IV.I.21 Mechanistic Studies of Activated Hydrogen Release from Amine Boranes

Larry G. Sneddon* (Penn),
Tom Baker** (Ottawa) PIs,
Dan Himmelberger (Penn student),
Giovanni Rachiero,
William Wright (Ottawa postdoctorals)

*Department of Chemistry, University of Pennsylvania, Philadelphia PA 19104-6323
Phone: 215-898-8632; Fax: 215-573-6743;
E-mail: lsneddon@sas.upenn.edu

**Department of Chemistry, University of Ottawa, Ottawa, ON, Canada K1N 6N5
Phone: 613-562-5698
E-mail: rbaker@uottawa.ca

Research Scope and Objectives

Effective storage of hydrogen presents one of the most significant technical gaps to successful implementation of the hydrogen economy, particularly for transportation applications. Amine boranes, such as ammonia borane H_3NBH_3 and ammonia triborane $H_3NB_3H_7$ have been identified as promising, high-capacity chemical hydrogen storage media containing potentially readily released protic (N-H) and hydridic (B-H) hydrogens. At the outset of our studies, dehydrogenation of ammonia borane had been studied primarily in the solid state, but our work carried out under the previous grant clearly demonstrated that ionic liquids, base-initiators and/or metal-catalysts can each significantly increase both the rate and extent of hydrogen release from amine boranes under moderate conditions. Our studies have also shown that depending upon 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 is to develop a fundamental understanding of each of these hydrogen-release mechanisms and to elucidate the important controlling factors for each type of reaction. Such detailed understanding is vital to the continued discovery and optimization of new chemical-hydride based hydrogen release systems.

Recent Progress

The high hydrogen release capacity that could potentially be achieved by ammonia triborane **1** oxidative-hydrolysis, (9.7 materials-wt% H_2) or thermolysis (17.7 materials-wt% H_2), has made it an attractive candidate for chemical hydrogen storage. Although $NH_3B_3H_7$ was first synthesized over 50 years ago, owing to the lack of a suitable method for its efficient and safe synthesis, its reactivities and properties have not been intensively explored. Of the fewer than 30 previous publications on **1**, many were stimulated by the apparent contradiction between the computational studies that predict a symmetric single hydrogen-bridged C_s-symmetric structure, and the early single crystal X-ray determination of **1** that showed an asymmetric structure with perhaps two bridging-hydrogens. In a recently published paper [1] we presented: (1) a new, efficient preparation of **1** that now makes this compound easily available; (2) a new crystallographic study of the solid-state structure of **1**, along with a structural determination of the **1**•18-crown-6 adduct, that resolves the contradictions with computational structural predictions; and (3) a description of the hydrolytic hydrogen release properties of **1**.

Iodine oxidation of $B_3H_8^-$ in glyme solution to produce (glyme)B_3H_7, followed by displacement of the coordinated glyme by reaction with anhydrous ammonia provides a safe and convenient preparation of ammonia triborane. X-ray crystallographic determinations and DFT computational studies of both $NH_3B_3H_7$ and the $NH_3B_3H_7$•18-crown-6 adduct demonstrate that while computations predict a symmetric single bridging-hydrogen conformation, $NH_3B_3H_7$ has a highly asymmetric structure in the solid-state that results from intermolecular $N-H^+$--H^--B dihydrogen bonding interactions.

Studies of its hydrolytic reactions showed that upon the addition of acid or an appropriate transition metal catalyst, aqueous solutions of **1** rapidly release hydrogen, with the rate of H_2-release controlled by both the catalyst loadings and temperature. The hydrolysis reaction of a highly concentrated 22.7 wt% sample yielded 6.1 materials-wt% H_2 making an ammonia triborane based hydrolytic system competitive with both NH_3BH_3 and $NaBH_4$ based hydrolysis systems. As will be discussed in future publications, the development of an efficient synthesis of **1** is now enabling systematic investigations of the chemistry and applications of this unique compound.

We have previously shown that ionic liquids provide advantageous media for ammonia borane
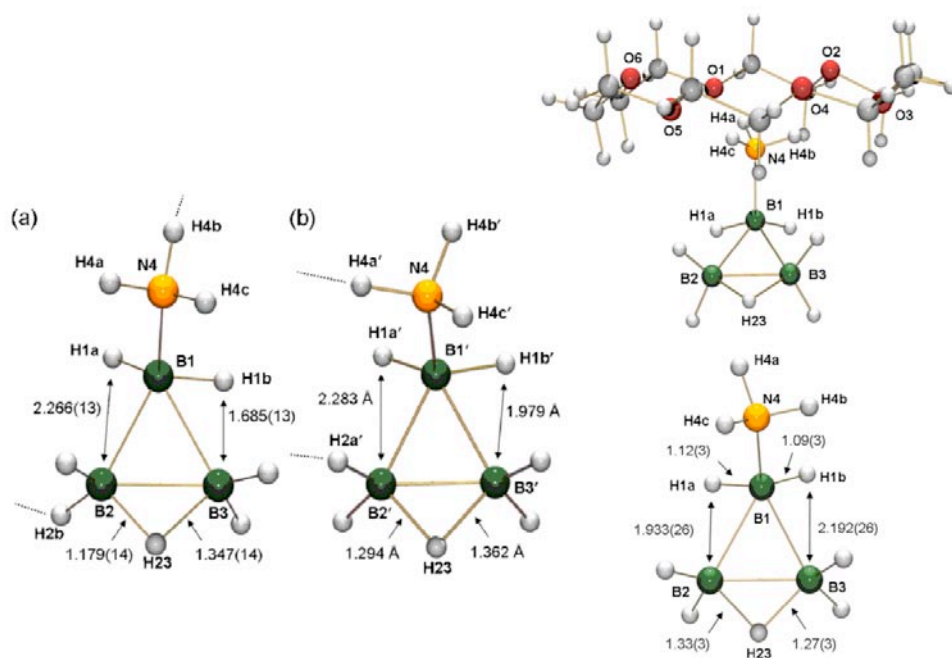
FIGURE 1. **Left:** Comparison of (a) the solid-state structure of **1** with (b) the DFT-optimized **1** structure. Dashed lines indicate the positions of the dihydrogen bonding interactions. **Right:** (top) X-ray crystal structure of **1**•18-crown-6 (molecule a); (bottom) selected distances in the ammonia triborane fragment of **1**•18-crown-6 (molecule a).

dehydrogenation in which both the extent and rate of dehydrogenation are significantly increased [2]. Furthermore, in contrast to the results found for solid-state reactions, when ammonia borane dehydrogenation was carried out in ionic liquids, no induction period was observed. Work in the last year [3] has focused on using both solid-state and ionic-liquid solution NMR studies to identify the mechanistic pathways and key intermediates involved in AB H_2-release in ionic-liquids. These studies have provided strong evidence for the mechanistic pathway illustrated in Figure 3 involving the initial ionic liquid promoted formation of the diammoniate of diborane (DADB) followed by the reaction of DADB with additional AB to produce saturated polyaminoborane polymers. At the outset of our studies, we thought that subsequent dehydrogenation of this polymer could occur along either of two main mechanistic pathways. As shown on the left, H_2-release could proceed by cyclization and chain-branching reactions, ultimately yielding saturated materials that preserve the sp^3 framework. However, the NMR studies strongly favor instead the process on the right, involving H_2-elimination from adjacent polyaminoborane BH and NH groups to produce B=N unsaturated polyiminoboranes that furtherreact to form cross-linked sp^2-bonded polyborazylene materials.

Other synthetic, mechanistic and computational studies conducted in the last year have also demonstrated that strong nitrogen bases, such as Proton Sponge (1,8-bis(dimethylamino)naphthalene) [4], induce H_2-release from ammonia borane by a different mechanistic pathway involving the initial deprotonation of AB to produce the $H_2NBH_3^-$ anion. This anion then induces anionic dehydropolymerization of additional ammonia borane to produce a growing polyaminoborane polymer with a resulting significant increase in the hydrogen release rate.

Previous work on metal-catalyzed dehydrogenation of ammonia borane (AB) indicated that some catalysts afforded aminoborane oligomers, $(NH_2BH_2)_n$, and one equivalent of H_2 whereas others gave borazine, $(NHBH)_3$, BN cross-linked borazine (polyborazylene, BNHx) and > 2 equiv. H_2. Post-catalysis characterization of soluble Ir^5 and Ru^6 complexes showed that both processes involve homogeneous catalysis and theoretical treatments proposed a variety of activation mechanisms [7-9]. Detailed in situ multinuclear NMR studies of substituted amine-boranes and external trapping studies using cyclohexene demonstrated that ejection of reactive aminoborane, NH_2BH_2 [10], from the metal center leads to rapid trapping by AB to afford the BN analog of ethylcyclobutane [B-(cyclodiborazanyl)amine borane, CDBAB, Scheme 1).

Conversion of CDBAB to borazine and subsequent cross-linking to polyborazylene affords more than 2 equiv. H_2 per AB (Scheme 2). In collaboration with
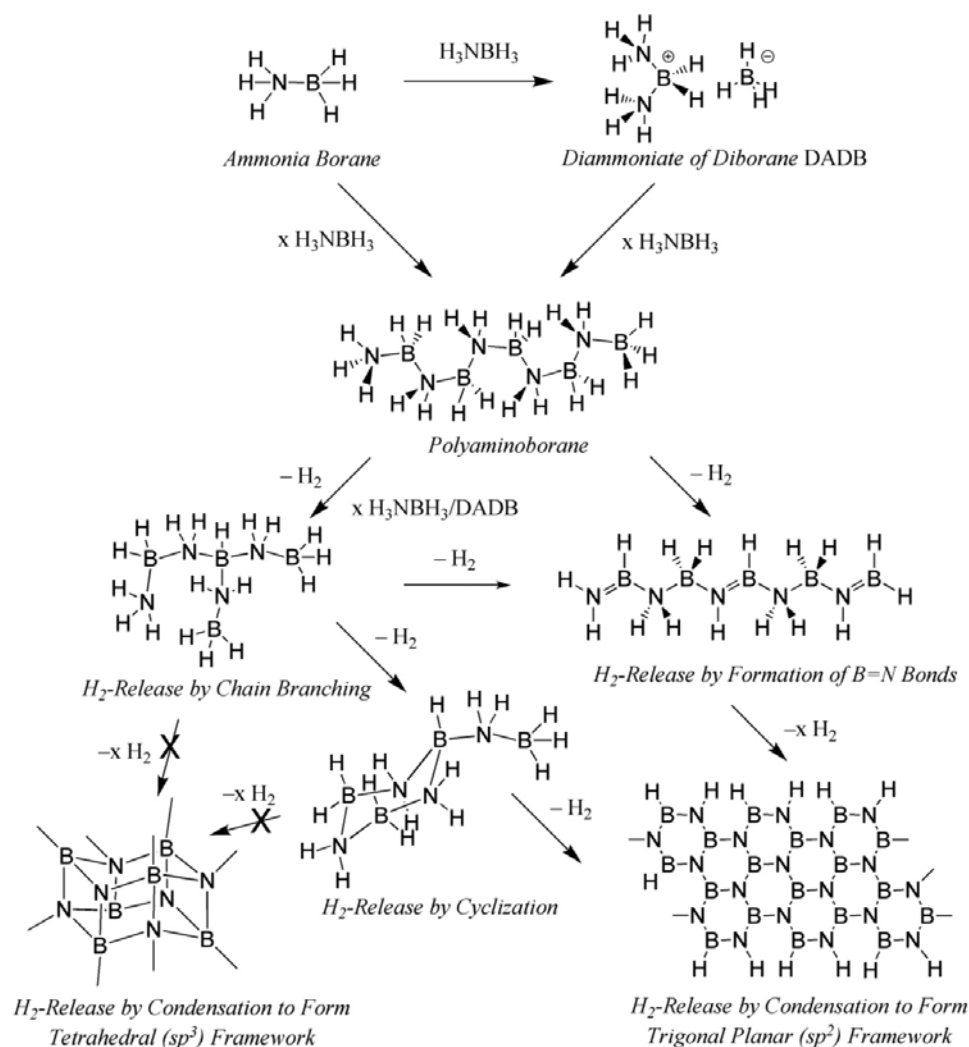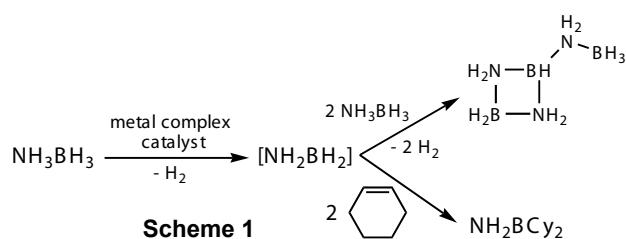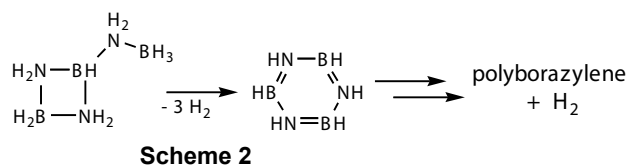
FIGURE 2. Ammonia-Borane H_2-Release Mechanism in Ionic Liquids

Scheme 1

Scheme 2

Heinz Berke (University of Zurich, Switzerland) we have now used reactive imines to prepare CDBAB in good yield (Equations 1 and 2).

$$ArN=CHAr' + NH_3BH_3 \longrightarrow NHAr(CH_2Ar') + NH_2BH_2 \qquad (1)$$

$$3\ NH_2BH_2 \longrightarrow H_2B(NH_2)_2BHNH_2BH_3 \qquad (2)$$

Studies of the thermolysis and catalyzed dehydrogenation of CDBAB are in progress as are attempts to catalyze the cross-linking of borazine.

Inefficient ejection of aminoborane from the metal center leads to coordination complexes, $[M](NH_2BH_2)$, that limit the hydrogen released for AB to a single equivalent. Thus, cyclohexene trapping of NH_2BH_2 is not observed with $Cr(CO)_5(NMe_3)$ or the above-mentioned Ir complex catalyst. In collaboration with Jun Li and Don Camaioni (Pacific Northwest National Lab) we have now shown that the Cr catalyst effects AB dehydrogenation through a Lewis acid activation mechanism and the resulting aminoborane complex is predicted to exhibit a 90° Cr-NB angle (Figure 1A) due to the unusual sigma-backbonding interaction of a filled Cr d orbital with the empty p orbital on B (Figure 1B).
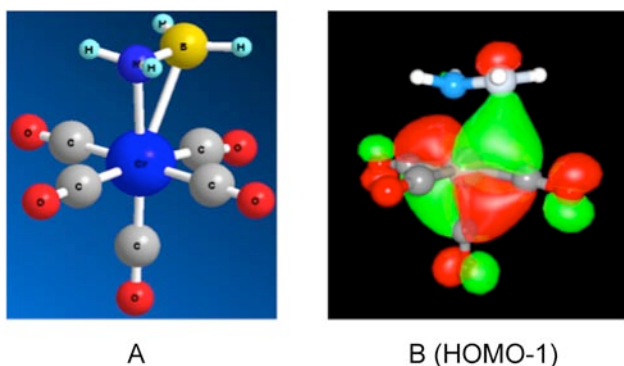
A   B (HOMO-1)

FIGURE 3. A) Electronic structure of $Cr(CO)_5(NH_2BH_2)$ from DFT calculation (B3LYP/6311+G**; B) HOMO-1 orbital depicting sigma back-bonding interaction.

We have now isolated the first aminoborane coordination complexes, $[M](NH_2BH_2)$, with $M = Cr(CO)_5$ and $[Mn(CO)_5]+$ and are investigating their reactivity with additional AB to test our proposed dehydrocyclization pathway (Scheme 3) to give cyclopentaborazane, $(NH_2BH_2)_5$. Confirmation of the structure of this pentamer using variable field, variable temperature solidstate NMR is in progress and we are also trying to co-crystallize the compound with crown ethers.

Scheme 3
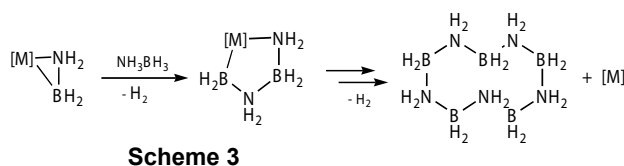
Future studies include detailed mechanistic studies of the reactions and interactions of amine-boranes, including ammonia borane, the diammoniate of diborane, $[(NH_3)_2BH_2^+]BH_4^-$ and ammonia triborane $NH_3B_3H_7$, with a range of potential dehydrogenation promoters and/or catalysts. Computational and experimental studies involve kinetic measurements, isotope labeling studies and the quantification of H_2-release, along with product characterizations by ^{11}B NMR and DFT/GIAO calculations and mass spectral analyses of both the solid and volatile dehydrogenation products. In situ monitoring of reactions by ^{11}B NMR in room temperature ionic liquids are again being used for direct observation of any differences in mechanistic steps and intermediates. Having identified disparate mechanisms for hydrogen release from AB using ionic liquids (cationic or anionic oligomerization) and metal catalysts (formation of reactive aminoborane), much of our future work will focus on metal catalysis in ionic liquids in order todevelop catalysts that are effective for releasing more than two equivalents of hydrogen per AB.

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