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

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Contract Number: DE-FG02-05ER15719-AO  
Project Period:  
September 1, 2008 – August 30, 2011  
Current Period:  
September 1, 2008 – August 30, 2009  
Report Date: April 24, 2009

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$_3$NBH$_3$ and ammonia triborane H$_5$NBH$_7$, 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$_3$B$_2$H$_6$ 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 50 previous publications on 1, many were stimulated by the apparent contradiction between the computational studies that predict a symmetric single hydrogen-bridged C$_5$-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$_3$H$_7$ in glyme solution to produce (glyme)B$_3$H$_7$, 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$_3$B$_2$H$_6$ and the NH$_3$B$_2$H$_6$•18-crown-6 adduct demonstrate that while computations predict a symmetric single bridging-hydrogen conformation, NH$_3$B$_2$H$_6$ 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$_3$BH$_4$ 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...
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 H₂-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, H₂-release could proceed by cyclization and chain-branching reactions, ultimately yielding saturated materials that preserve the sp³ framework. However, the NMR studies strongly favor instead the process on the right, involving H₂-elimination from adjacent polyaminoborane BH and NH groups to produce B=N unsaturated polyaminoboranes that further react to form cross-linked sp²-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 H₂-release from ammonia borane by a different mechanistic pathway involving the initial deprotonation of AB to produce the H₂NBH₃⁻ 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, (NH₂BH₂)n, and one equivalent of H₂ whereas others gave borazine, (NH₂BH)₃, BN cross-linked borazine (polyborazylene, BNHₓ) and > 2 equiv. H₂. Post-catalysis characterization of soluble Ir₅ and Ru₆ 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, NH₂BH₁ [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. H₂ per AB (Scheme 2). In collaboration with

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

$$\text{ArN}=\text{CHAr'} + \text{NH}_3\text{BH}_3 \rightarrow \text{NHAr(CH}_2\text{Ar')} + \text{NH}_3\text{BH}_2 \quad (1)$$

$$3 \text{NH}_3\text{BH}_2 \rightarrow \text{H}_2\text{B(NH}_2\text{)}_3\text{BHNH}_2\text{BH}_3 \quad (2)$$

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$_2$BH$_2$), that limit the hydrogen released for AB to a single equivalent. Thus, cyclohexene trapping of NH$_3$BH$_2$ 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).
We have now isolated the first aminoborane coordination complexes, [M][NH₂BH₃], 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, (NH₃BH)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.

Future studies include detailed mechanistic studies of the reactions and interactions of amine-boranes, including ammonia borane, the diammoniate of diborane, [(NH₃)₂BH₃]⁺BH₄⁻ and ammonia triborane NH₃BH₂H₄⁺ with a range of potential dehydrogenation promoters and/or catalysts. Computational and experimental studies involve kinetic measurements, isotope labeling studies and the quantification of H₂ release, along with product characterizations by ¹¹B NMR and DFT/GIAO calculations and mass spectral analyses of both the solid and volatile dehydrogenation products. In situ monitoring of reactions by ¹¹B 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 to develop catalysts that are effective for releasing more than two equivalents of hydrogen per AB.

References


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