

Hydrogen Storage Materials for the Future: Synthesis and Dehydrogenation Studies of Ammonia Borane

MARIAN UNIVERSITY
Indianapolis

Thomas M. Sublett and Roderick M. Macrae
Marian University, Indianapolis

IGSS'10
The Institute for Green and Sustainable Science

Abstract

Ammonia borane is an efficient hydrogen storage material of considerable current interest, with a storage capacity of 19.4 wt. %. In this work we present synthesis of ammonia borane using the recently developed method of Ramachandran and Gagare^[1], study of the thermolytic dehydrogenation of ammonia borane by Fourier transform infrared spectroscopy, and proof-of-principle demonstrations of a gas burette apparatus for hydrogen collection by base hydrolysis of sodium borohydride.

Introduction

In the search for new fuels and energy storage materials for a post fossil-fuel economy, hydrogen is one of the most promising candidates: not only does H₂ possess the highest fuel value of any material at 120 kJ/g (LHV), but its combustion reaction leads only to water as a product, it can be burned directly or used in electrochemical fuel cells, and while not readily available on Earth in elemental form it can be produced electrolytically from water in a "green" fashion using solar energy (although the most common current production method is steam reforming of hydrocarbons).

The problem with hydrogen lies in its containment. Hydrogen is a gas at STP, leading to a low energy density (about 10 kJ/L). Pressurization to 800 bar is required in order to yield a volumetric energy density 1/3 that of gasoline. At such pressures hydrogen must be kept in steel containers weighing 100 times as much as the hydrogen they contain, and presents a severe explosion hazard in case of catastrophic tank failure. (Liquid hydrocarbons, by contrast, can be contained in simple thin-walled tanks.) Liquefaction of hydrogen is another possibility, but loss through venting makes this strategy impracticable for automobile use.

What is needed is a containment system in which hydrogen can be stably stored at high volumetric density at temperatures close to ambient temperature and without excessive applied external pressure, but from which hydrogen can be released in a facile manner at mildly elevated temperatures. Several alternative methods for hydrogen storage have been proposed in recent years; these include complex metal hydrides such as sodium alanate^[2], porous sorbent materials such as metal organic frameworks (MOFs)^[3], and dehydrogenation of light molecules containing a large mass fraction of covalently bound hydrogen. In this study we focus on ammonia borane, which has in the last few years become a material of acute interest as its intrinsic hydrogen storage capacity (19.4 wt. %, of which about 14 % can be chemically liberated via dehydrogenation reactions) already exceeds the targets set by the Department of Energy for 2015^[4,5].

Synthesis

Ammonia borane was first synthesized by Shore and Parry in 1955 by two methods, reaction of ammonia with the "diammoniate of diborane" ($[\text{H}_2\text{B}(\text{NH}_3)_2]^+ [\text{BH}_4]^-$) and reaction of lithium borohydride with ammonium chloride, from the latter of which they obtained a yield of around 45 %^[6]. Subsequent work either refined this latter procedure, for example through the use of sodium borohydride instead of lithium borohydride^[7], or through an alternative direct reaction between diborane and ammonia^[8]. Quite recently, as a result of the strong interest in a low-cost efficient synthesis of this candidate hydrogen storage material, a systematic optimization study of the borohydride synthetic strategy was carried out by researchers at Purdue University^[1], which showed that optimal synthetic timescales (down to 2 hours) and yields (up to 95%) were obtained using ammonium bicarbonate and sodium borohydride with THF or 1,4-dioxane as solvent.

Following the procedure of [1], sodium borohydride (0.385 g, 10 mmol) and ammonium bicarbonate (1.601 g, 20 mmol) were combined in a 100 mL double-necked flask. 50 mL of sodium-dried THF was added to the flask and the contents were stirred under argon for 24 hours at 40 ° C. The procedure was carried out in a well-ventilated fume hood. The reaction mixture was cooled to room temperature and filtered, whereupon the filtrate was concentrated under vacuum to yield ammonia borane. The THF was removed with a rotary evaporator. A very small amount (less than 10 mg) of white solid remained after evaporation. Boiling THF was then added to the flask, which was then immersed in an ice bath to facilitate crystal growth. The solution was then filtered with an ultra-fine sintered glass funnel to remove any contaminants. An infrared spectrum of the product was obtained by allowing a sample of the original filtrate to dry by evaporation on a salt disc. A melting temperature evaluation was performed, but the solid did not melt below 350 ° C.



Figs. 1 and 2. Synthesis apparatus

Thermolysis

Hydrogen evolution from ammonia borane can be accomplished through several reaction paths, including thermolytic dehydrogenation, hydrolysis, and methanolysis. In thermolysis, NH₃BH₃ is thought to go through three stages: induction, nucleation, and growth. In induction phase the dihydrogen bonding is disrupted, creating a mobile phase of NH₃BH₃ in which rearrangement can occur. Diammoniate of diborane (DADB) forms from the mobile phase, starting the nucleation stage. In the growth stage, DADB reacts with NH₃BH₃ to evolve H₂. This process continues until a polymer-like aminoborane chain is formed^[9]. At temperatures $\geq 90^\circ\text{C}$ H₂ production commences after about 15 minutes, but at temperatures even 10 ° C lower the induction phase can last several hours^[10].

An initial thermolysis run at 80 ° C in laboratory air led to sample ignition (Fig. 3). Subsequent trials were conducted under argon. A sample of 0.1003 g of NH₃BH₃ (Aldrich, 97%) under a dry argon atmosphere was held in a water bath at 80-90 ° C. The sample was heated for 15-25 minutes, then removed from the hot water bath and placed in an ice bath to stop further reaction. The process was then repeated. Four IR spectra were obtained using KBr salt discs prepared as described in the next section, over a period of about one hour and thirty minutes (Fig. 4)

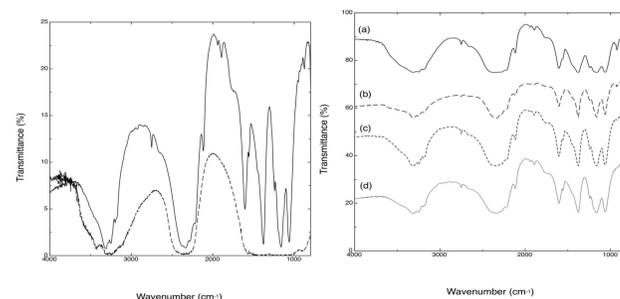


Figure 3. Comparison of combusted (dashed line) vs. thermolyzed (solid line) NH₃BH₃

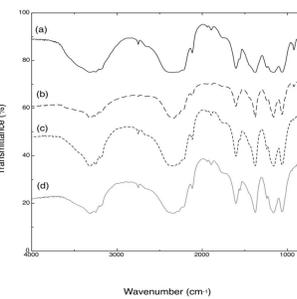


Figure 4. Comparison of IR spectra obtained via thermolysis of NH₃BH₃. (a) Initial spectrum. (b) Spectrum after 25 minutes. (c) Spectrum after 45 minutes. (d) Spectrum after 90 minutes.

Sample Characterization

All infrared spectra were measured using a Shimadzu FTIR-8400S at a resolution of 4 cm⁻¹. Standard spectra were obtained using a sample of ammonia borane obtained from Aldrich. Figure 5(a) shows a spectrum obtained from a powder sample of NH₃BH₃ combined with dry KBr using a Wig-L-Bug grinding mill and compacted into a disc of 7 mm diameter and about 1 mm thickness using a mechanical press. Figure 5(b) shows a spectrum obtained by dissolving NH₃BH₃ in dry THF and allowing the sample to evaporate onto a salt disc. The primary difference between these spectra is a broad feature on the high-frequency side of the peak at 3300 cm⁻¹ in spectrum (b), most likely due to residual THF.

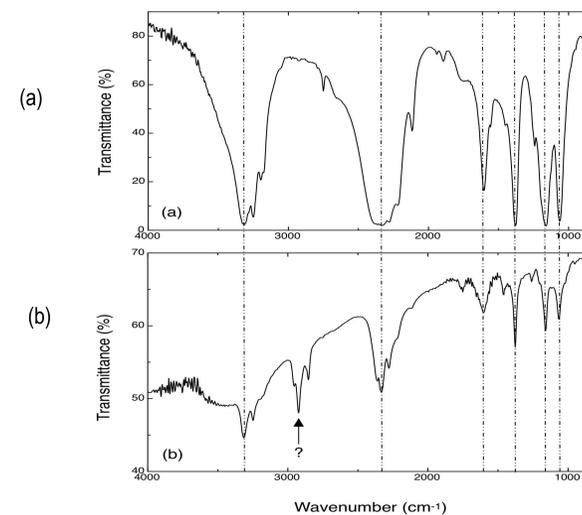


Figure 5. Comparison of stock powder sample NH₃BH₃ (a) and synthesized NH₃BH₃ (b).

IR spectra of solid ammonia borane have proved difficult to assign because of substantial bond length changes (and accompanying frequency changes) that occur in the transition from the gas phase to the solid^[11]. The vibrational modes observed in the room temperature tetragonal crystal phase are otherwise similar to those in the gas phase^[12]. The principal observed modes are NH stretches in the region of 3300 cm⁻¹, BH stretches in the region of 2300 cm⁻¹, NH₃ deformation in the region of 1600 cm⁻¹ and 1325 cm⁻¹, and BH₃ deformations in the 1100-1200 cm⁻¹ region. The spectra are complicated by the presence of two boron isotopes. The spectrum of the synthesized product shows the expected peaks, but also exhibits what appear to be impurity peaks in the vicinity of 2900 cm⁻¹. A computed spectrum of single-molecule NH₃BH₃ appears in Figure 6, showing the expected features in the gas phase spectrum.

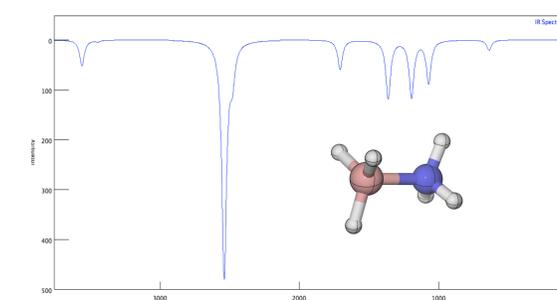


Figure 6. Calculated infrared spectrum of single-molecule NH₃BH₃

Volumetric Hydrogen Evolution

Hydrogen gas measurement was tested using base hydrolysis of NaBH₄. An apparatus (Hydride Analysis Kit) was assembled for measuring the amount of hydrogen being released with a gas burette and collection vessel (Fig. 7). Two trial runs were performed using a double-necked 250 mL round bottomed flask. For both trials, NaBH₄ was dissolved in 10 mL of 1M NaOH. For trial 1, 0.0378 g (1 mmol) of NaBH₄ was dissolved. The flask was heated to 40 ° C and stirred. Slowly, 10 mL of 6M aqueous HCl was added via syringe. Hydrogen evolution occurred and 47 mL was measured in the gas burette. In the second trial, 0.0378 g (1 mmol) of NaBH₄ was used. 40 mL was observed in the gas burette, corresponding to about 2 mmol of H₂.



Figure 7. Apparatus used for hydrolysis of NaBH₄

Future Work

Future work will include:

- Gas evolution studies of ammonia borane hydrolysis, with direct measurement of pressure and gas volume flow;
- Improvement of thermolysis technique;
- Development of an instrumental method superior to IR for the determination of where bond induction, nucleation, and growth occur;
- Improved synthesis technique for larger quantities of ammonia borane, with solvent recovery;
- Improved methods of product extraction and purification.

Discussion

IR spectra demonstrate successful synthesis of ammonia borane by the method of Ramachandran and Gagare. Hydrolysis measurements on NaBH₄ indicate that our apparatus can quantify H₂ evolved in the reaction. In the ammonia borane thermolysis, we were not able to observe significant differences between the spectra using standard FT-IR. This may be due to the removal of the flask to and from the heat source, to the KBr disc preparation method, or to intrinsic limitations of the IR method. A method of performing the same procedure at constant well-controlled temperature should improve the results of the IR spectra, but better measurements should be possible using different instrumental approaches such as Raman spectroscopy or ¹¹B NMR with in-situ sample temperature variation.

References

- [1] P. V. Ramachandran, P. D. Gagare, *Inorg. Chem.* 46, (2007), 7810.
- [2] A. Zaluska, L. Zaluski, J. O. Strom-Olsen, *J. Alloys Compd.* 298, (2000), 125.
- [3] A. G. Wong-Foy, A. J. Matzger, O. M. Yaghi, *J. Amer. Chem. Soc.* 128, (2006), 3494.
- [4] C. W. Hamilton, R. T. Baker, A. Staubitz, I. Manners, *Chem. Soc. Rev.* 38, (2009), 279.
- [5] S. Satyapal, J. Petrovic, C. Read, G. Thomas, G. Ordaz, *Catal. Today* 120, (2007), 246.
- [6] S. G. Shore, R. W. Parry, *J. Amer. Chem. Soc.*, 80, (1958), 8.
- [7] M. G. Hu, J. M. Van Paaschen, R. A. Geanangel, *J. Inorg. Nucl. Chem.* 39, (1977), 2147.
- [8] E. Mayer, *Inorg. Chem.* 12, (1973), 1954.
- [9] A. C. Stowe, W. J. Shaw, J. C. Linehan, B. Schmid, T. Autrey, *Phys. Chem. Chem. Phys.* 9, (2007) 1832.
- [10] D. J. Heldebrand, A. Karkamkar, N. J. Hess, M. Bowden, S. Rassant, F. Zheng, K. Rappe, T. Autrey, *Chem. Matter* 20, (2008), 5333.
- [11] J. Dillen, P. Verhoveven, *J. Phys. Chem. A* 107, (2003), 2570.
- [12] N. J. Hess, M. E. Bowden, V. M. Parvanov, C. Mundy, S. M. Kathmann, G. K. Schenter, T. Autrey, *J. Chem. Phys.* 128, (2008), 034508.

Contact Information

Thomas M. Sublett - tsublett444@marian.edu Dr. Roderick M. Macrae - macrae@marian.edu