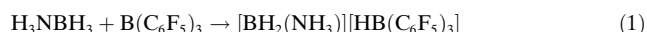
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On-board storage is a major technical barrier to the use of hydrogen as a transportation fuel.^[1,2] Ammonia–borane (H_3NBH_3 , **1**) has a hydrogen capacity of 19.6 wt %, exceeding that of gasoline and making it an attractive candidate for chemical hydrogen-storage applications.^[3] At temperatures up to 100°C, solid **1** affords a single equivalent of H_2 and aminoborane oligomers, $[\text{H}_2\text{NBH}_2]_n$.^[4] While both rate and extent of dehydrogenation are increased in nanoscaffolds^[5] and concentrated ionic-liquid solutions of **1**,^[6] catalysts will be required to meet the demands of transportation-based hydrogen storage.^[7] Transition-metal catalysts have shown promise,^[8–11] but the presence of a metal in the BNH_x “spent fuel” may complicate the required chemical regeneration of **1**. Herein we present a unique catalytic process for releasing H_2 from ammonia–borane, wherein the dehydrocoupling of **1** is initiated by small amounts of strong Lewis or Brønsted acids.

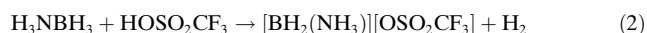
Denis et al. demonstrated that dehydrocoupling of phosphine–boranes $\text{H}_2\text{RP}\cdot\text{BH}_3$ can be catalyzed by addition of the Lewis acid tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$).^[12] They proposed formation of the reactive intermediate $\text{H}_2\text{PhP}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ by ligand exchange. Because $\text{B}(\text{C}_6\text{F}_5)_3$ is more Lewis acidic than BH_3 ,^[13] the protic character of the P–H bond is increased, enhancing its reactivity with the hydridic B–H bond of $\text{H}_2\text{PhP}\cdot\text{BH}_3$.

Although Manners and co-workers reported that $\text{B}(\text{C}_6\text{F}_5)_3$ does not catalyze the dehydrocoupling of dimethylamine–borane,^[8b] we observed reaction upon mixing of this Lewis acid with **1** with concomitant H_2 release. The ^{11}B NMR spectrum of the reaction mixture displayed a prominent peak

at $\delta = -25$ ppm, a doublet ($J_{\text{BH}} = 90$ Hz) characteristic of the anion $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ resulting from hydride abstraction [Eq. (1)].^[14] Addition of 25 mol % $\text{B}(\text{C}_6\text{F}_5)_3$ to **1** resulted in

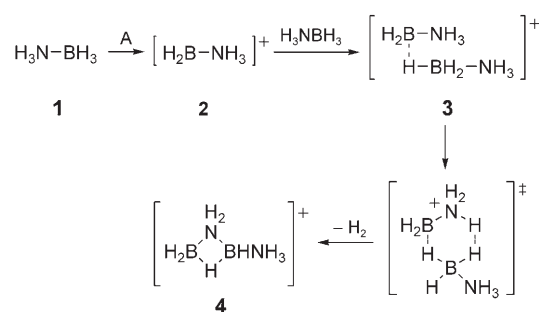


consumption of the starting material after about 24 h at 60°C with concomitant formation of an insoluble, colorless solid^[4] and 0.6 equivalents of H_2 .^[15] Similar products were obtained when the strong Brønsted acid trifluoromethanesulfonic acid (HOSO_2CF_3)^[16] was utilized. Protonolysis of the B–H bond occurred, resulting in liberation of 0.25 equivalents of H_2 (an amount equal to the catalyst loading) and generating the boronium cation $[\text{BH}_2(\text{NH}_3)(\text{L})]^+$ (**2**; $\text{L} = \text{solvent}$) [Eq. (2)].^[17–19] Subsequent dehydropolymerization liberated an additional 0.6 equivalents of H_2 .^[15]



Stoichiometric, slow addition of a dilute solution of **1** in diethyl ether to a solution of $[\text{H}(\text{OEt}_2)_2][\text{B}\{3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\}_4]^{20}$ in diethyl ether resulted in formation of the boronium salt $[\text{BH}_2(\text{NH}_3)(\text{OEt}_2)][\text{B}\{3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\}_4]$ (**2a**) in 84 % yield. The electron-deficient boron center is stabilized by one solvent molecule ($\text{L} = \text{Et}_2\text{O}$). The ^{11}B NMR chemical shift ($\delta = 0.21$ ppm) and coupling constant ($J_{\text{BH}} = 125$ Hz) are consistent with a four-coordinate boronium cation in solution.^[21] Isolation of this initiator will be invaluable for future studies of reaction kinetics and isotope effects.

The initial step of the reaction pathway is likely the interaction of boronium **2** with one equivalent of **1** to form intermediate **3** (Scheme 1). This configuration appears well-



Scheme 1. Reaction of **1** with a Lewis or Brønsted acid (**A**) results in formation of boronium cation **2**. Subsequent reaction with another equivalent of **1** results in formation of **3** with subsequent expulsion of H_2 and concomitant formation of **4**. A proposed transition state for the conversion of **3** into **4** is shown. Solvent and anion interactions have been removed for clarity.

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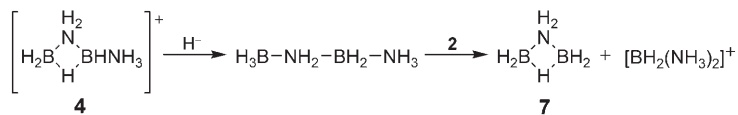
[**] We thank the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy for funding. F.H.S. thanks Los Alamos National Laboratory for a postdoctoral fellowship. D.A.D. thanks the Robert Ramsay Fund at the University of Alabama for partial support. All calculations were completed at the Alabama Super-computer Center. Martin Bluhm, Mark Bradley, and Larry Sneddon are thanked for their assistance with hydrogen quantification and helpful discussions.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

positioned for loss of H₂ with concomitant B–N bond formation. We investigated the reaction pathway in detail using density functional theory (DFT; gas phase) at the B3LYP/DZVP2 level^[22–24] utilizing the program Gaussian03.^[25] Calculations indicate that formation of intermediate **3** is strongly exothermic (–191 kJ mol^{–1}), consistent with stabilization of a cation by interaction with a neutral species (Scheme 2). In contrast, loss of hydrogen from **3** to form **4** is approximately thermoneutral ($\Delta H(298) = 5.2$ kJ mol^{–1}), and is driven by entropy ($\Delta G(298) = -23.0$ kJ mol^{–1}). Subsequent additions of **1** to the growing chain afford amino-bridged species for which four-coordination at boron is maintained after loss of H₂. The less-substituted boronium cation **5b** is favored thermodynamically ($\Delta\Delta H = -58$ kJ mol^{–1}) over the more-substituted boronium cation **5a**. The chain structure with the fewest branches (**6d**) is the most stable, although the branched structure investigated is similar in energy (**6c**: –291 kJ mol^{–1}; **6d**: –309 kJ mol^{–1}).^[26]

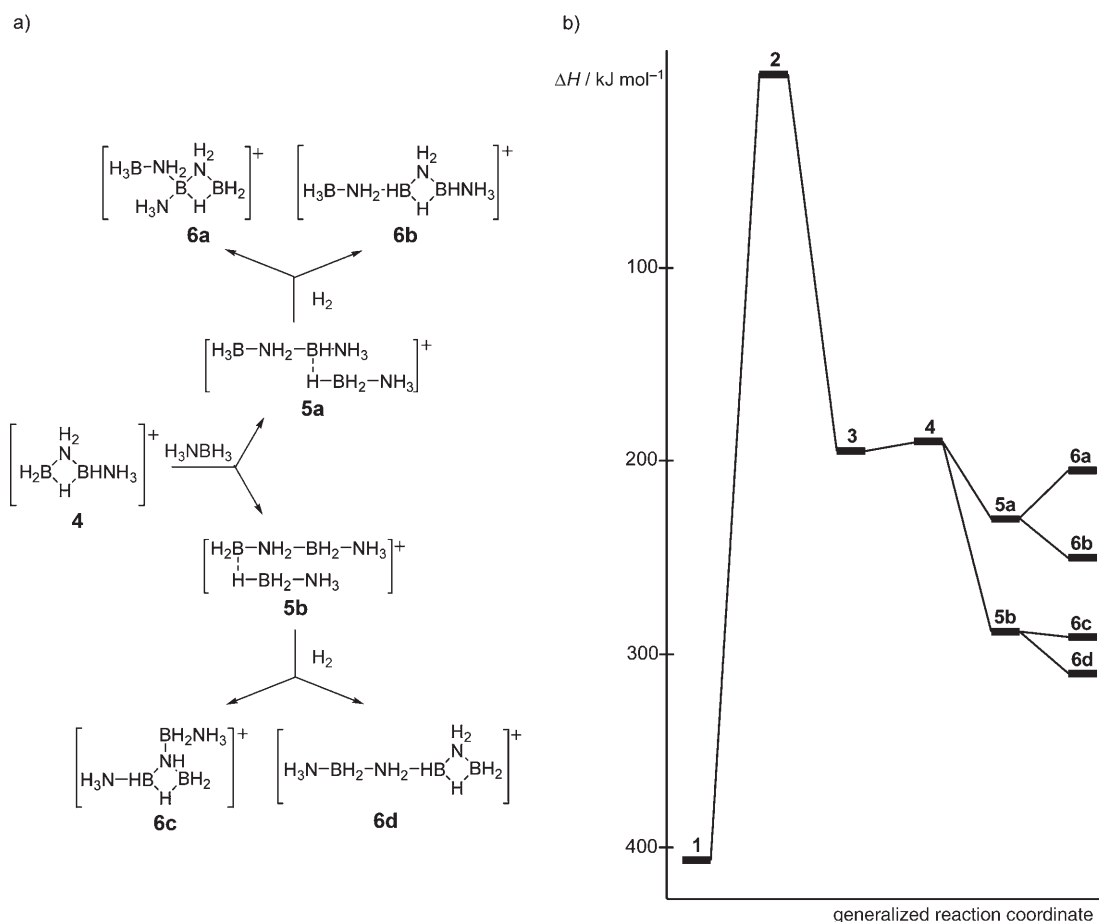
The ¹¹B NMR spectra of the product mixtures are similar to those obtained in ionic liquids where no catalyst was added.^[6] The boronium borohydride [BH₂(NH₃)₂][BH₄], an isomer of **1** that is chemically similar to **2**, has been implicated as the reaction initiator in the thermolysis of **1** in ionic liquids. As validated by ¹¹B NMR chemical shift calculations, the

species observed here and in ionic liquids are a mixture of linear and branched acyclic aminoborane oligomers. Observation of these neutral oligomers from acid-initiated dehydrogenation of **1** is indicative of rapid chain termination by hydride abstraction from **1** (or other neutral oligomers; Scheme 3).



Scheme 3. Chain termination can occur by hydride abstraction or by base transfer. Chain transfer results in termination when the cation **4**, for example, abstracts H[–] from **1** or neutral oligomers. Boronium cation **2** can abstract NH₃ from neutral species to form μ -aminodiborane **7** without H₂ evolution.

As dehydrocoupling of **1** progresses utilizing 10 mol % or more acid, a broad triplet is observed in the ¹¹B NMR spectrum at $\delta = -24$ ppm. On the basis of variable-temperature ¹¹B NMR spectroscopy, this triplet is consistent with the parent μ -aminodiborane [B₂H₅(μ -NH₂)] (**7**),^[27] not (primarily) species **4** or **6**. Formation of **7** is consistent with base (NH₃) transfer from neutral oligomers to **2** due to a rate mismatch of



Scheme 2. a) Possible reaction pathways investigated using DFT calculations. b) Calculated gas-phase energies $\Delta H(298 \text{ K})$ (and free energies $\Delta G(298)$ in parentheses) of possible reaction intermediates and products. Energies (in kJ mol^{–1}) are relative to that for **2** + [HB(C₆F₅)₃][–] at 0 kJ mol^{–1} for the following ions: **1** + B(C₆F₅)₃, –407 (–377); **3**, –195 (–146); **4**, –190 (–218); **5a**, –230 (–185); **5b**, –288 (–249); **6a**, –205 (–235); **6b**, –250 (–275); **6c**, –291 (–318); **6d**, –309 (–377).

the initiation and propagation steps. As in the chain-transfer mechanism, the reaction depicted in Scheme 3 results in consumption of **1** without formation of additional H₂ [Eq. (3),



a simplification of Scheme 1 and 2]. By reducing the ratio of acid to **1**, then, we should reduce the formation of **7** and increase the amount of hydrogen evolved. Indeed, use of 0.5 mol% B(C₆F₅)₃ resulted in significantly less **1** being diverted to **7** and a larger amount (ca. 1.1 equiv) of H₂ generated (Table 1).

Table 1: Reactivity of **1** with acids.

Acid	Loading [mol %]	Conc. of 1 [M]	T [°C]	t [h]	H ₂ [equiv]
B(C ₆ F ₅) ₃	25	0.14 ^[a]	60	24	0.6
B(C ₆ F ₅) ₃	0.5	2.6 ^[b]	60	20	1.1
HOSO ₂ CF ₃	25	0.13 ^[a]	60	18	0.8
HOSO ₂ CF ₃	0.5	6.2 ^[c]	60	18	1.3
HCl	0.5	2.9 ^[c]	60	20	1.2

[a] Reaction in glyme. [b] Reaction in tetraglyme. [c] Reaction in diglyme.

Cyclic products are generated in these reactions, whereas preliminary calculations (Scheme 2) indicated linear and branched acyclic products. To probe this apparent dichotomy, synthesis of [H₂NBH₂]_n using the method of Wolf and co-workers^[4b] was undertaken followed by solution thermolysis of this species. The ¹¹B NMR spectra of [H₂NBH₂]_n indicated limited solubility in diglyme, but revealed cyclic products after as little as 2.5 h at 60 °C. This differs from solid-state thermolysis, whereby no decomposition of [H₂NBH₂]_n is observed at temperatures below about 120 °C.^[4c] An examination of the linear species BH₃NH₂BH₂NH₂BH₂NH₃ (**8**) at the DFT and molecular orbital theory levels indicates that cyclization can be initiated by coiling.^[28] Formation of a short B–H···H–N interaction,^[29,30] oriented to release H₂, stabilizes **8** by 97.1 kJ mol^{−1}. Therefore, in solution dehydrocyclization is facile, whereas the same process is precluded in the solid state as a result of hindered molecular motion.

In summary, we have shown that strong Lewis and Brønsted acids initiate dehydrocoupling of **1** under mild conditions. The novel hydride-abstraction pathway differs from that proposed by Denis et al. for dehydropolymerization of phosphine–boranes proceeding via a H₂RP·B(C₆F₅)₃ intermediate.^[12] This difference likely stems from the stronger B–N versus B–P dative bonds.^[31,32] The formation of acyclic aminoborane oligomers by chain transfer is followed by facile dehydrocyclization above 60 °C to afford borazine and additional H₂. The boronium borohydride [BH₂(NH₃)₂][BH₄][−] implicated in thermolyses of **1** in ionic liquids is structurally similar to the boronium cations discussed here, and isolation of boronium salt **2a** will permit further studies. As we have been able to effect these reactions using the low-molecular-weight acid HCl in nonvolatile polyethers, and we postulate that use of nonvolatile acids such as polyphosphoric acid or

solid-supported acids will initiate dehydropolymerization of **1**, this chemistry may be promising for automotive applications if energy-efficient regeneration processes can be developed.

Experimental Section

General method for the reaction of **1** with acids: A solution of an acid was prepared in diglyme and placed in a Schlenk flask. With the side arm of the Schlenk flask attached to the gas burette, solid **1** was rapidly added using a Merlic solid addition funnel. The reaction vessel was then heated using an oil bath. A detailed synthetic protocol and analytical information for **2a** can be found in the Supporting Information along with variable-temperature ¹¹B NMR data supporting the assignment of compound **7**.

Computational details: Geometries were optimized and frequencies were calculated to ensure minima using density functional theory (DFT) with the B3LYP exchange–correlation functional^[22,23] and the polarized double-ζ/DZVP2 basis set.^[24] The NMR chemical shifts were calculated at the DFT level in the gauge-invariant atomic orbital (GIAO) formalism^[33] with a polarized triple-ζ basis set^[34] and the B3LYP functional. All calculations were done with the program Gaussian03^[25] on a Cray XD1 computer. Estimates of the salt-formation energies for [2][X] (X[−] = CF₃SO₂O[−], [HB(C₆F₅)₃][−]) were made on the basis of the relationship given by Jenkins et al.^[35,36] Calculated geometries of **1–6** can be found in the Supporting Information.

Received: August 11, 2006

Published online: November 28, 2006

Keywords: Brønsted acids · cations · density functional calculations · hydrogen · Lewis acids

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