Hydrolytic Cleavage of Ammonia Borane Complex for Hydrogen Production

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ABSTRACT:

Ammonia-borane (AB) complex is a chemical hydride that is stable in air and water, and contains very high hydrogen content (19.6 wt%). AB is a promising material as a hydrogen carrier especially for power generation utilizing proton exchange membrane fuel cells (PEMFC). Release of hydrogen in the AB complex can occur by either thermolysis or hydrolysis. Thermolysis of AB generates, in addition to hydrogen, species such as borazine, monomeric aminoborane, and diborane, among others that have adverse effect on the PEMFC operation. In this paper, we present a new process for generating hydrogen via near room temperature hydrolysis of AB complex using small amounts of several platinum group metal catalysts. The kinetics of the AB hydrolysis in the presence of $K_2Cl_6Pt$ catalyst was studied using in situ $^{11}B$-NMR spectroscopy. The GC/MS analysis of the product gas showed that the amount of ammonia detected in the reactor effluent was significantly less when phosphoric acid was used as a sequestering agent.

KEYWORDS: Ammonia Borane, Hydrogen Storage, Chemical Hydrides, Hydrolysis, Catalyst.

Introduction

Compounds represented by the empirical formula $B_xN_xH_y$ have been known and used as high capacity hydrogen ($H_2$) carriers. Hydrogen generators based on such carriers can be employed for hydrogen on-demand applications. However, the hydrogen is often too impure for the proton exchange membrane fuel cell (PEMFC) applications, the process yield is low, the process requires high temperatures (above 100°C) for reasonable yield, and/or environmentally harmful materials are required.¹

Ammonia borane (AB) complex has the highest material hydrogen content (about 19.6 wt%) with a system-level $H_2$ energy storage density of about 2.74 kWh/L (vs. 2.36 kWh/L for a liquid hydrogen Dewar). At near room temperatures and atmospheric pressure, AB is a white crystalline solid, and is stable in both water and ambient air.

Thermolysis has been used as a method of choice to generate hydrogen from AB complex. There are several drawbacks to thermolytic release of hydrogen from AB complex. Ammonia borane pyrolysis begins at temperatures below 140°C. However, to release substantial amount of the hydrogen contained in AB complex, temperatures above 500°C are needed. The overall process is exothermic, but requires heat to be added to activate the AB complex. The overall reaction can be written as follows:

$$\text{NH}_3\text{BH}_3 + \text{Heat} \rightarrow \text{BN} + 3\text{H}_2 \quad (1)$$

Complete pyrolysis of ammonia borane complex provides 3 moles of hydrogen per mole of AB. In practice, thermolysis of AB involves competing reactions leading to the formation of various by-products. For example, FTIR analysis of the evolved gases from the thermolysis of AB complex has shown that monomeric aminoborane (BH$_2$NH$_2$), borazine, and diborane is also produced. The aminoborane comprises poly-(aminoborane), (BH$_2$NH$_2$)$_n$.

Poly-(aminoborane), the inorganic analog of polyethylene, is a nonvolatile white solid. These compounds are undesirable impurities that make hydrogen from direct thermolysis of AB complex unfit for PEMFC applications. Furthermore, formation of these species lowers $H_2$ yield from direct thermolysis of AB complex.

An alternative to thermolysis is provided by hydrolysis or methanolyis of AB complex. Hydrolytic or methanolic cleavage of amine borane complexes provides 3 moles of hydrogen per mole of AB complex.² ³ Although this process has been used in the field of modern synthetic organic chemistry and for
pharmaceutical applications, only recently has it been applied as a way of utilizing AB complex for the storage of hydrogen. Corresponding reactions are given below:

\[
\begin{align*}
\text{NH}_3\text{BH}_3 + 3\text{H}_2\text{O} &\rightarrow \text{NH}_3 + \text{H}_3\text{BO}_3 + 3\text{H}_2 \\
\text{NH}_3\text{BH}_3 + 3\text{CH}_3\text{OH} &\rightarrow \text{NH}_3 + \text{B(OCCH}_3)_3 + 3\text{H}_2
\end{align*}
\]

As noted above, AB complex is a stable adduct. Therefore, to date, the hydrogen generating reactions (2) and (3) have involved harsh acidic condition such as, refluxing in aqueous HCl or the use of heterogeneous catalysts based on palladium or nickel. In this paper, we describe a method for catalytic hydrolysis of AB complex for production of high purity hydrogen at low temperatures.

**Experimental**

**General.** AB complex (NH$_3$BH$_3$) and catalysts used in this work were obtained from Aldrich Chemicals and used without further treatment.

**Characterization and Analysis.** The X-ray Photoelectron Spectroscopy (ESCA) analysis was done using a Physical Electronic 5400 spectrometer and a Mg anode, at 300 W power, high resolution scans from 1100 to 0 eV step size 0.1 eV, dwell time 50 ms. In situ $^{11}$B-NMR measurements were conducted using a Varian VXR300. The GC/MS experiments were performed on a JEOL GCmate-II GC/MS-MS instrument. The carrier gas was He flowing at a rate of 2.0 mL/min. All GC runs were carried out in the splitless mode. The GC injector port and interface with MS were set at 60$^\circ$C and 250$^\circ$C, respectively.

**Hydrolytic Dehydrogenation Experiments.** In a typical reaction, the catalyst was dissolved in water and then added to as received AB. The amount of hydrogen was measured volumetrically.

**Kinetic Studies Using In Situ $^{11}$B-NMR.** 0.01 g of AB complex was added to 7 mL of 5 mM, 10mM, 30 mM, and 40 mM K$_2$Cl$_6$Pt in D$_2$O at 25$^\circ$C, 30$^\circ$C, and 35$^\circ$C. The NMR tube cap was modified to allow hydrogen release.

**Results & Discussions**

A. **Catalyst Screening for Hydrolytic Cleavage of AB Complex.** At near room temperatures, AB complex was found to readily undergo hydrolytic cleavage in the presence of various platinum group metal (PGM) salts such as, (NH$_4$)$_2$RuCl$_6$, K$_2$Cl$_6$Pt, (NH$_4$)$_2$PtCl$_6$, and Na$_3$RhCl$_6$. Figure 1 depicts the volume of hydrogen generated vs. time for several PGM salts. It can be seen that among all the catalysts screened, Na$_3$RhCl$_6$ had the highest catalytic activity. For all catalysts tested, the reaction is fast and exothermic.

![Figure 1. Hydrogen evolution vs. time for the hydrolytic dehydrogenation of AB complex (0.05g) by 0.1 mL of 19 mM solution of various PGM catalysts at room temperature.](image)
The rate of hydrolysis can be affected by varying the rate at which the catalyst solution is introduced to the AB powder. The reaction rate can also be affected by the reaction temperature and heat transfer within the reacting material. Figure 2 shows the amount of evolved H\textsubscript{2} as a function of time for hydrolytic dehydrogenation of AB complex at three different reaction conditions. Prior research has shown that AB bond cleavage is the rate-limiting step followed by rapid hydrolysis of BH\textsubscript{3}.\textsuperscript{3} Elevating the reactor temperature slightly from room temperature to 35°C for 5 min, significantly increased the rate of hydrolysis of AB complex compared to that resulting from either insulated reactor or isothermal reactor set at 30°C.

\begin{center}
\textbf{Figure 2.} H\textsubscript{2} production vs. time for hydrolytic dehydrogenation of AB complex (0.3 g) by 0.1 mL H\textsubscript{2}O and 0.44 mL of 19 mM K\textsubscript{2}Cl\textsubscript{6}Pt solution supplied at the rate of 0.02 mL/min at three different heating conditions.
\end{center}

\textbf{B. Kinetic Studies Using In Situ \textsuperscript{11}B-NMR.} In aqueous solutions of K\textsubscript{2}Cl\textsubscript{6}Pt, hydrolysis of the AB complex is first-order with respect to [AB]. The apparent first-order rate constant varies with the catalyst concentration as shown in Figure 3. Figure 4 depicts the rate of the AB hydrolysis vs. time for [K\textsubscript{2}Cl\textsubscript{6}Pt] in the range of 0.005-0.03 M. The data indicate that hydrolysis of AB complex is second order with respect to concentration of the catalyst. Therefore, the overall rate of K\textsubscript{2}Cl\textsubscript{6}Pt catalyzed hydrolysis of AB complex is third-order and can be expressed as: –d[AB]/dt = k'[AB][K\textsubscript{2}Cl\textsubscript{6}Pt]\textsuperscript{2}. It is assumed that the concentration of water remains constant throughout the reaction, thus, k′=k[H\textsubscript{2}O].

\begin{center}
\textbf{Figure 3.} Rate of hydrolysis of the AB complex as a function of time at various concentration of the K\textsubscript{2}Cl\textsubscript{6}Pt in the solution (0.005, 0.01 & 0.03 M). The rate is first order with respect to [NH\textsubscript{3}BH\textsubscript{3}].
\end{center}
Figure 4. Rate of NH$_3$BH$_3$ hydrolysis in D$_2$O solutions at 25°C for 0.005-0.03 M K$_2$Cl$_6$Pt catalyst concentration, slope = 2.27 (correlation coefficient = 0.92), $v_0 = k'[AB]$.

Figure 5 shows the temperature dependency (in the range of 25-35°C) of the AB hydrolysis reaction rates. The first-order rate constants increase as the temperature increased from 25-35°C (see Table 1).

Figure 5. Rate constant of NH$_3$BH$_3$ hydrolysis at 25, 30, and 35°C for a first order reaction with respect to [NH$_3$BH$_3$] using 0.01 M K$_2$Cl$_6$Pt solutions.

Using the information given in Table 1, the pre-exponential factor ($A$) and the activation energy ($E_a$) were determined from Figure 6 using the Arrhenius equation, $lnk = lnA - E_a/RT$, to be: $A = 1.6 \times 10^{11}$ Lmol$^{-1}$s$^{-1}$ and $E_a = 86.6$ kJmol$^{-1}$.

Table 1. Rate constants and correlation coefficients for the AB hydrolysis at $T = 25$, 30, and 35°C.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>k (Lmol$^{-1}$s$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.18 $\times$ 10$^{-3}$</td>
<td>0.999</td>
</tr>
<tr>
<td>30</td>
<td>1.42 $\times$ 10$^{-3}$</td>
<td>0.999</td>
</tr>
<tr>
<td>35</td>
<td>3.69 $\times$ 10$^{-4}$</td>
<td>0.987</td>
</tr>
</tbody>
</table>

C. ESCA Analysis of Spent Catalyst. Figure 7 depicts the ESCA spectra used to determine the state of Pt in the spent catalyst. The two binding energy peaks at 71.3 and 74.6 in the spectra are in good agreement with Pt$^0$ metal.$^6$ Results suggest that the platinum salt was reduced from Pt$^{4+}$ to Pt$^0$ within the course of the reaction. We note that the metallic state of the PGM catalysts did not show significant catalytic activity for hydrolysis of AB complex.
Figure 6. The Arrhenius plot for the hydrolysis of AB complex using $K_2Cl_6Pt$ as the catalyst, correlation coefficient = 0.86.

Figure 7. Pt 4f ESCA spectra of spent material from catalytic hydrolysis of AB complex.

D. Ammonia Sequestration. Hydrolytic cleavage of AB complex produces one equivalent weight of ammonia per equivalent weight of AB complex (Eq. 2). Ammonia can be split catalytically to generate more hydrogen (Eq. 4):

\[
2NH_3 \rightarrow N_2 + 3H_2 \quad (4)
\]

But, presently, there are no ammonia decomposition catalysts that provide high yields of hydrogen at temperatures below 400°C. For small portable fuel cell applications, ammonia decomposition at high temperatures is not generally feasible. It is, therefore, necessary to sequester NH$_3$ to avoid degradation of the PEMFC performance. Ammonia can be readily sequestered using sulfuric or phosphoric acid. For example, the stoichiometry for the production of hydrogen from AB complex using H$_3$PO$_4$ is as follows:

\[
NH_3BH_3 + 3H_2O + \frac{1}{3}H_3PO_4 + PGM \text{ catalyst} \rightarrow \frac{1}{3}(NH_4)_3PO_4 + B(OH)_3 + 3H_2 \quad (5)
\]

Figure 8 depicts the GC/MS spectra for the total ammonia ion count (TIC) for the gas samples taken from the head space of the AB hydrolysis reactor from tests with and without H$_3$PO$_4$ in the solution. The amount of
ammonia detected in the reactor effluent was significantly less when phosphoric acid was used as the sequestering agent.

![GC/MS spectra](image)

Figure 8. GC/MS spectra depicting the total ammonia ion counts for the gas samples AB hydrolysis reaction (a) without phosphoric acid and (b) with phosphoric acid

**Conclusions**

Near room temperature hydrolysis of AB complex has been carried out using small amounts of several PGM salts. The AB hydrolytic reaction is exothermic and can be extremely fast, kinetically. The rate of the reaction can be controlled by varying the flow rate of the catalyst solution into the reactor that contains a bed of AB powder. The rate of hydrogen production is also affected by heat transfer to and from the reaction zone and reaction temperatures. ESCA analysis of the spent material showed that the PGM in the catalyst is reduced to metallic state during the reaction and as such PGM did not display any catalytic activity.

The kinetics of the AB hydrolysis in the presence of K$_2$Cl$_6$Pt catalyst was studied using *in situ* $^{11}$B-NMR spectroscopy. The overall reaction-order was estimated to be three with an apparent activation energy $E_a = 86.6$ kJmol$^{-1}$.

The GC/MS analysis of the product gas showed that the amount of ammonia detected in the reactor effluent was significantly less when phosphoric acid was used as the sequestering agent.

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**References**


