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Communication

Enabling Ammonia-Borane: Co-oligomerizaiton of Ammonia-Borane and Amine-Boranes Yield Liquid Products

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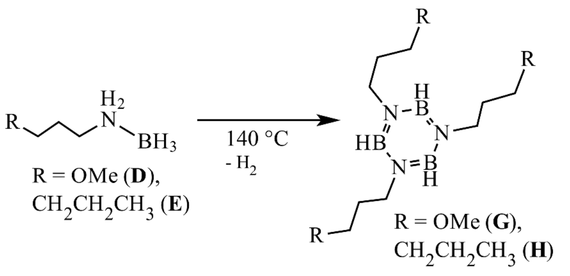
In contrast to neat ammonia borane (AB), the thermal decomposition of AB with N-substitutted amine-boranes yields a liquid product after extended heating and H_2 release. NMR and GPC data indicate that co-oligomerization has occurred. These results show promise for developing high energy density AB-based fuel formulations for automotive applications.

In an effort to supplant the current fossil fuel-based energy paradigm for transportation, the United States Department of Energy (US-DOE) greatly increased its focus on hydrogen (H_2) as an alternative in 2005.[1, 2] As a result many automobile manufacturers now have a proton exchange membrane-based fuel cell vehicle operating on compressed H_2.[3] US-DOE recognized that deployment of compressed H_2 technologies would be an interim solution due to insufficient gravimetric and volumetric capacities, and set forth rigorous system and material standards to find a longer term answer.[4, 5] Initially championed by the pioneering work of Wolf[6-8] and continued by US-DOE, ammonia-borane (H_3BNH_3, AB) was shown as promising next generation H_2 storage medium, primarily because of the large quantity of H_2 stored (19.6 wt. % H_2, ~15% usable) and good stability.[9] The solid-state nature of AB impedes loading/unloading from a vehicle; even 'liquid' formulations became solid after extensive H_2 release.[10-12] Although long-term efforts are underway to address more fuel needs,[13] the most promising ideas still suffer from low energy density, instability, or high cost.[2, 13-15] Chemical hydrogen storage also requires off-board regeneration, a topic discussed extensively elsewhere.[16, 17] Based on previous work demonstrating reaction of AB with amineboranes solvent-free[18, 19] and in solvents,[19, 20] we saw an opportunity to develop AB based fuels with higher energy density that did not solidify after H_2 evolution.



Scheme 1. Substituted borazines (G, H) formed after heating amineboranes (D, E)

To make an inexpensive fuel, amineboranes derived from abundant alkyl and ether functionalized amines were targeted using a preparation similar to that described in the literature.[21] The resulting 3-methoxypropylamine borane (**D,** 3.9 usable wt. % H_2) and hexylamineborane (**E,** 3.5 usable wt. % H_2) were obtained in high yields as viscous, colorless oils.[22] **D** and **E** release H_2 slowly, only losing 0.2-0.5% mass (7-13% stored H_2 if only H_2 is released) after 24 h @ 30 °C (see ESI); this poses an issue on a larger scale as periodic venting to the fuel cell would be required. DSC experiments indicate two exothermic events for each amineborane, without the endotherm attributed to AB melting.[6] The magnitude of the first exotherm, -26.8 kJ/mol H_2 for **E** and -22.9 kJ/mol H_2 for **D**, is consistent with theoretical predictions[13] and similar to that measured for AB (-21.7 kJ/mol H_2).[6] and other amineboranes, except ethylenediamine-bisborane.[23]

To gauge whether these amineboranes can release their stored H_2 and remain liquid for facile removal from a vehicle, each was heated for a prolonged period (140 °C, 8 h). In all cases the product is a colorless oil. ^{11}B NMR for the product of **E** indicates a broad peak at 34 ppm, in the same region as borazine[24] and

AB:R-NH$_2$ Ratio	**D**	**E**
1:3	oil	oil
1:1	oil	oil
3:1	solids	solids

Table 1. Phase of final products (T = 25 °C) from AB/amineborane decomposition

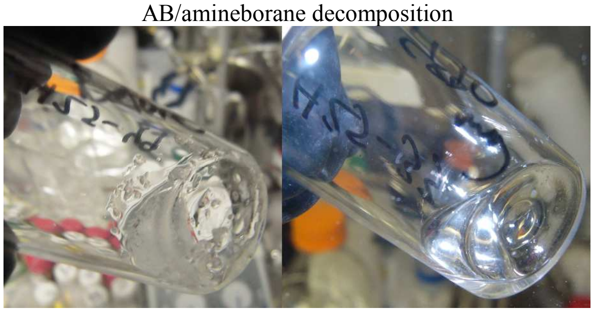


Fig. 1. 1:1 blend of AB:**E** before H_2 release (left) and after extended heating (right)

substituted borazines.[21, 24] Unlike previous borazines, no splitting information could be obtained from the coupled ^{11}B NMR experiment, however, a $^1H\{^{11}B\}$ NMR experiment identifies a peak at +4.8 ppm resulting from the B-H resonance. Integration yields a 1:2.3:2.4:6.5:2.7 ratio, consistent with the $B(H)NCH_2(CH_2)_3CH_3$ empirical formula. MS confirms the existence of **G** and **H**; **G** readily ionizes with ESI-MS, showing a parent peak at 320.1 m/z, corresponding to the hypothesized borazine plus sodium. **H** is observed by APCI-MS as M+K as 372.3 (see ESI). FTIR shows the expected absorbances for C-H and B-H bonds, with the absence of N-H stretches. Taken together, these results suggest a tri-N-substituted borazines have formed (Scheme 1).

By themselves, **D** and **E** store insufficient amounts of H_2 (3.5-3.9 wt. usable % material) to be used in automotive applications, since a minimum of 7.8 wt. % material is required for liquid materials.[5] For these amineboranes to be viable as fuels, a blend with another H_2 storage material is necessary. **D** and **E** can be blended with AB to yield a slurry fuel with improved capacity, for instance a 1:1 molar mixture of **D**:AB theoretically yields 6.0 wt. % H_2 if one assumes no further borazine crosslinking (2.0 equiv. H_2 from each AB). Of paramount importance, however, is that the spent fuel remain flowable in the wide operating range specified by the DOE (-40 to 60 °C). Amineborane/AB blends were initially screened by observing the state of the products after sustained heating (140 °C, 12 h+). When the molar ratio was ≤ 1, the AB/amineborane blends resulted in homogeneous oils (Table 1, Fig. 1) which did not exhibit freezing points down to -60 °C (ESI). NMR affords evidence that AB and D/E reacted together to form mixed N-substituted borazines: $^1H\{^{11}B\}$ NMR show additional resonances between G/H (4.74, 4.83 ppm) and borazine (4.47 ppm), while ^{11}B NMR has new peaks upfield of the N,N',N"-trisubstitutedborazine resonance (Fig 2). This observation, paired with the knowledge that neat AB forms solid products after extended heating,[11, 25] suggests that co-oligomerization or dissolution has occurred. Work by Mal et al. on sec-butylamineborane and AB blends did not indicate co-oligomerization, although product insolubility may have hampered characterization.[19]

Evidence for co-olgomerization was obtained thru GPC analysis. Since GPC has only been performed on a limited number of B-N materials,[26, 27] **G** was examined first, yielding M_p = 346, which compares favourably to the predicted 294 (17% higher, Table 3, Run #1, ESI) for a tris-N-(3-methoxypropyl)borazine. When **H** was analysed M_p = 489 was obtained, significantly higher than the predicted 330 (48% higher, Table 3, Run #4, ESI) for tris-N-hexylborazine. Since the ^{11}B NMR for **H** does not contain multiple resonances consistent with asymmetric boron environments, product/column interactions are likely the source for these higher values.[26]

When blends of **D** or **E** and AB fuel blends are thermally decomposed GPC indicates higher molecular species are forming (Table 3, ESI). As the ratio of **D**/AB goes from 3:1 to 1:1, the M_w grows from 440 to 550 and M_n from 392 to 433 (Runs #2, #3). A similar trend is observed for **E**/AB, with M_w growing from 630 to 710 and M_n from 570 to 592. These are admittedly small values on the low end of the GPC scale, but still suggest that co-oligmerization has occurred, corroborating the macroscopic observations. DLS experiments were also performed but all samples exhibited a single peak with a diameter of < 1 nm, confirming there are not higher molecular weight species and the molecular weights are at/below our 550 Mw PMMA standard.

While evaluating AB/amineborane fuel blends, we wanted to see what impact the functionalized amineborane would have on impurities typically observed in neat AB, such as ammonia, borazine, and diborane. We postulated that cooligomerization would reduce the amount of borazine. In addition, we wanted to measure any impact of making fuel blends with smaller AB particle sizes. To test this idea, AB was dissolved in freshly distilled THF, filtered thru a fine porosity glass frit, and then rapidly mixed with hexanes (2:1 ratio) precipitating the AB as a fine powder. Optical and SEM images indicate that the as received AB particles went from ~100 μm to ~10 um in size using this process. The AB/amine-borane fuel blends were then rapidly dehydrogenated (~10°/min ramp) in a pressure vessel before the resultant H_2 was analysed. Despite the particle size change, there was no appreciable impact on impurity levels. One impurity we did not expect, methane, was observed in appreciable levels when **D** was dehydrogenated under these conditions.

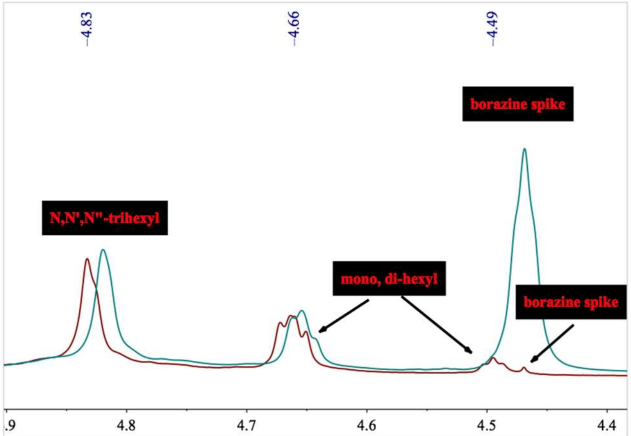


Fig. 2. $^1H\{^{11}B\}$ of decomposed **E**/AB mixture (blue); with borazine spike (red)

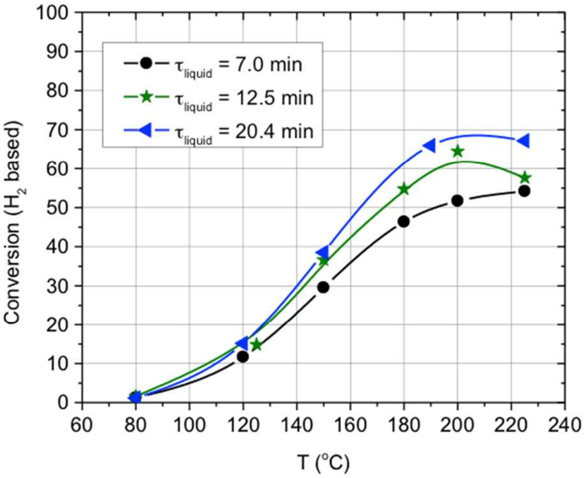


Fig. 3. Conversion of **D** as a function of space-time and temperature for flow-through reactor studies

Although AB and its derivatives are often evaluated with a slow heating profile using thermogravimetric techniques, in a practical application, the fuel will experience a rapid heat flow, even more pronounced than used in the aforementioned particle size/impurity experiments. In conjunction with the Hydrogen Storage Engineering Center of Excellence, we evaluated the performance of neat liquid **D** in downward flow reactors.[28] At the highest temperatures and slowest flow rates we only observed a maximum conversion around 66% (Fig 3). ^{11}B NMR confirms that some of the fuel is not releasing its stored H_2 (see ESI). Changes in the reactant space-time and reactor design did not result in improved conversions. Given that the conversion is < 1, we suspect that at elevated reactor temperatures (>180 °C) the vapour pressure of **D** becomes appreciable resulting in removal of unreacted **D** from the reactor prior to dehydrocoupling. ^{11}B NMR of the spent fuel supports this idea with resonances for **D**, as well as an intermediate borazanes (~-5 ppm) and N-substituted borazines (~34 ppm).

Conclusions

We have demonstrated that blends of functionalized amineboranes and AB can store appreciable amounts of H_2 (6.8 wt. %) and form liquid products after H_2 release when the AB/amine-borane ratio is ≤ 1. The products also do not freeze down to -60 °C, allowing these formulations to be readily moved on/off an automobile under a wide range of conditions. GPC analysis shows higher molecular weight species have formed, indicating that the dehydrocoupling reactions occur between AB and the amineboranes. Using a first generation reactor design to rapidly release the stored H_2, 66% of the stored H_2 can be released. Although these fuel blends do not currently meet the DOE specifications for vehicular applications (11 wt. % min stored H_2 for slurries), the development of non-volatile analogs may allow for better reactor conversions. Reports on optimization and new fuel blends are forthcoming.

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Notes and references

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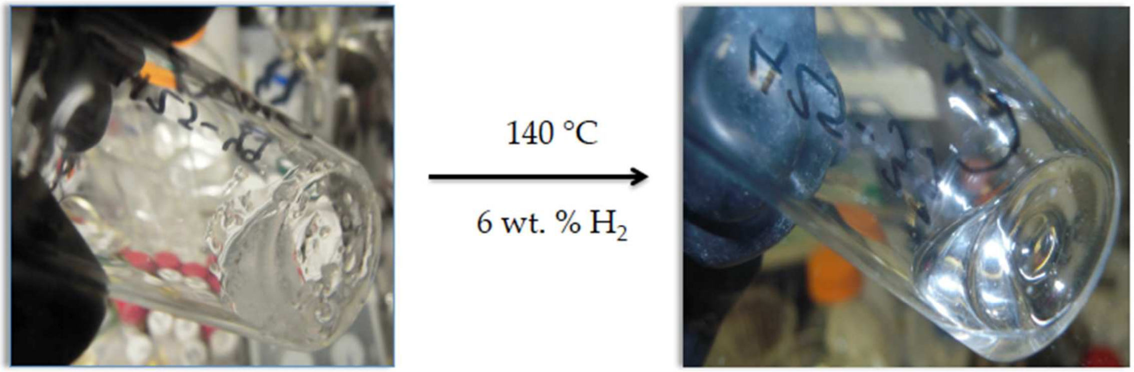
1. DOE-EERE, *2012 Interim Update - Technical Plan - Storage*, Department of Energy, Washington, D.C., 2013. http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/storage.pdf
2. S. McWhorter, C. Read, G. Ordaz and N. Stetson, *Curr. Opin. Solid State Mater. Sci.*, 2011, **15**, 29-38.
3. R. von Helmolt and U. Eberle, *J. Power Sources*, 2006, **165**, 833-843.
4. 2009 System Targets. https://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf
5. D. Anton, T. A. Semelsberger, D. Siegal, K. Brooks and B. Hardy, Hydrogen Storage Materials Requirements to Meet the 2017 On Board Hydrogen Storage Technical Targets, https://www1.eere.energy.gov/hydrogenandfuelcells/webinar_archives_2013.html#date062513.
6. G. Wolf, J. Baumann, F. Baitalow and F. P. Hoffmann, *Thermochim. Actta*, 2000, **343**, 19-25.
7. F. Baitalow, J. Baumann, G. Wolf, K. Jaenicke-Robler and G. Leitner, *Thermochim. Actta*, 2002, **391**, 159-168.
8. J. Baumann, F. Baitalow and G. Wolf, *Thermochim. Actta*, 2005, **430**, 9-14.
9. C. W. Hamilton, R. T. Baker, A. Staubitz and I. Manners, *Chem. Soc. Rev.*, 2009, **38**, 279-293.
10. L. G. Sneddon, Amineborane-Based Chemical Hydrogen Storage, 2010. http://www.hydrogen.energy.gov/pdfs/review10/st039_sneddon_2010_o_web.pdf
11. D. W. Himmelberger, C. Won Yoon, M. E. Bluhm, P. J. Carroll and L. G. Sneddon, *J. Am. Chem. Soc.*, 2009, **131**, 14101-14110.
12. W. Luo, P. G. Campbell, L. N. Zakharov and S. Liu, *J. Am. Chem. Soc.*, 2013, **135**, 8760.
13. For example the Joint Center for Artificial Photosynthesis, http://www.solarfuelshub.org
14. L. P. and Q. X., *Energy Environ. Sci.*, 2012, **5**, 9698-9725.
15. W. Luo, P. G. Campbell, L. N. Zakharov and S. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 19326-19329.
16. Y. Tan and X. Yu, *RSC Advances*, 2013, **3**, 23879.
17. O. T. Summerscales and J. C. Gordon, *Dalton Trans.*, 2013, **42**, 10075-10084.
18. A. Staubitz, A. Presa Soto and I. Manners, *Angew. Chem. Int. Ed.*, 2008, **47**, 6212-6215.
19. S. S. Mal, F. H. Stephens and R. T. Baker, *Chem. Comm.*, 2011, **47**, 2922-2924.
20. B. L. Dietrich, K. I. Goldberg, D. M. Heinekey, T. Autrey and J. C. Linehan, *Inorg. Chem.*, 2008, **47**, 8583-8585.
21. E. Framery and M. Vaultier, *Hetero. Chem.*, 2000, **11**, 218-225.
22. B. L. Davis, Fluid Phase H2 Storage Material Development, Arlington, VA, 2013. http://www.hydrogen.energy.gov/pdfs/review13/st040_davis_2013_o.pdf
23. D. Neiner, A. Karkamkar, M. Bowden, Y. J. Choi, A. Luedtke, J. Hollday, A. Fisher, N. Szymczak and T. Autrey, *Energy Environ. Sci.*, 2011, **4**, 4187-4193.
24. P. J. Fazen, J. S. Beck, A. T. Lynch, E. E. Remsen and L. G. Sneddon, *Chem. Mater.*, 1990, **2**, 96-97.
25. D. W. Himmelberger, L. R. Alden, M. E. Bluhm and L. G. Sneddon, *Inorg. Chem.*, 2009, **48**, 9883-9889.

26. A. Staubitz, M. E. Sloan, A. P. M. Robertson, A. Friedrich, S. Schneider, P. J. Gates, J. Schmedt auf der Gunne and I. Manners, *J. Am. Chem. Soc.*, 2010, **132**, 13332-13345.
27. P. J. Fazen, E. E. Remsen, J. S. Beck, P. J. Carroll, A. R. McGhie and L. G. Sneddon, *Chem. Mater.*, 1995, **7**, 1942-1956.
28. T. A. Semelsberger, B. L. Davis, B. D. Rekken, B. Paik and J. I. Tafoya, Chemical Hydrogen Rate Modeling, Validation and System Demonstration, Arlington, VA, 2013. http://www.hydrogen.energy.gov/pdfs/review13/st007_semelsberger_2013_o.pdf

Slurries of Ammona-borane and functionalized amine-boranes form liquid spent fuels after heating in batch or flow-thru reactors



Broader Context

The recent media attention placed on new natural gas reserves might cause the lay person to ask, “Do we have an energy problem?” If we neglect the impact of methane losses during production and the large amount of carbon dioxide formed on combustion, the answer is probably no. Realistically, however, we need to shift our energy infrastructure to one with less impact on climate. New energy paradigms, like those based on hydrogen that may be sustained produced from alternative sources, may allow our transportation infrastructure to continue without the large climate footprint it has today.

Several researchers have been exploring new materials to store hydrogen in forms more dense than the current state of the art (compressed). The goal is to acquire an inexpensive material that doesn’t dramatically alter our current fueling infrastructure and can be reused. Toward this end we describe liquid amine-borane materials that can be blended with ammonia-borane. In contrast to previous amine-borane based fuels, these materials release H2 and react together to form liquid products. This result represents substantial progress toward making an alternative, H2 carrying fuel that is readily loaded/unloading from a vehicle.