

Will We Soon Be Fueling our Automobiles with Ammonia–Borane?*

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boron · hydrogen storage · sustainable chemistry

As we burn our way through the petroleum resource which took many millions of years to form, and we generate large amounts of the greenhouse gas, CO₂, as well as other pollutants in the process, the issues of economics and politics as well as social and environmental questions have led to the search for new fuels, especially for use in transportation. Hydrogen, which would be potentially the cleanest of fuels, producing only water as an oxidation product, has attracted much attention,^[1] and of course, there is the potential to derive this fuel from water itself, should an attractive alternative to electrolysis be developed (e.g., an efficient photocatalytic process^[2]). However, the question of how to store large enough amounts of hydrogen in a light weight “tank” for use in automobiles has presented a major stumbling block to its widespread use. The current goal, in this regard, is to develop an entire system for on-board storage and controlled release of hydrogen, which is capable of allowing a vehicle to travel approximately 300 miles (500 km) without refueling. The hydrogen release should occur preferably at temperatures below about 350 K, so as to make use of the waste heat generated in polymer-electrolyte-membrane (also known as proton-exchange-membrane or PEM) fuel cells. Other important features of such a system include the means by which the refueling will take place (i.e., the infrastructure required and how it differs from current petrol (gasoline) delivery), as well as the potential to regenerate the material to achieve an environmentally friendly and sustainable fuel system. This latter point is especially challenging.

Transport and storage of hydrogen as a gas or liquid are not without dangers, and the compression process to achieve the pressures necessary to reach a high density requires energy and does not solve the hazard issue. In addition, the densities of either compressed H₂ (40 g L⁻¹ at 700 bar) or liquefied H₂ (70 g L⁻¹ at 20 K) are below those required for the above goal.^[3]

Thus, there has been an intense effort to find means by which to “store” hydrogen in a convenient and especially high-density form from which it can be released on demand at reasonable temperatures and rates so as to use it in a fuel cell in cars, buses, and trucks. Several very different approaches have been investigated in recent years, and it is beyond the scope of this Highlight to review them all. One material which has attracted much attention is ammonia–borane,^[3–5] H₃NBH₃, which is known in the community as AB, as it contains 19.6 weight % H, and is thermally stable enough at ambient temperatures to transport and store. It is solid at room temperature, water stable and indeed, owing to its polarity, quite soluble in water.^[6] I will concentrate on AB, and recent advances in AB chemistry, as the US Department of Energy (DOE) has set a target of 9 weight % hydrogen by 2015 (for the entire hydrogen storage and delivery system)^[24], and AB is *potentially* consistent with this target if progress can be made on a number of fronts. I will also mention a few other recent and very interesting advances involving novel aspects of H₂ chemistry.

The major challenges are as follows: 1) the system has to be able to release H₂ at an appropriate rate, whether the “tank” is full or nearly empty; 2) the system has to be able to release most (ca. 2.5 equiv) of the available H₂ to achieve the gravimetric requirements stipulated above; 3) the system must produce a minimum of volatile by-products, such as borazine, which can poison the PEM fuel cells; and 4) an economically viable method must be developed for regeneration of AB if it is to become a sustainable fuel. Indeed, this latter point may be the ultimate barrier to its use, and an area which certainly requires significant research.

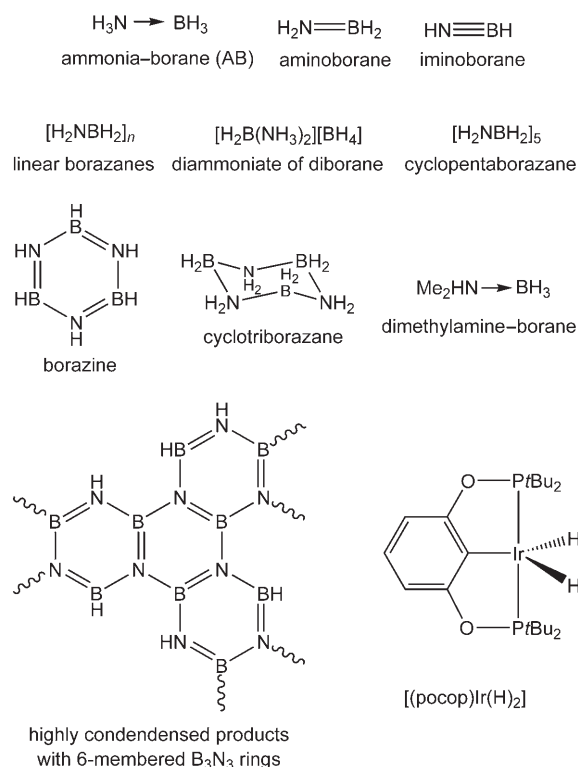
Neat AB, of course, contains 19.6 weight % H; however, if the release mechanism requires a solvent, the actual density of H₂ in the system is significantly lowered. AB is relatively stable to hydrolysis in aqueous solution at neutral or basic pH values, but it is rapidly hydrolyzed in acid, and this process can be catalyzed by metals or promoted by solid acids.^[7] However, the unfavorable thermodynamics of regeneration of AB from the resulting borate products is a major drawback to this approach. Similarly, if AB is incorporated into a scaffold (e.g., high-surface-area mesoporous silica,^[8]), the H₂ density is reduced considerably, even at 1:1 loading. Neat AB releases H₂ only slowly at elevated temperatures, and undesirable borazine is formed upon thermolysis of AB in tetraglyme solution at 393–413 K.^[9] The thermodynamics of release of H₂ from AB and subsequent H₂ release from

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partially dehydrogenated products has been examined,^[10] suggesting that dehydrogenation reactions are both enthalpically and entropically favorable, and thus regeneration through H₂ pressure seems unfeasible. Therefore, alternatives, such as digestion of the products followed by reduction back to BH₃ using other hydrides, are being investigated.^[11] However, depending on how the H₂ release is promoted, whether the AB is neat or in solution, in an ionic liquid,^[12] or encapsulated into a mesoporous material,^[8] different series of dehydrogenation products are formed, making comparisons among the approaches somewhat difficult!

With these points in mind, much recent work has focused on catalyzing the release of H₂ from AB. The first two examples of transition-metal catalyzed dehydrogenation of amine–borane adducts were reported by Roberts et al. in 1989,^[13a] using 10% palladium on charcoal, and then by Manners et al. in 2001,^[13b] as part of their wider research program on metal-catalyzed dehydrocoupling reactions.^[13c] This research was extended to include AB itself in 2003^[14a] using 0.6 mol% of $[\text{Rh}(1,5\text{-cod})(\mu\text{-Cl})_2]$ (cod = cyclooctadiene) as catalyst precursor, either in diglyme or tetraglyme at 328 K, giving borazine along with nonvolatile products (presumably oligomeric and/or polymeric boron–nitrogen-containing species) via the cyclic trimer (H₂NBH₂)₃ and μ -aminodiborane $[(\mu\text{-NH}_2)\text{B}_2\text{H}_5]$ intermediates. Catalyst-poisoning experiments using mercury in the related MeH₂NBH₃ dehydrogenation reactions, along with TEM studies, suggested heterogeneous catalysis and the presence of small (ca. 2 nm) rhodium clusters.^[14] Autrey et al.^[15] examined Me₂HNBH₃ dehydrogenation using $[\text{Rh}(1,5\text{-cod})(\mu\text{-Cl})_2]$, and suggested the presence of toluene-soluble Rh₆ clusters and small amounts (< 1%) of other rhodium species. Thus, it is not completely clear what the active species is in these reactions, or how sensitive this may be to conditions or the exact nature of the substrate. More recently, Manners et al. reported^[16] the homogeneous titanocene-catalyzed dehydrocoupling of Me₂HNBH₃, and the mechanism of this process has been studied theoretically by Luo and Ohno.^[17] A stepwise mechanism was computed to be the lowest in energy, in which binding of a BH group to titanium as a σ -complex was followed by NH oxidative addition. Heinekey, Goldberg et al. reported^[18] that the iridium pincer complex $[(\text{pocop})\text{Ir}(\text{H})_2]$ (pocop = $[\eta^3\text{-}1,3\text{-(OPtBu}_2)_2\text{C}_6\text{H}_3]$, see Scheme 1) catalyzes the release of one equivalent of H₂ from AB within 14 minutes at room temperature at 0.5 mol% loading. This rate is approximately 2–3 orders of magnitude faster than with previous catalysts, and is the first system which is close to meeting the rate requirements for automobile applications. No inhibition of the catalysis was observed upon addition of mercury, suggesting that the catalytic process is homogeneous. Two mechanisms for catalyzed dehydrogenation using the iridium pincer complex were examined by DFT calculations by Paul and Musgrave,^[19] one involving iridium(I) activation of AB following predissociation of H₂ from the iridium(III) dihydride complex, the second involving direct attack of AB on the iridium(III) dihydride species. Their calculations support the second mechanism being the lower in energy of the two, and they proposed a concerted process, transferring simultaneously a



Scheme 1. Important species related to ammonia–borane dehydrogenation. pocop = $[\eta^3\text{-}1,3\text{-(OPtBu}_2)_2\text{C}_6\text{H}_3]$.

hydridic BH hydrogen to the iridium center and an acidic NH hydrogen to an Ir–H ligand, which contrasts with the mechanism for ethane dehydrogenation with the same catalyst system. Both theoretical studies^[17,19] clearly show the effects of the polarity of AB, and the importance of having both hydridic and acidic hydrogen atoms in the same molecule, in contrast to the situation in ethane. Baker et al. recently reported^[20] that in situ treatment of $[\text{Ni}(\text{cod})_2]$ with a suitable NHC ligand (NHC = N-heterocyclic carbene) affords long-lived catalysts which release an “unprecedented extent” of H₂ (> 2.5 equiv) from AB in diglyme solvent at 333 K, giving a soluble cross-linked borazine product. Interestingly, deuteration studies showed kinetic isotope effects of 1.7 for deuteration at boron, 2.3 for deuteration at nitrogen, and 3.0 for deuteration at both boron and nitrogen, suggesting a concerted mechanism for H₂ release from AB with this catalyst system.

Lewis or Brønsted acids, such as B(C₆F₅)₃, HOSO₂CF₃, or HCl, all at 0.5 mol% loading, catalyze the release of 1.1–1.3 equivalents of H₂ from AB in nonvolatile polyether solvents (e.g., tetraglyme or diglyme) at 333 K in about 18–20 h.^[21] Cyclic products are formed, probably via (H₂NBH₂)₂ precursors which, in the polyether solutions (in contrast to the solid-state^[22]) undergo dehydrocyclization at 333 K. The potential to use nonvolatile acid catalysts, such as polyphosphoric acid or supported acids, to initiate dehydropolymerization of AB was proposed, but again, the need for efficient regeneration processes was noted.

While these recent efforts show that there has been much progress on new promoters for the controlled release of H₂

from AB under mild conditions, the main issues for future research will be minimizing the formation of volatile products and developing economically viable methods for regeneration of AB; the latter, of course, depends on what products the catalysts produce. An alternative, namely finding new uses for the AB dehydrogenation products, would defeat the sustainability objective while depleting the world's borate deposits fairly quickly. It is worth noting that there are a number of other types of hydrogen-storage materials which are under investigation, and it is beyond the scope of this Highlight to discuss them. It remains to be seen which, if any, of these materials will eventually satisfy all of the economic and technical requirements for use as a fuel source.

Finally, this Highlight would not be complete without mentioning the very exciting new findings by Stephan et al.^[23] of metal-free phosphorus/boron systems which reversibly activate H₂. While not likely to be of direct relevance to automobile fuels, these novel systems provide a new pathway for H₂ activation, and are likely to lead to novel applications.

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