

## IV.H.18 Mechanistic Studies of Activated Hydrogen Release from Ammonia-Borane

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### Objectives

- Develop a fundamental understanding of the various thermolytic hydrogen release mechanisms (using acid and base initiators, ionic liquid activators, or metal complex catalysts) for ammonia-borane (AB) and to elucidate the important controlling factors for each type of reaction.
- Apply this understanding to achieve rapid, controlled release of pure hydrogen from an AB-based liquid fuel formulation.

### Technical Barriers

- While thermolytic hydrogen release from AB can afford >10 wt% hydrogen, the dehydro-oligomerization process is complicated, with different products being obtained depending on the phase (solid vs. solution), initiator (acid or base), activator (ionic liquids) or catalyst (metal complex or supported metal/metal boride) employed.

- Demonstrated engineering solutions for controlled hydrogen release involve passing a liquid fuel (with concomitant reduced gravimetric storage) over a heterogeneous catalyst bed.
- Volatile impurities in the hydrogen stream need to be less than ppm levels to ensure long fuel cell catalyst lifetime.

### Abstract

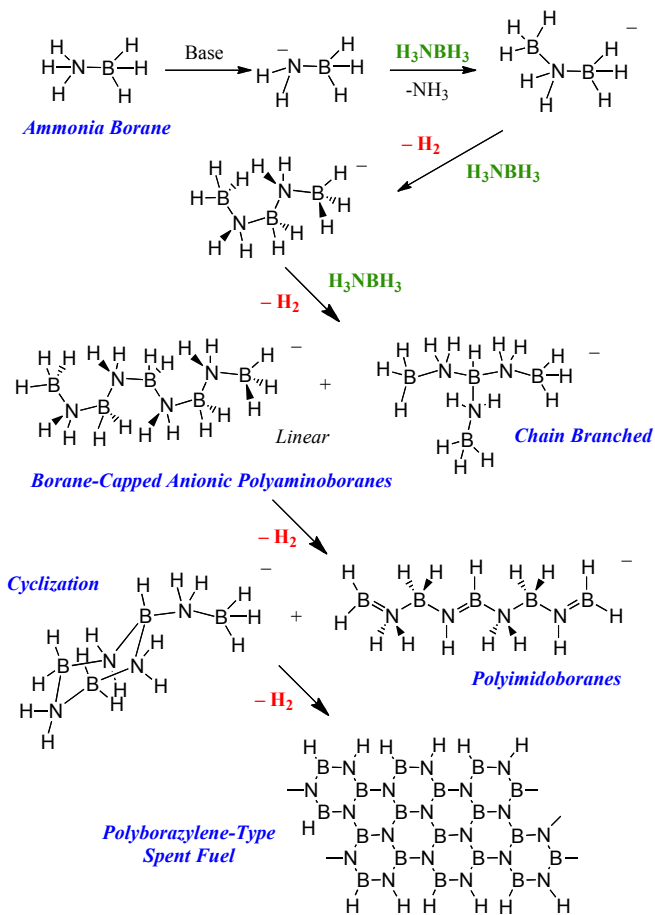
Significant advances have been made in our understanding of various hydrogen release mechanisms from AB in glycol methyl ether and ionic liquid [1,2] solutions. In previous work, we demonstrated that addition of 5 mol% bis(dimethylamino)naphthalene base (proton sponge) to a solution of AB accelerated the release of the second equivalent of hydrogen at 85°C affording >5 material wt% in 40 min [3]. Using Verkade's base, P[N(i-Bu)CH<sub>2</sub>CH<sub>2</sub>]<sub>3</sub>N, we have now demonstrated that stepwise anionic chain growth produces both linear and branched borane-capped oligomers, with the 'trimer' analogs isolated and fully characterized by multinuclear magnetic resonance spectroscopy and single crystal X-ray diffraction [4]. Further thermal dehydrogenation of these oligomers affords a mixture of BN analogs of benzene (borazine) and polyaromatic hydrocarbons (known collectively as polyborazylene [5]). In another study combining the activation effects of ionic liquids (ILs) [1,2] with catalytically active Ru complexes, we showed that AB dehydrogenation can be selectively 'tuned' by altering the donor strength of the IL anion [6]. Remarkably, nearly 2 equiv. of hydrogen are obtained even in tetraalkylphosphonium chloride ILs where the Cl<sup>-</sup>/Ru ratio is >100! Whereas metal complex catalysts that effect rapid (minutes) AB dehydrogenation are usually limited in extent of hydrogen release (1 equiv.) due to formation of insoluble poly(aminoborane) [7,8] we showed that most selective catalysts produce initially a mixture of the BN cyclohexane and ethylcyclobutane isomers [9]. In a more detailed investigation of the second equivalent of hydrogen release, we have now identified catalysts that dehydrogenate *both isomers* to borazine and polyborazylene. Turning our attention to inexpensive, earth-abundant catalysts, we have now discovered that FeH<sub>2</sub>(depe)<sub>2</sub> [depe = 1,2-bis(diethylphosphino)-ethane] is an efficient catalyst for poly(amino-borane) formation while mixtures of AB and FeCl<sub>2</sub> afford nanoparticle iron boride catalysts that release >2 equiv. hydrogen and can be reused for multiple cycles in glycol methyl ether or ionic liquid solutions without loss of activity or selectivity.

## Progress Report

**Introduction:** Effective storage of hydrogen presents one of the most significant technical gaps to successful implementation of the hydrogen economy, particularly for transportation applications [10]. AB,  $\text{H}_3\text{NBH}_3$ , has been identified as a promising, high-capacity chemical hydrogen storage medium containing potentially readily released protic (N-H) and hydridic (B-H) hydrogens [11-13]. The dehydro-oligomerization process, however, is complicated, with different products being obtained under different reaction conditions. At the outset of our studies in 2005, AB dehydrogenation had been studied primarily in the solid state, but our work clearly demonstrated that ionic liquids, acid and base initiators, and metal complex-catalysts can each significantly increase both the rate and extent of hydrogen release from AB under moderate conditions. Our studies have also shown that depending on the activation method, hydrogen release from amine-boranes can occur by very different mechanistic pathways and yield different types of spent-fuel materials. The goal of the current project was to develop a fundamental understanding and to elucidate the important controlling factors for each type of reaction. This information is vital to the continued refinement and optimization of chemical-hydride based hydrogen release systems.

**Base Initiators:** In previous work, we demonstrated the efficiency of non-nucleophilic strong bases such as proton sponge (PS) in promoting the rate and extent of hydrogen release from AB [3]. In addition, reactions of the triethylborane-capped model compound  $[\text{Et}_3\text{BNH}_2\text{BH}_3]^- \text{Li}^+$  with AB showed evidence of chain-growth, providing support for a PS-promoted anionic dehydro-polymerization of AB. In our most recent study, use of Verkade's base,  $\text{P}[\text{N}(\text{i-Bu})\text{CH}_2\text{CH}_2]_3\text{N}$ , demonstrated that stepwise anionic chain growth occurs by a mechanism involving both linear and branched borane-capped oligomers (Figure 1), with the 'trimer' analogs isolated and fully characterized by multi-nuclear NMR spectroscopy and single crystal X-ray diffraction [4] (Figure 2).

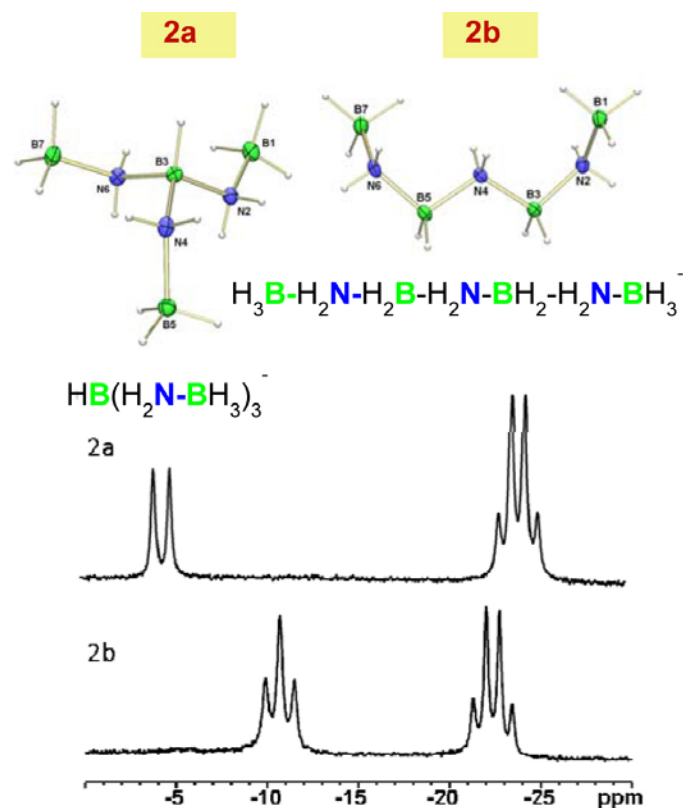
**Metal Complex Catalysts in Ionic Liquids:** In previous work combining the activation effects of ionic liquids [1,2] with catalytically active Ru complexes, we showed that AB dehydrogenation can be selectively 'tuned' to avoid formation of insoluble poly(aminoborane) (Figure 3) by altering the donor strength of the IL anion [6]. In more recent studies, IL cation effects were also noted, which could be partially correlated with the IL viscosity that greatly affects the rates of intermolecular aminoborane oligomerization. Remarkably, the Ru catalyst retained its activity even in phosphonium halide ILs and hydrogen release approaching 5 wt% was achieved, albeit at impractical rates. Further studies suggested that a fast initial rate of AB dehydrogenation could raise the reaction temperature sufficiently to allow for



**FIGURE 1.** Anionic AB polymerization mechanism

efficient activation of the subsequent  $\text{H}_2$  release steps by the ionic liquid solvent.

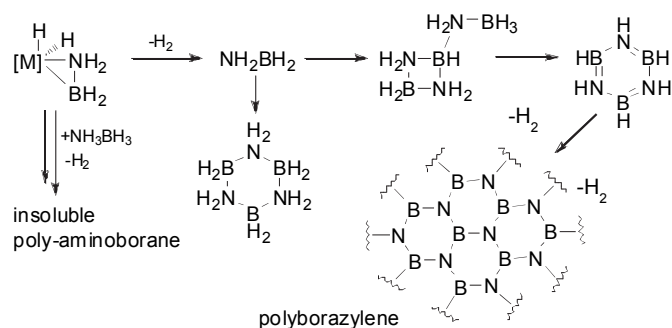
**Investigating the Second Equivalent of  $\text{H}_2$  Release:** Over the last seven years, a multitude of papers have appeared describing metal complex catalysts for AB dehydrogenation, including some with rapid rates and excellent selectivity to poly(aminoborane) [14-16] (1 equiv.  $\text{H}_2$ ), and others that form exclusively borazine and polyborazylene [17,18] (>2 equiv.  $\text{H}_2$ ). The reaction pathways traversed by the latter selective catalysts involve cyclic aminoborane intermediates such as the BN cyclohexane analog, cyclotriborazane (CTB) and its BN ethylcyclobutane (ECB) isomer that we reported previously (Figure 3) [9]. While CTB is easily prepared from borazine, all synthetic routes to ECB that we developed led to significant contamination from Ni or Fe metal. After significant effort, we finally discovered that use of Schwartz's reagent,  $\text{Cp}_2\text{ZrHCl}$ , affords ECB in 40% yield contaminated only by ca. 10-20% of its CTB isomer. With samples of ECB in hand we were able to show first that thermolysis of ECB leads primarily to CTB, but a competing pathway affords borazine and AB via a hydrogen redistribution reaction [19].



**FIGURE 2.**  $^{11}\text{B}$  nuclear magnetic resonance spectra and molecular structures of borane-capped aminoborane oligomers

Secondly, we found that some metal catalysts converted ECB cleanly to borazine and polyborazylene, leaving CTB untouched, while others effectively dehydrogenated both isomers.

**Iron Catalysts for AB Dehydrogenation:** In previous work on iron amido phosphine bifunctional catalysts, we discovered the most active base metal AB dehydrogenation catalyst that was selective for poly(aminoborane) formation, but it exhibited limited lifetime due to unwanted reactivity of the diamido ligand [20]. Using less bulky bis(phosphine) ligands, we have now identified stable Fe catalysts,  $\text{FeH}_2(\text{P-P})_2$ , where P-P is depe or dmpe, that react with a variety of primary amine-boranes to afford the poly(aminoborane)s exclusively. Further work is underway with chiral bis(phosphine) ligands to assess tacticity and concomitant microstructure control in the resulting BN polymers. Finally, in extended studies of AB dehydrogenation catalyzed by metal-containing Lewis acids, we recently found that mixtures of AB and  $\text{FeCl}_2$  afford nanoparticle iron-on-iron-boride catalysts that release  $>2$  equiv. hydrogen. These are the most promising heterogeneous catalysts yet reported for AB dehydrogenation and can be reused for multiple cycles in glycol methyl ether or ionic liquid solutions without loss of activity or selectivity. Further work in this area involves detailed investigations of hydrogen purity and use of oxygen-



**FIGURE 3.** Observed dehydrogenation products from metal complex-catalyzed AB dehydrogenation

free BN supports to prepare practical heterogeneous catalysts for use with ionic liquid/AB fuels.

### Future Directions

Although this Basic Energy Sciences project has been completed, the PIs are working with Los Alamos National Lab and DOE's Engineering Hydrogen Storage Center of Excellence to develop a working ammonia-borane-based liquid-fuel/spent-fuel combination working in concert with an iron-based heterogeneous catalyst to achieve rapid, controlled release of pure hydrogen streams.

### References

1. Bluhm, M.E.; Bradley, M.G.; Butterick, R.; Kusari, U.; Sneddon, L.G. *J. Am. Chem. Soc.* **2006**, *128*, 7748-9.
2. Himmelberger, D.; Yoon, C.W.; Bluhm, M. E.; Carroll, P.J.; Sneddon, L.G. *J. Am. Chem. Soc.* **2009**, *131*, 14101-14110.
3. Himmelberger, D.W.; Alden, L.R.; Bluhm, M.E.; Carroll, P.J.; Sneddon, L.G. *Inorg. Chem.* **2009**, *48*, 9883-9889.
4. Ewing, W.C.; Marchione, A.; Himmelberger, D.W.; Carroll, P.J.; Sneddon, L.G. *J. Am. Chem. Soc.* **2011**, *133*, 17093-17099.
5. Fazen, P.J.; Remsen, E.E.; Beck, J.S.; Carroll, P.J.; McGhie, A.R.; Sneddon, L.G. *Chem. Mater.* **1995**, *7*, 1942-1956.
6. Wright, W.H.R.; Berkeley, E.; Baker, R.T.; Sneddon, L.G. *Chem. Commun.*, **2011**, *47*, 3177-3179.
7. Staubitz, A.; Presa Soto, A.; Manners, I. *Angew. Chem., Int. Ed.* **2008**, *47*, 6212-6215.
8. Staubitz, A.; Sloan, M.E.; Robertson, A.P.M.; Friedrich, A.; Schneider, S.; Gates, P.J.; Günne, J.S. a. d.; Manners, I. *J. Am. Chem. Soc.*, **2010**, *132*, 13332-13345.
9. Pons, V.; Baker, R.T.; Linehan, J.; Matus, M.H.; Dixon, D.A., *Chem. Commun.* **2008**, 6597-6599.
10. Satyapal, S.; Petrovic, J.; Read, C.; Thomas, G.; Ordaz, G. *Catal. Today* **2007**, *120*, 246-256.
11. Stephens, F.H.; Pons, V.; Baker, R.T. *Dalton Trans.*, **2007**, 2613-2626.

12. Hamilton, C.W.; Baker, R.T.; Staubitz, A.; Manners, I. *Chem. Soc. Rev.*, **2009**, 38, 279-293.
  13. Staubitz, A.; Sloan, M.E.; Robertson, A.P.M.; Manners, I. *Chem. Rev.* **2010**, 110, 4079-4124.
  14. Denney, M.C.; Pons, V.; Hebden, T.J.; Heinekey, D.M.; Goldberg, K.I. *J. Am. Chem. Soc.* **2006**, 128, 12048-12049.
  15. Blaquiere, N.; Diallo-Garcia, S.; Gorelsky, S.I.; Black, D.A.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, 130, 14034-14035.
  16. Käß, M.; Friedrich, A.; Drees, M.; Schneider, S. *Angew. Chem., Int. Ed.* **2009**, 121, 922-924.
  17. Keaton, R.J.; Blacquiere, J.M.; Baker, R.T. *J. Am. Chem. Soc.*, **2007**, 129, 1844-1845.
  18. Conley, B.L.; Guess, D.; Williams, T.J. *J. Am. Chem. Soc.*, **2011**, 133, 14212-14215.
  19. A paper on hydrogen redistribution from AB to bulky aminoborane monomers appeared recently: Robertson, A.P.M.; Leitao, E.M.; Manners, I. *J. Am. Chem. Soc.* **2011**, 133, 19322-19325.
  20. Baker, R.T.; Gordon, J.G.; Hamilton, C.W.; Henson, N.J.; Lin, P.-H.; Maguire, S. *J. Am. Chem. Soc.* **2012**, 134, 5598-5609.
- Recent Publications (including patents) acknowledging the grant or contract**
1. "Tuning the Selectivity of Transition Metal-Catalyzed Ammonia-Borane Dehydrogenation in Ionic Liquids," Wright, W.R.H.; Menant, C.L.; Baker, R.T., submitted to *Inorganic Chemistry*, 2012.
  2. "Synthesis, Characterization and Reactivity Study of B-(cyclo-diborazanyl)aminoborohydride: the Second Dehydrogenation Step in Ammonia-Borane Dehydrogenation," Gaertner, F.; Kalviri, H.; Baker, R.T., submitted to *Chemical Science*, 2012.
  3. "Iron Complex-Catalyzed Ammonia-Borane Dehydrogenation. A Potential Route Towards B-N Containing Polymer Motifs Using Earth Abundant Metal Catalysts," Baker, R.T.; Gordon, J.G.; Hamilton, C.W.; Henson, N.J.; Lin, P.-H.; Maguire, S. *J. Am. Chem. Soc.* 2012, 134, 5598-5609.
  4. "Syntheses and Structural Characterizations of Anionic Borane-Capped Ammonia-Borane Oligomers: Evidence for Ammonia Borane H<sub>2</sub>-Release via a Base-Promoted Anionic Polymerization Mechanism," Ewing, W.C.; Marchione, A.; Himmelberger, D.W.; Carroll, P.J.; Sneddon, L.G. *J. Am. Chem. Soc.* 2011, 133, 17093-17099.
  5. "Transition Metal-Catalysed Ammonia-Borane Dehydrogenation in Ionic Liquids," Wright, W.H.R.; Berkeley, E.; Baker, R.T.; Sneddon, L.G. *Chem. Commun.*, **2011**, 47, 3177-3179 (Invited for special Hydrogen issue).
  6. "Ammonia Triborane: A New Synthesis, Structural Determinations and Hydrolytic Hydrogen-Release Properties," Yoon, C.W.; Carroll, P.J.; Sneddon, L.G. *J. Am. Chem. Soc.* **2009**, 131, 855-864.
  7. "Base Promoted Ammonia Borane Hydrogen Release," Himmelberger, D.W.; Yoon, C.W.; Bluhm, M.E.; Carroll, P.J.; Sneddon, L.G. *J. Am. Chem. Soc.* **2009**, 131, 14101-14110.
  8. "Ammonia Borane Hydrogen Release in Ionic Liquids," Himmelberger, D.W.; Alden, L.R.; Bluhm, M.E.; Carroll, P.J.; Sneddon, L.G. *Inorg. Chem.* **2009**, 48, 9883-9889.
  9. "B-N Compounds for Chemical Hydrogen Storage," Hamilton, C.W.; Baker, R.T.; Staubitz, A.; Manners, I. *Chem. Soc. Rev.*, **2009**, 38, 279-293. (invited review for thematic issue on Renewable Energy).
  10. "Mechanistic Studies of Metal-Catalyzed Amine-Borane Dehydrogenation: Selectivity Dictates Extent of Hydrogen Release from Ammonia-Borane," Pons, V.; Baker, R.T.; Linehan, J.; Matus, M.H.; Dixon, D.A. *Chem. Commun.* **2008**, 6597-6599.
  11. "Soluble Boron-Nitrogen High Polymers from Metal Complex-Catalyzed Amine Borane Dehydrogenation," Pons, V.; Baker, R.T. *Angew. Chem. Int. Ed.*, **2008**, 47, 9600-9602.