VIP Hydrogen Storage

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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, $[H_2NBH_2]_n$.[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 $H_2RP{\cdot}BH_3$ can be catalyzed by addition of the Lewis acid tris(pentafluorophenyl)borane ($B(C_6F_5)_3$).[12] They proposed formation of the reactive intermediate $H_2PhP{\cdot}B(C_6F_5)_3$ by ligand exchange. Because $B(C_6F_5)_3$ 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 $H_2PhP{\cdot}BH_3$.

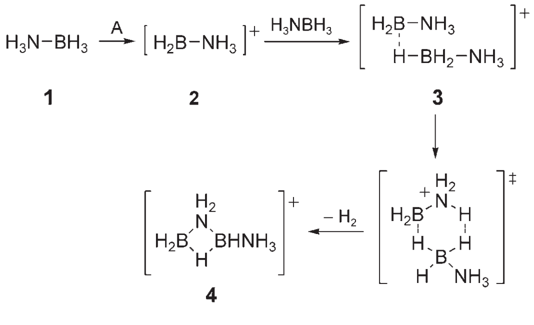
Although Manners and co-workers reported that $B(C_6F_5)_3$ does not catalyze the dehydrocoupling of dimethylamine–borane,[8b] we observed reaction upon mixing of this Lewis acid with **1** with concomitant H_2 release. The ^{11}B NMR spectrum of the reaction mixture displayed a prominent peak at $\delta = -25$ ppm, a doublet ($J_{B,H} = 90$ Hz) characteristic of the anion $[HB(C_6F_5)_3]^-$ resulting from hydride abstraction [Eq. (1)].[14] Addition of 25 mol% $B(C_6F_5)_3$ 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 $[BH_2(NH_3)(L)]^+$ (**2**; L = solvent) [Eq. (2)].[17–19] Subsequent dehydropolymerization liberated an additional 0.6 equivalents of H_2.[15]

$$H_3NBH_3 + B(C_6F_5)_3 \rightarrow [BH_2(NH_3)][HB(C_6F_5)_3] \qquad (1)$$

$$H_3NBH_3 + HOSO_2CF_3 \rightarrow [BH_2(NH_3)][OSO_2CF_3] + H_2 \qquad (2)$$

Stoichiometric, slow addition of a dilute solution of **1** in diethyl ether to a solution of $[H(OEt_2)_2][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$[20] in diethyl ether resulted in formation of the boronium salt $[BH_2(NH_3)(OEt_2)][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ (**2a**) in 84% yield. The electron-deficient boron center is stabilized by one solvent molecule (L = Et_2O). The ^{11}B NMR chemical shift ($\delta = 0.21$ ppm) and coupling constant ($J_{B,H} = 125$ 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 borenium 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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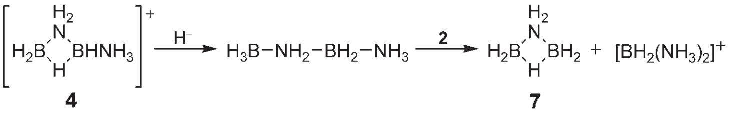
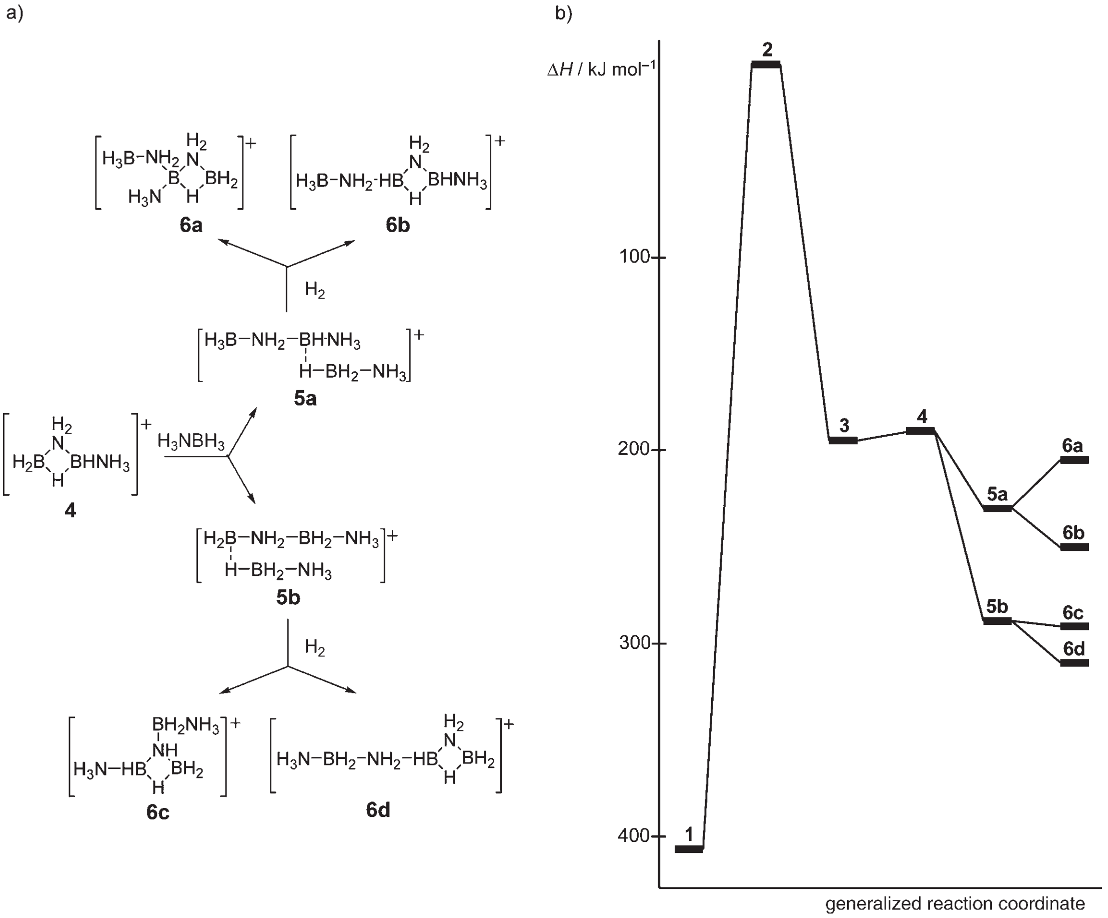
positioned for loss of H_2 with concomitant B–N bond formation. We investigated the reaction pathway in detail using density functional theory (DFT; gas phase) at the B3LYP/DZVP2 level[22–24] utilizing the program Gaussian03.[25] Calculations indicate that formation of intermediate **3** is strongly exothermic ($-191\ \mathrm{kJ\,mol^{-1}}$), 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 ($\Delta H(298) = 5.2\ \mathrm{kJ\,mol^{-1}}$), and is driven by entropy ($\Delta G(298) = -23.0\ \mathrm{kJ\,mol^{-1}}$). Subsequent additions of **1** to the growing chain afford amino-bridged species for which four-coordination at boron is maintained after loss of H_2. The less-substituted borenium cation **5b** is favored thermodynamically ($\Delta\Delta H = -58\ \mathrm{kJ\,mol^{-1}}$) over the more-substituted borenium cation **5a**. The chain structure with the fewest branches (**6d**) is the most stable, although the branched structure investigated is similar in energy (**6c**: $-291\ \mathrm{kJ\,mol^{-1}}$; **6d**: $-309\ \mathrm{kJ\,mol^{-1}}$).[26]

The ^{11}B NMR spectra of the product mixtures are similar to those obtained in ionic liquids where no catalyst was added.[6] The boronium borohydride $[BH_2(NH_3)_2][BH_4]$, 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 ^{11}B 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 NH_3 from neutral species to form μ-aminodiborane **7** without H_2 evolution.

As dehydrocoupling of **1** progresses utilizing 10 mol % or more acid, a broad triplet is observed in the ^{11}B NMR spectrum at $\delta = -24$ ppm. On the basis of variable-temperature ^{11}B NMR spectroscopy, this triplet is consistent with the parent μ-aminodiborane $[B_2H_5(\mu\text{-}NH_2)]$ (**7**),[27] not (primarily) species **4** or **6**. Formation of **7** is consistent with base (NH_3) 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 ΔH(298 K) (and free energies ΔG(298) in parentheses) of possible reaction intermediates and products. Energies (in $\mathrm{kJ\,mol^{-1}}$) are relative to that for **2** + $[HB(C_6F_5)_3]^-$ at $0\ \mathrm{kJ\,mol^{-1}}$ for the following ions: **1** + $B(C_6F_5)_3$, −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 H_2 [Eq. (3),

$$3\,H_3NBH_3 + \text{acid} \rightarrow H_2 + [BH_2(NH_3)_2]^+ + B_2H_5(\mu\text{-}NH_2) \qquad (3)$$

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% $B(C_6F_5)_3$ resulted in significantly less **1** being diverted to **7** and a larger amount (ca. 1.1 equiv) of H_2 generated (Table 1).

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

Acid	Loading [mol%]	Conc. of **1** [M]	T [°C]	t [h]	H_2 [equiv]
$B(C_6F_5)_3$	25	0.14[a]	60	24	0.6
$B(C_6F_5)_3$	0.5	2.6[b]	60	20	1.1
$HOSO_2CF_3$	25	0.13[a]	60	18	0.8
$HOSO_2CF_3$	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 $[H_2NBH_2]_n$ using the method of Wolf and co-workers[4b] was undertaken followed by solution thermolysis of this species. The ^{11}B NMR spectra of $[H_2NBH_2]_n$ 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 $[H_2NBH_2]_n$ is observed at temperatures below about 120 °C.[4c] An examination of the linear species $BH_3NH_2BH_2NH_2BH_2NH_3$ (**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 H_2, 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 $H_2RP{\cdot}B(C_6F_5)_3$ 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 H_2. The boronium borohydride $[BH_2(NH_3)_2][BH_4]$ 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 ^{11}B 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] ($X^- = CF_3SO_2O^-$, $[HB(C_6F_5)_3]^-$) 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.

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