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Chemical Hydrogen Storage

Efficient Regeneration of Partially Spent Ammonia Borane Fuel**

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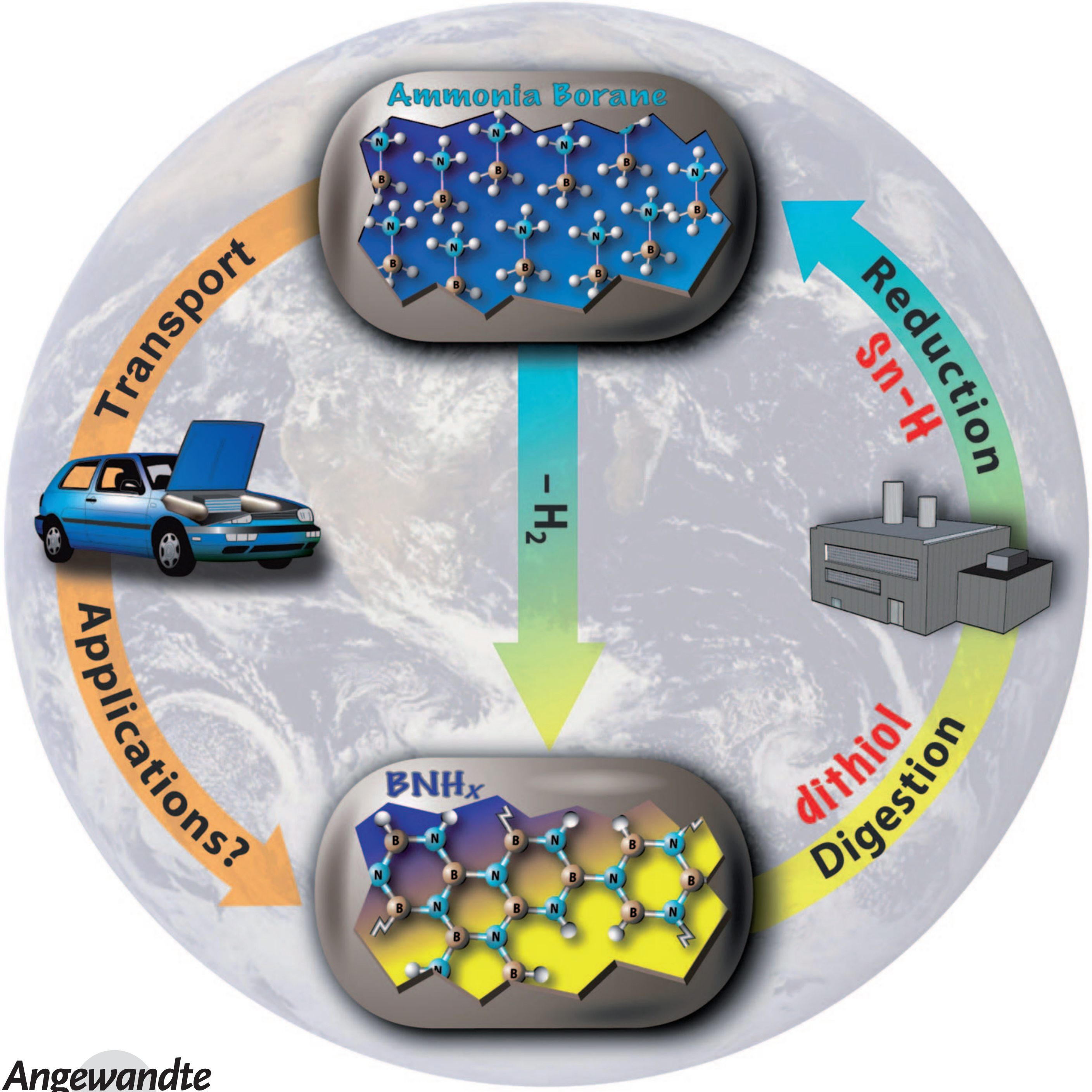

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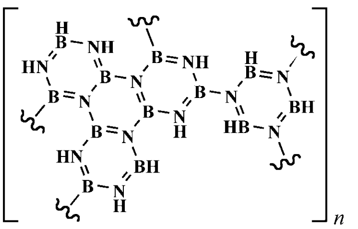
A necessary target in realizing a hydrogen economy is the storage of H_2 for controlled delivery, presumably to an energy-producing fuel cell.[1] In this vein, the U.S. Department of Energy's (DOE) Centers of Excellence (CoE) in Hydrogen Storage have pursued different methodologies, including metal hydrides, chemical hydrides, and sorbents, for the expressed purpose of supplanting gasoline's current driving range of over 300 miles (ca. 500 km). Chemical hydrogen storage has been dominated by one appealing material, ammonia borane ($H_3B{-}NH_3$, AB), owing to its high gravimetric capacity of hydrogen (19.6 wt %) and low molecular weight (30.7 $g\,mol^{-1}$). AB has both hydridic and protic moieties, yielding a material from which H_2 can be readily released.[2] As such, a number of publications have described H_2 release from amine boranes, yielding various rates depending on the method applied.[3–6] The viability of any storage system is critically dependent on efficient recyclability, but reports on the latter subject are sparse.[1,7–10] For example, the DOE recently decided to no longer pursue the use of $NaBH_4$ as a H_2 storage material, in part because of inefficient regeneration. We thus endeavored to find an energy-efficient regeneration process for the spent fuel from H_2-depleted AB.

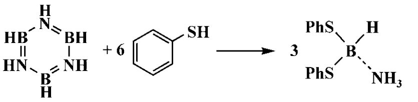
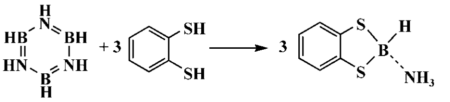
Although spent fuel composition depends on the dehydrogenation method,[3,5] we have focused our efforts on the spent fuel resulting from metal-based catalysis, which has to date shown the most promise to meet the DOE H_2 storage requirements for release rate and extent.[11] Although the first transition-metal-catalyzed dehydrogenation of AB generated many products,[12] more recent metal catalysts have produced single products, the fastest rates for a single equivalent of H_2 released from AB,[13] and the greatest extent of H_2 release (up to 2.5 equiv of H_2 can be produced within 2 h).[5] While ongoing work is being carried out to tailor the composition of spent AB fuel, we have developed a method for regenerating the predominant product, polyborazylene (PB, Scheme 1), resulting from dehydrogenation by nickel carbene catalysts.

Our approach utilizes reagents which avoid the formation of thermodynamically stable B–O bonds and the subsequent need for high-energy reducing agents. Thiols were attractive, as B–S bonds are weaker than analogous B–O bonds and the acidity of the SH moiety could aid the reaction. On the basis of DFT calculations for the gas phase, coupled with experimental data or estimates of the heats of vaporization, benzenedithiol was predicted to be a better reagent than thiophenol for the reaction with borazine, a computational surrogate for PB, where the products are presumed to retain the B–H bond (Table 1, see the Supporting Information for details).



Scheme 1. Representative structure of polyborazylene (PB).

Table 1: Estimates of reaction energies for digestion.

Reaction	ΔH (298 K)[a]
	42.2/25.1
	−20.4/0.5

[a] Condensed-phase/gas-phase values in $kcal\,mol^{-1}$.

When benzenedithiol and PB were heated at reflux in THF, 90 % of the PB had reacted after 12 h, as judged by the ^{11}B NMR spectrum, which showed two new resonances. The upfield resonance ($\delta = -5.6$, d, $^{1}J_{B\text{-}H} = 128$ Hz) was identified as $(C_6H_4S_2)B{-}H{\cdot}(NH_3)$ (**1**) by independent synthesis as well as by comparison to the chemical shift calculated by DFT (see the Supporting Information). The downfield resonance ($\delta =$ 10.5 ppm, s) exhibits a similar chemical shift to $Li[B(C_6H_4S_2)_2]$,[14] suggesting that $[NH_4][B(C_6H_4S_2)_2]$ is formed (this assignment is consistent with the calculated NMR spectrum, see the Supporting Information). Attempts to make this product independently from $(C_6H_4S_2)B{-}H{\cdot}(NH_3)$ and benzenedithiol failed to produce a pure material even under driving conditions (heat and gas removal by freeze–pump–thaw cycles). When $Li[B(C_6H_4S_2)_2]$ was prepared independently according to the literature procedure and examined by ^{11}B NMR spectroscopy, the same resonance ($\delta =$ 10.5 ppm) was observed, in contrast to that reported ($\delta =$ 12.1 ppm) in the literature.[14] Both resonances (at $\delta = -5.6$ and 10.5 ppm) are also observed in the reaction of borazine and benzenedithiol, along with concomitant H_2 formation. This observation suggests that $[NH_4][B(C_6H_4S_2)_2]$ might originate from reaction of benzenedithiol and $(C_6H_4S_2)$-$B{-}H{\cdot}(NH_3)$ as well as any H_2-depleted boron contained within the spent fuel. The full digestion reaction supported by our observations is depicted in Scheme 2. A feature of the first step in this cycle requires highlighting: some of the

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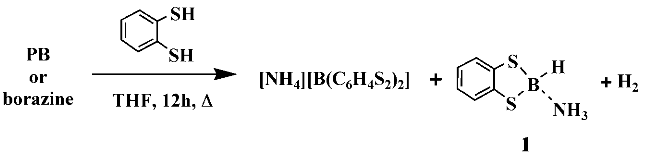
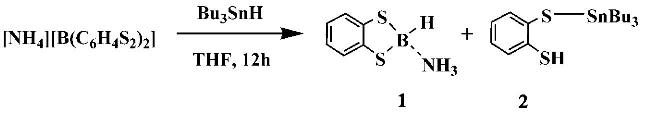


Scheme 2. Digestion of PB or borazine with benzenedithiol.

nitrogen in the spent fuel is transformed into NH_3, which is subsequently retained by $(C_6H_4S_2)B{-}H{\cdot}(NH_3)$. This process contrasts with other proposed methods, which solely generate NH_4^+ salts (which require thermal cracking to release and recycle NH_3).[8]

To transform the products of Scheme 2 into AB, a reductant is required. Bu_3SnH was judged to be a good starting point, as the reagent is commercially available and a literature report suggested a possible Bu_3SnH regeneration method by decarboxylation of a tin formate.[15] When Bu_3SnH is added to the mixture of products in Scheme 2, $[NH_4][B(C_6H_4S_2)_2]$ is fortuitously transformed into $(C_6H_4S_2)B{-}H{\cdot}(NH_3)$ (Scheme 3, ^{11}B NMR spectrum in Figure 1). The other product is $C_6H_4SH(S{-}SnBu_3)$ (**2**), as observed by ^{119}Sn NMR spectroscopy and verified by an independent synthesis from benzenedithiol and Bu_3SnH (Figure S1 in the Supporting Information). Thus in two steps, we can convert PB into a single new boron-containing product.



Scheme 3. Reduction of $[NH_4][B(C_6H_4S_2)_2]$ with Bu_3SnH.

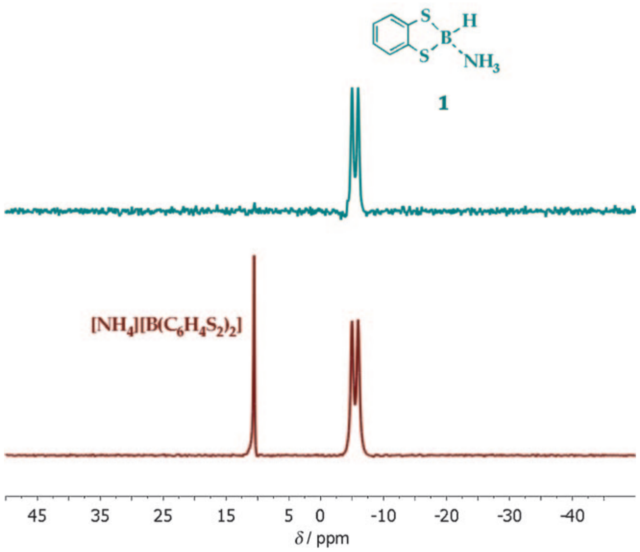
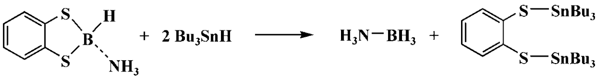
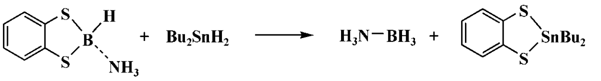


Figure 1. Reduction of $[NH_4][B(C_6H_4S_2)_2]$ with Bu_3SnH. Bottom plot is the ^{11}B NMR spectrum of $(C_6H_4S_2)B{-}H{\cdot}(NH_3)$ (**1**) and $[NH_4][B(C_6H_4S_2)_2]$; top plot is the spectrum of the resulting $(C_6H_4S_2)B{-}H{\cdot}(NH_3)$ after reduction with Bu_3SnH.

Table 2: Estimates of reaction energies for reduction.

Reaction	ΔH (298 K)[a]
	−3.7/2.8
	−9.7/0.8

[a] Condensed-phase/gas-phase values in kcal mol^{-1}.

Subsequent replacement of the dithiolate ligand in $(C_6H_4S_2)B{-}H{\cdot}(NH_3)$ with hydride to regenerate AB proved more difficult. A series of hydride sources were examined, all of which either over-reduced the boron to borohydride or did not react at all. We hypothesized that overcoming the chelate effect of the dithiolate ligand in the first reaction shown in Table 2 might be a substantial problem and thus screened suitable hydrides using theory. DFT calculations of the reactions of Bu_3SnH and Bu_2SnH_2 (Table 2) were consistent with this hypothesis and predicted that Bu_2SnH_2 should react more favorably on the basis of thermodynamics. Experiments subsequently confirmed that $(C_6H_4S_2)B{-}H{\cdot}(NH_3)$ was transformed into AB using a slight excess of Bu_2SnH_2 (Figure 2), with concomitant formation of $Bu_2Sn(C_6H_4S_2)$ (**3**, Figure 2 in the Supporting Information). The absence of borohydride in this hydride transfer makes this reaction very significant.

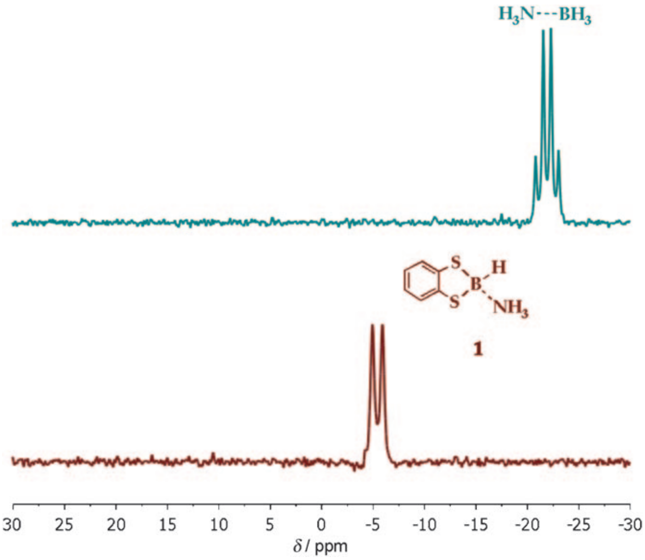
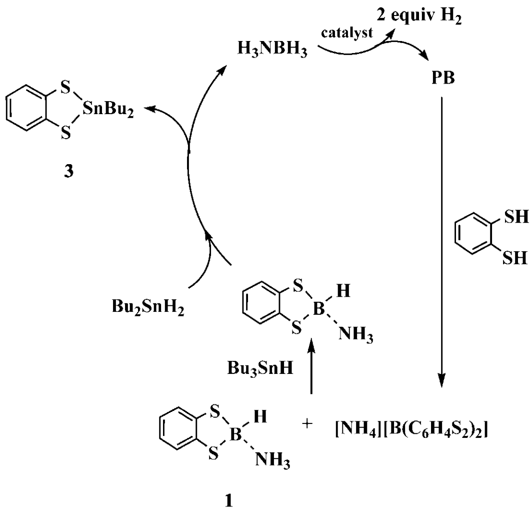


Figure 2. Reduction of $(C_6H_4S_2)B{-}H{\cdot}(NH_3)$ (**1**) with Bu_2SnH_2. Bottom plot is the ^{11}B NMR spectrum of $(C_6H_4S_2)B{-}H{\cdot}(NH_3)$, top plot is the spectrum of AB after reduction.

Practically, the first step in this regeneration cycle is difficult to optimize because of the apparent side reaction that results in $[NH_4][B(C_6H_4S_2)_2]$ formation. Therefore, to obtain an estimate of the best possible AB yield, excess Bu_3SnH was used after the digestion step both to consume unreacted benzenedithiol and to convert any $[NH_4][B(C_6H_4S_2)_2]$ into

$(C_6H_4S_2)B{-}H{\cdot}(NH_3)$. The thermal instability of Bu_2SnH_2 prompted stepwise addition of excess reductant in the final step to ensure maximum yield of AB. Using this methodolgy, an overall yield of 67 % isolated AB was obtained on our first attempt. The complete regeneration cycle is shown in Scheme 4.



Scheme 4. Demonstrated off-board regeneration scheme for spent ammonia borane.

As part of the DOE Chemical Hydrogen Storage CoE, we would like to have a method for differentiating (to a first approximation) the various regeneration schemes in the literature and estimating which processes might be inefficient if thoroughly evaluated with all reagents recycled. To estimate the optimum energetic efficiency for AB regeneration schemes, Equation (1) has been developed on the basis of the energy of oxidation for one mole of H_2 to form H_2O (57.8 kcal).

$$\text{efficiency} = \frac{(\text{equiv } H_2 \text{ stored})(57.8)}{(\text{equiv } H_2 \text{ used})(57.8) + \sum(\Delta H_{\text{endo}}) - (\%\ \text{heat recovery}) \sum(-\Delta H_{\text{exo}})} \quad (1)$$

Using Equation (1), our regeneration process in which all reagents and by-products are recycled has a theoretical peak energy efficiency that is higher than that of the only other peer-reviewed account of AB regeneration (Table 3, see the Supporting Information for complete equations). We realize that other factors (upscale yield, engineering) will play a significant role in the implementation of any regeneration process on a large scale.

Table 3: Efficiency estimates for AB regeneration.

Regeneration process	Efficiency (0 % heat recovery)
$NH_4B(OMe)_4 + 3\,H_2 \rightarrow H_3N{-}BH_3 + 4\,MeOH$[10]	46 %
$\frac{1}{3}\,B_3N_3H_6 + 2\,H_2 \rightarrow H_3N{-}BH_3$	65 %

In conclusion, we have shown that one form of spent AB fuel, polyborazylene, can be regenerated efficiently in a one-pot process by the stepwise addition of appropriate digesting and reducing agents. A unique feature of the described process is the formation of NH_3, which is retained by some of the digested species. Future reports will detail a more complete regeneration cycle, including the recycling of the tin by-product, use of H_2 as the energy source, and improved overall efficiencies.

Experimental Section

Synthetic details and characterization of compounds **1**–**3** are given in the Supporting Information. All reactions were performed in an inert atmosphere using standard Schlenk line and glovebox techniques. Ethereal solvents and toluene were distilled from Na/benzophenone ketyl radical. ^1H (400 MHz), ^{13}C (100 MHz), ^{11}B (128 MHz), and ^{119}Sn (149 MHz) NMR spectra were recorded at room temperature (unless otherwise noted) on a Bruker AVANCE 400 MHz spectrometer. ^1H spectra were referenced to the signal of residual ^1H nuclei in the deuterated solvent and ^{13}C NMR to solvent ^{13}C signal. ^{119}Sn NMR spectra were referenced to Me_4Sn. ^{11}B NMR spectra were referenced to an internal $BF_3{\cdot}$etherate standard placed in a stem coaxial insert (Wilmad). 1,2-benzenedithiol (96 % Acros) was sublimed prior to use and stored cold (−20 °C). Polyborazylene (PB) was formed by the slow decomposition of borazine, received from Gelest. $n\text{Bu}_2SnH_2$ was prepared by the literature method, distilled, and stored in the absence of light at −20 °C.[16]

Regeneration of AB from polyborazylene: PB (0.049 g, 0.61 mmol) was dissolved in THF (20 mL) and combined with 1,2-benzenedithiol (0.260 g, 1.83 mmol). This mixture was heated overnight at 60 °C. ^{11}B NMR spectroscopy indicated consumption of PB and formation of two new peaks corresponding to **1** and $[NH_4][B(C_6H_4S_2)_2]$. Excess Bu_3SnH (240 μL, 0.9 mmol) was added to reduce $[NH_4][B(C_6H_4S_2)_2]$ to **1** and convert unreacted benzenedithiol to **3**. This solution was heated to 60 °C before the addition of $n\text{Bu}_2SnH_2$ (1020 μL, 4.86 mmol) in four portions over 40 min, reducing **1** to AB (0.038 g, 67 %), which was isolated by washing with toluene. ^{11}B and ^{119}Sn NMR spectra indicate no undesirable by-products with the isolated AB.

Reaction of borazine and 1,2-benzenedithiol: Borazine (0.015 g, 0.186 mmol) and 1,2-benzenedithiol (0.080 g, 0.559 mmol) were combined in THF (0.75 mL) and heated to 65 °C overnight. The resulting ^{11}B NMR spectrum revealed two resonances, $\delta = 10.5$ ppm (s) and $\delta = -5.6$ ppm (d, 128 Hz). When the headspace gas was sampled by GC, more H_2 gas was detected than in the control sample (only borazine and solvent).

Computational details: The calculations were performed at the DFT level as described in the Supporting Information. Heats of formation in the gas-phase compounds were obtained from isodesmic reactions, and COSMO-RS predictions[17] of the boiling points were used to estimate vaporization enthalpies to obtain heats of formation of the liquid.

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