

Quantitative Analysis of Hydrogen Evolution from Ammonia Borane and Sodium Borohydride

Abstract

We study the acid-catalyzed hydrolysis reactions of ammonia borane and sodium borohydride, two materials of interest from the perspective of a post-fossil-fuel economy in which hydrogen plays a leading role. The reaction stoichiometries for complete hydrolysis are



Introduction (Edit)

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).

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^[1], porous sorbent materials such as metal organic frameworks (MOFs)^[2], and dehydrogenation of light molecules containing a large mass fraction of covalently bound hydrogen. In this study we focus on sodium borohydride and ammonia borane, the latter of 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^[3,4].

Two methods have been proposed for the liberation of hydrogen from ammonia borane; of these, the more explored has been thermolysis, which occurs above about 85° C and has the benefit of producing only H₂ gas but leads to potential complications in the recycling of the residual solid mixed aminoborane polymer product^[6-12]. We focus instead here on hydrolysis, which also efficiently produces H₂ gas but which additionally yields NH₃ as an unwelcome by-product which requires removal from the gaseous product stream^[9,10,13,14]. Additionally, we pursue comparative studies on sodium borohydride, NaBH₄, another candidate hydrogen storage material of slightly lower storage capacity than ammonia borane^[15].

Hydrolysis

Using a hydrolysis analysis kit, several tests were performed to determine both the flow rate of hydrogen gas evolved from a hydrolysis reaction and pressure from evolved gas. Runs were performed with both NaBH₄ and NH₃BH₃. Initial runs were performed to determine if pH had an influence upon gas evolution. It was determined that the ideal molarity to use for subsequent hydrolysis reactions was 1.5 M HCl obtained as a stock sample. NaBH₄ was measured first, initially to determine visually the amount of gas evolved. All measurements of volume were taken from a gas buret.

All measurements were done with around 1 mmol of solute (0.0378 g NaBH₄) and 10 mL of 1.5 M HCl. Flow rate was determined with the use of a McMillan Model 101 FLO-SENSOR which converted gas flow to volts by using a small flywheel. (The inertia of the flywheel is a potential source of measurement error, as the wheel continues to spin down for some seconds after gas flow ceases.)



Figure 1: Hydrolysis analysis apparatus.

Figure 2: Flow meter

Figure 3 shows a trial run using 0.0377 g SBH and 10 mL 1.5 M HCl.

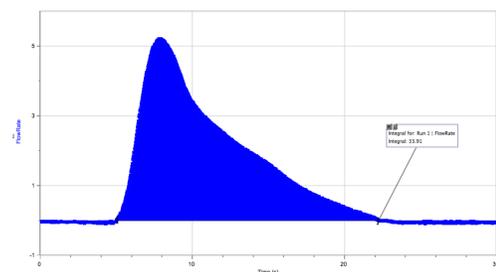


Figure 3. NaBH₄ demonstrating integral of flow rate

The gas flow data show a smooth curve that tapers exponentially mainly due to the slowing of the wheel. The volume of gas directly measured using the gas buret was ~35 mL. This value can be compared with a value computed using the gas flow readings which are obtained from the meter voltage using the formula:

$$\text{VDC} \times \frac{100\text{mL} / \text{min}}{1\text{volt}} \times \frac{1\text{min}}{60\text{sec}} = \frac{dV}{dt}$$

where dV/dt is the gas flow rate in mL/sec. The corrected curve was then integrated over time (in seconds) to generate the total volume change (ΔV) The calculated volume for this experiment was 33.91 mL, which agrees well with the observed volume of 35 mL.

The AB reaction followed the same procedure, but the utilization of a Vernier gas pressure sensor was added. 0.031 g AB and 10 mL of 1.5 M HCl were combined in a round bottom flask. 21 mL of gas were observed in the gas buret. The same process was repeated above to analyze the data. In addition to that, the quantity of gas evolved was also calculated with a time-integrated version of the equation presented below:

$$\frac{P(\text{kPa}) \times \Delta V(\text{mL})}{8.314 \frac{\text{J}}{\text{molK}} \times 298\text{K} \times 1000} = \Delta n(\text{moles})$$

By this calculation, 0.0004641 moles (0.4641 mmols) of gas were generated in the reaction, which converted to a volume at STP amounts to 11.38 mL. This agrees poorly with the directly observed gas volume of 21 mL. (It should be noted that the gas evolution process is more complex in the case of ammonia borane than in sodium borohydride, as both hydrogen and ammonia are generated during ammonia borane hydrolysis, the latter gas being water-soluble.)

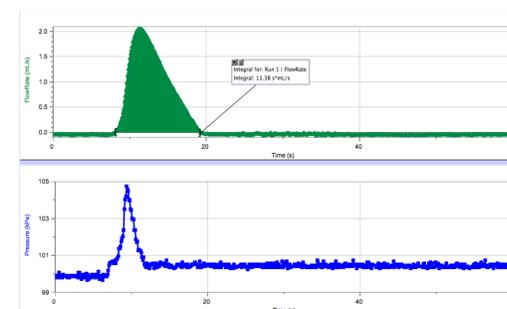


Figure 4. (Top) Integral of flow rate vs. time. (Bottom) Pressure in kPa vs. time.

IR Characterization

IR spectra were generated to determine the amount of ammonia generated via hydrolysis of AB. All infrared spectra were measured using a Shimadzu FTIR-8400S: gas phase spectra used a resolution of 0.8 cm⁻¹, while solid state spectra used 4 cm⁻¹ resolution. An IR spectrum for solid ammonia borane was performed using AB obtained from Sigma Aldrich, employing a powder sample directly loaded onto the ZnSe prism of a McCarthy ATR apparatus. The sample (Figure 5) exhibit peaks around 2300 cm⁻¹ and 3300 cm⁻¹, representing collective stretches of the N-H bonds.

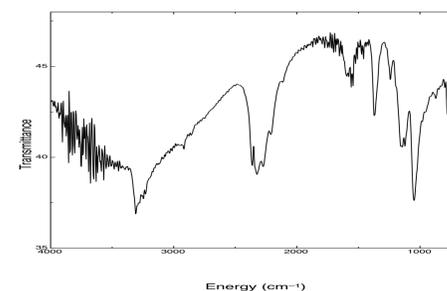


Figure 5. Spectrum of ammonia borane (ATR)

Next, IR spectra were obtained to study the evolution of ammonia during the hydrolysis. An ammonia reference spectra was obtained using vapor sampled above stock ammonia solution (27%) (Figure 8a). Ammonia vapor samples were injected into a McCarthy 10 cm demountable gas tube (Figure 7) for measurement of spectra.



Figure 7. Gas Tube for IR

Subsequently, a hydrolysis reaction was performed to liberate gas for sampling and IR spectral measurement. 0.0132 g AB was used with 10 mL 1.5 M HCl. (Figure 8c.) The spectrum is considerably less intense than the reference spectrum, but clearly exhibits the same band progressions.

To study the mechanism of the reaction a further spectrum (Figure 8b) was obtained as above, but using 10 mL of 1.5 M DCl made from stock DCl solution (35%) and D₂O, together with 0.016 g of AB. Major shifts in the bands are evident, clearly showing the formation of N-D bonds and suggesting that the dominant product is NH₂D. We believe that this represents new direct evidence that the nitrogen center of AB is directly involved in the acid-catalysed hydrolysis reaction^[13].

Figure 8: Gas phase IR spectra. Note the similarities between 8a and 8c and the shifting of lines in 8b in the 2600 cm⁻¹ region.

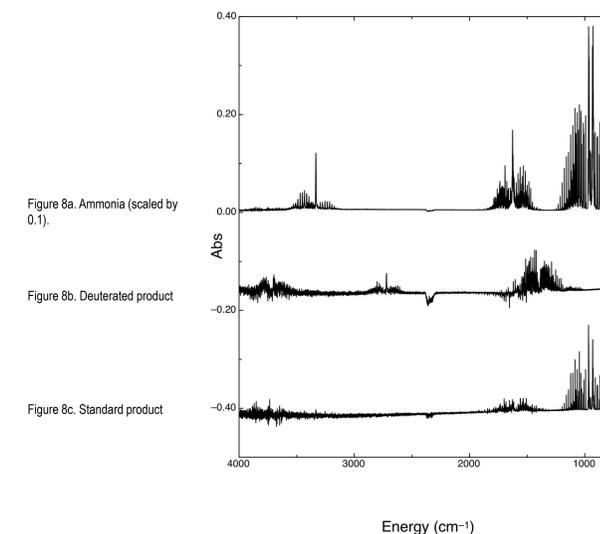


Figure 8a. Ammonia (scaled by 0.1).

Figure 8b. Deuterated product

Figure 8c. Standard product

Future Work

In the future, more work could be done in the characterization of the components of the evolved gas product of the ammonia borane hydrolysis reaction, including a search for deuteration of the H₂ gas evolved.

Additionally, studies could be done to compare thermolytic, hydrolytic, and other dehydrogenation reactions of AB from the perspective of determining the comparative ease of recycling the products to regenerate AB fuel for repeated use.

Discussion and Conclusion

We were able to determine, using the combination of a flow meter, a pressure sensor, and a gas buret, both the volume and the molar quantity of gas evolved in the acid-catalysed hydrolysis of NaBH₄ and NH₃BH₃.

We were able to generate usable spectra of solid ammonia borane using the ATR method, with much lower effort than in previous studies using pellet-pressed samples.

Using gas phase infrared spectroscopy we observed new direct evidence of the direct involvement of the nitrogen center of AB in the hydrolysis mechanism.

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