

Hydrazine Borane: A Promising Hydrogen Storage Material

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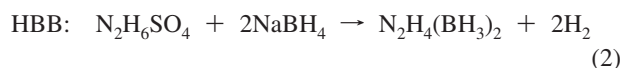
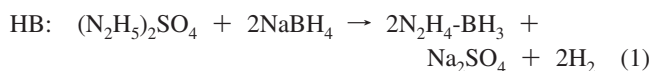
Abstract: We describe an easy method of improving the promising hydrogen storage capabilities of hydrazine borane by adding an equimolar amount of lithium hydride. The resulting mixture contains 14.8 wt % H₂. The hydrogen release behavior of both the pure hydrazine borane and the LiH mixture was studied at various temperatures and showed excellent hydrogen release rates at a reasonable temperature range of 100–150 °C.

Introduction

With oil reserves running low and oil demand rising, the search for alternative fuels is a matter of great importance. Hydrogen in combination with a fuel cell is generally seen as the most attractive option.¹ However, two major obstacles for a widespread use of hydrogen especially for mobile applications have proven to be critical: hydrogen production and hydrogen storage. Efficient processes for a large-scale production of hydrogen need to be developed, preferably using “clean” energy (e.g., photochemical water splitting²). Since storing pure hydrogen (either as a liquid or as a compressed gas) is out of question for a variety of reasons (volumetric energy density being a major one),³ one of the key steps on the road to a working hydrogen economy will be the development of an efficient hydrogen storage material. A lot of money and effort is being put into finding a material that meets the standards set by the DOE in 2007.⁴ One of the most promising candidates seems to be ammonia borane (AB).⁵ AB has a gravimetric hydrogen storage capacity of 19.6 wt % consisting of three hydridic (H⁻) and three protic (H⁺) atoms bound to a nitrogen and a boron atom that form a Lewis acid–base complex. There are various ways to release hydrogen from AB: hydrolysis in water,⁶ dehydrocoupling in ionic liquids⁷ or organic solvents,⁸ and thermal decomposition of the solid.⁹ Recently, progress was made regarding the regeneration of spent AB, which can be

seen as a breakthrough toward practical applications.¹⁰ However, several problems remain: While the dehydrogenation reaction in solution was significantly improved by using a variety of catalysts,¹¹ the hydrogen release from solid AB is still comparably slow and includes a long induction period during which very little hydrogen is released. Byproducts of the reaction include volatile borazine, which is undesired in combination with a fuel cell. Foaming of the substance during hydrogen release causes additional technical difficulties.

The closely related compounds hydrazine borane N₂H₄–BH₃ (HB) and hydrazine bisborane N₂H₄(BH₃)₂ (HBB) contain 15.37 wt % (4H⁺, 3H⁻) and 16.88 wt % (4H⁺, 6H⁻) of hydrogen, respectively. Both compounds are easily prepared from a reaction of either hydrazine sulfate (leading to HBB) or dihydrazine sulfate (leading to HB) with sodium borohydride in cyclic ethers such as dioxane:¹²



Results and Discussion

Studies on the hydrogen release from solid HBB were performed with some success (up to 10 wt % H₂ at 150 °C) in our group. They showed that the substance decomposes explosively upon rapid heating and at temperatures over 160 °C, rendering the material unsuitable as a hydrogen source for mobile, widespread applications unless it can be stabilized (this approach was followed by U.S. army researchers in the 1980s).¹³ Therefore, our work concentrated on HB which reportedly

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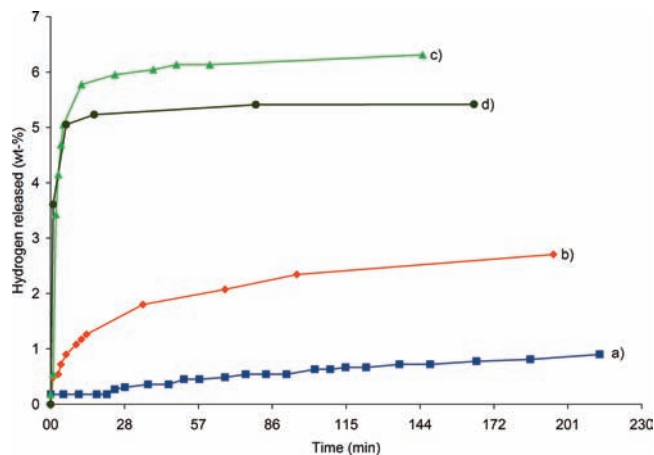


Figure 1. Hydrogen release of pure HB at (a) 65 °C, (b) 100 °C, (c) 140 °C, and (d) 150 °C.

releases hydrogen in a controlled manner even at temperatures as high as 200 °C.¹²

The thermal decomposition of solid HB was first studied by Ricker and Goubeau in 1961,¹² and further investigations on the reaction kinetics were published by Zhigach et al. in 1973.¹⁴ HB has a melting point of 61 °C, at which the decomposition slowly starts. The hydrogen release rates were studied at various temperatures ranging from 65 to 150 °C (Figure 1) by both volumetric methods and pressure monitoring. The H₂ release is slow and follows an almost linear course at low temperatures (65 °C). While the H₂ release at 100 °C is faster than at 65 °C during the first hour, it slows down to a similar rate after this time period. At elevated temperatures (>100 °C), the major amount of H₂ is released in a matter of minutes (12 min, 5.8 wt %) after which further release is slow. The total amount of hydrogen released as well as the time in which most of the hydrogen is released are better at higher temperatures. Surprisingly, HB releases more H₂ at 140 °C than at 150 °C. This might be due to the fact that the melt foams upon decomposition and solidifies rapidly above 140 °C, which could immobilize HB molecules in a way that intermolecular hydrogen release is hindered. The hydrogen release behavior supports this assumption: At 140 °C, the hydrogen release is quick in the beginning and slows down considerably afterward, steadily releasing H₂ for several more hours. At 150 °C, however, the hydrogen release stops almost completely after a few minutes. Contrary to ammonia borane, there is no induction period for the decomposition. The samples were kept at the chosen temperatures until the amount of released hydrogen ceased. The final amounts of H₂ released after prolonged heating are given in Table 1.

In October 2007, Diyabalanage et al. reported research on compounds of the composition Ca(NH₂BH₃)₂ made by a reaction of AB and the metal hydride in THF.¹⁵ Since HB has four protic hydrogens, but only three hydridic, this sparked the idea of adding light metal hydrides to HB to get equal amounts of protic and hydridic hydrogen atoms. Instead of doing so in solution, creating a compound M⁺(N₂H₃BH₃)⁻ and losing considerable

Table 1. Final Amounts of H₂ Released from HB and HB/LiH after Keeping the Substances at the Given Temperatures until No More H₂ was Released

substance	temperature (°C)	H ₂ release after prolonged heating (wt %)	time (h)
HB	65	3.1	43
HB	100	3.3	30
HB	140	6.5	16
HB	150	5.4	3
HB/LiH	100	8.1	45
HB/LiH	130	10.8	21
HB/LiH	150	11.9	4.5

amounts of hydrogen in the process (eq 3), a 1:1 mixture of solid LiH and solid HB was tested for its hydrogen release capabilities.



LiH/HB contains 14.8 wt % of hydrogen total and is able to release more than 11 wt % H₂ in only 45 min at 150 °C (Figure 2). At 100 °C, the H₂ release increases quickly before leveling out around 60 min at about 5.5 wt %. In the same time, the total amount of H₂ released increases to about 9 wt % at 130 °C. At 150 °C, both the release rate and the total amount of hydrogen produced are even better: ~10 wt % H₂ is evolved in the first 12 min, after which the release rate slows down and levels out at about 12 wt %. If the samples are kept at the chosen temperatures for longer times, even more H₂ is released at slow rates. The final amount of H₂ released for each temperature is given in Table 1. While the hydrogen release at 100 and 130 °C continues at very low rates for up to 2 days, yielding 8.1 wt % H₂ (100 °C) and 10.8 wt % H₂ (130 °C) in total, it is complete after only 4.5 h at 150 °C (11.9 wt % H₂).

The comparison of pure HB and HB/LiH at 150 °C (Figure 3) shows a drastic increase in the amount of hydrogen released. At 150 °C, an increase of ~110% in the hydrogen storage capacity of HB/LiH compared to pure HB can be seen after only 80 min, after which the amounts of H₂ produced do not change significantly any more. Not only does the addition of LiH increase the total amount of H₂ produced but it also speeds up the reaction considerably: at 100 °C, pure HB releases 2.1 wt % H₂ during the first hour (Figure 1), while HB/LiH releases 5.5 wt % in the same time (Figure 2). At 150 °C, pure HB releases 5.3 wt % H₂ during the first hour, while the H₂ release of HB/LiH amounts to 11.4 wt % in the same time (Figure 3).

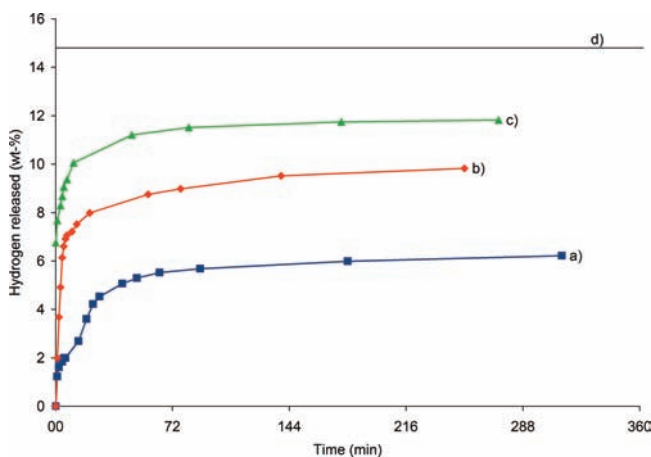


Figure 2. Hydrogen release of HB/LiH at (a) 100 °C, (b) 130 °C, and (c) 150 °C. The horizontal line at 14.8 wt % (d) shows the theoretical amount of H₂ that can be released from HB/LiH.

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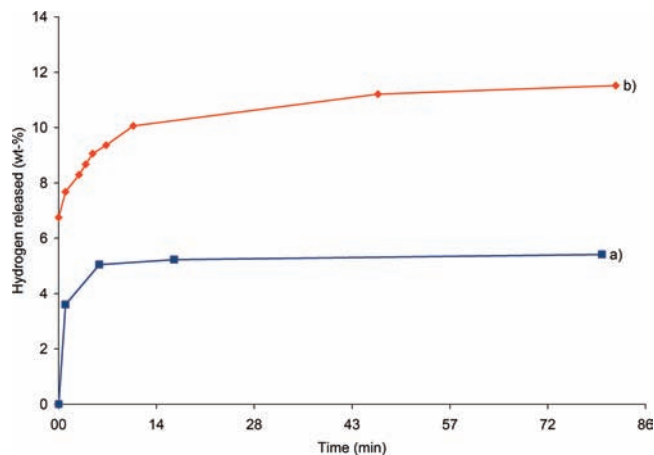


Figure 3. Comparison of the hydrogen release of (a) pure HB and (b) HB/LiH at 150 °C.

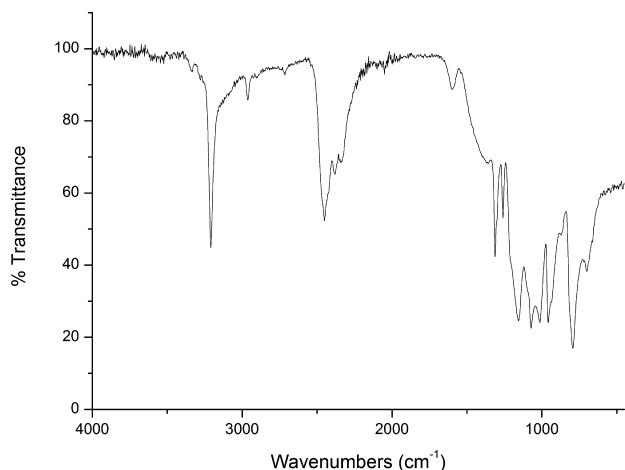


Figure 4. IR spectrum of the solid decomposition product of pure HB at 150 °C after the release of 1.5 equiv (6.5 wt %) of H₂.

This is consistent with recent studies on the ability of LiH to increase both the speed of the dehydrogenation and the final amount of H₂ released from ammonia borane considerably.¹⁶

The mechanism of the decomposition of HB and HB/LiH is complicated and difficult to investigate since both reactions yield solid substances that are insoluble in organic solvents, reactive with water, and amorphous to powder X-ray diffraction. The gaseous products were identified by IR spectroscopy and mass spectrometry and showed that only trace amounts of ammonia (<1 vol %) were produced. No borazine was detected. After the release of 1.5 equiv (6.5 wt %) of H₂ (Figure 4), the IR spectrum of the decomposition product of pure HB shows only one remaining strong signal in the region of $\nu(\text{NH})$, which indicates a polymeric structure in which all NH bonds are equal. The IR spectrum of the decomposed HB/LiH looks similar (Figure 5), but with a very broad peak in the region of $\nu(\text{NH})$, which indicates that the product is a not as well-defined polymer

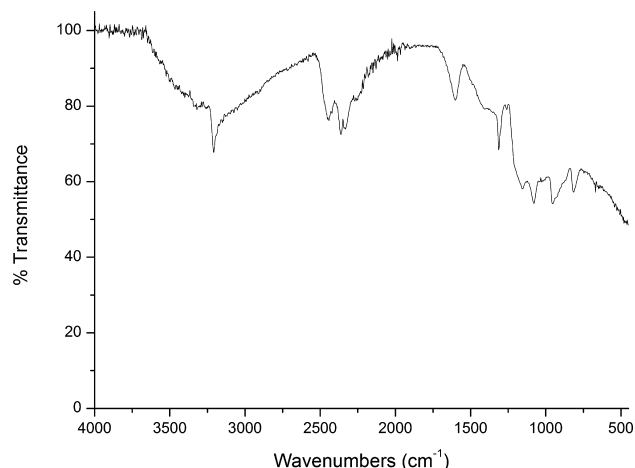


Figure 5. IR spectrum of the solid decomposition product of HB/LiH at 150 °C after the release of 2.9 equiv (11.9 wt %) of H₂

as the pure HB decomposition product. This could be due to cross-linking of the polymer chains.

Conclusions

In summary, we have shown that the already promising hydrogen storage capabilities of hydrazine borane (15.4 wt % H₂ total, 6.5 wt % H₂ release at 140 °C) can be significantly improved by adding an equal amount of lithium hydride, which yields a mixture containing 14.8 wt % H₂ that will release more than 11 wt % H₂ at 150 °C in less than an hour. Unsolved problems remaining include the tendency of the substances to foam upon decomposition at higher temperatures, the complete identification of the solid reaction products, and the regeneration of spent material. First tests of solid-phase catalysts to increase the hydrogen release rates especially of pure hydrazine borane show very promising results.

Experimental Section

The starting materials NaBH₄, LiH, N₂H₆SO₄, and N₂H₅OH were purchased from Merck Chemicals and used as received. HB and HBB were synthesized according to literature methods.¹² The purity of the samples was verified by NMR and IR spectroscopy.

Gas infrared spectra were recorded using a Shimadzu FTIR-8400S spectrometer and a gas IR cell. Solid-state ATR-FTIR spectra were taken using a Nicolet Nexus spectrometer with smart dura SamPLIR. MS spectra were obtained using a Balzers Quadstar 421 quadrupole mass spectrometer attached to glass vacuum line system.

All manipulations were performed in an inert atmosphere using either Schlenk techniques or an argon-filled glovebox. In a typical experiment, 1 mmol of both HB and LiH was ground together in a mortar and filled into glass tubes (5 mm outer diameter) with an attached side arm which was connected to either a gas buret or a glass vacuum line of known volume equipped with a manometer. The glass tube was inserted into a preheated tube furnace equipped with a tightly fitting aluminum piece with a cavity (6 mm diameter) in order to minimize the heat gradient. To identify the gaseous byproduct, the released gas was transferred either to a quadrupole mass spectrometer connected directly to the vacuum line or into an IR gas cuvette. In order to measure the amount of gaseous side products, a defined amount of gas was transferred into a calibrated gas IR cuvette.

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