

IV.B.1e Chemical Hydrogen Storage Using Polyhedral Borane Anions and Aluminum-Ammonia-Borane Complexes

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Objectives

- Develop heterogeneous catalysts for the controlled generation of hydrogen from the hydrolysis of salts of $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$ and $B_{11}H_{14}^{-}$ ions.
- Determine the kinetics and mechanism of these catalyzed borane anion hydrolysis reactions to provide design data for large-scale hydrogen generation devices.
- Optimize existing processes for the conversion of diverse >borohydride (B-H) sources to $Na_2B_{12}H_{12}$ and $Na_2B_{10}H_{10}$ for direct use in hydrogen generation without extensive purification.
- Investigate dehydrogenation of aluminum-ammonia-borane compounds $[Al(NH_2BH_3)_4]NH_4$ and $H_3N \cdot Al(NH_2BH_3)_3$ for hydrogen storage.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (E) Charging/Discharging Rates

Technical Targets

Data reported below are for hydrolysis of $(NH_4)_2B_{10}H_{10}$ with 25% mol of Rh metal catalyst at 80°C. The values are material-based where as the DOE targets are system-based.

Storage Parameter	UM 2007 Status	2010 Targets
System Gravimetric Capacity (kg H ₂ /kg System)	0.065 "In laboratory vessel" [(NH ₄) ₂ B ₁₀ H ₁₀ + water consumed + catalyst]	0.06
System Volumetric Capacity (kg H ₂ /l System)	0.0833 "In laboratory vessel" [(NH ₄) ₂ B ₁₀ H ₁₀ + water consumed + catalyst]	0.045
Charging/Discharging Rates H ₂ Flow Rate (g/s)/kW	0.025 (Material wt.)	0.02

Accomplishments

- Determined an active Rh metal catalyst for the hydrolysis of polyhedral borane anion salts.
- Optimized hydrogen release rate exceeding the DOE 2010 targets.
- Determined the rate and kinetics of the hydrolysis reaction. The rate of hydrolysis is first-order with respect to the concentration of borane anion salts and surface area of Rh metal catalyst.
- Investigated the probable mechanism of hydrolysis of borane anions and by investigating various derivatives of polyhedral borane anions.



Introduction

Hydrolysis of Polyhedral Borane Anions

Hydrolysis of borohydride compounds offer the potential for significant hydrogen storage capacity, but most work to date has focused on one particular anion, BH_4^- , which requires high pH for stability and large energy costs for regeneration. Other borohydride compounds, in particular polyhedral borane anions, may offer comparable hydrogen storage capacity without requiring high pH media and with significantly reduced energy costs for regeneration.

Aluminium Amidotrihydroborates

The ammonia borane molecule (AB) is a demonstrated source of chemically stored hydrogen (19.6 wt%) which meets DOE performance parameters except for its regeneration from spent AB and elemental hydrogen. The presence of an aluminum center bonded to multiple AB residues might combine the efficiency of AB dehydrogenation with an aluminum mediated hydrogenation process leading to reversibility. This work is just begun and will constitute phase II of the project. This annual report will primarily focus on the hydrolysis of polyhedral borane anions.

Approach

Hydrolysis of Polyhedral Borane Anions

This project provides the overall program focal point for the investigation of polyhedral borane anions $B_nH_n^{2-}$ ($n = 10$ and 12), $B_{11}H_{14}^-$ and their derivatives as reservoirs for stored electrons available for hydrogen release upon catalyzed hydrolysis. Due to their inherent stability, a transition metal catalyst is necessary for the hydrolysis. Transition metal ions such as cobalt, nickel, palladium and rhodium are known to form metal borides in the presence of reactive borane species. The rate of hydrolysis depends upon a) choice of polyhedral borane anion, b) metal catalyst, c) concentration of polyhedral borane anion, d) concentration of metal catalyst and e) temperature and pH of the reaction. For initial exploration, rhodium, nickel, cobalt, ruthenium, palladium, platinum and iridium catalyst were examined. It was found that cobalt-boride and nickel-boride were able to hydrolyse $B_{11}H_{14}^-$ but not $B_nH_n^{2-}$ ($n = 10$ and 12). Only rhodium was able to catalyze all polyhedral borane anions investigated for this project.

Aluminum Ammonia Boranes

For this study we will investigate dehydrogenation of $H_3N \cdot Al(NH_2BH_3)_3$ and $[Al(NH_2BH_3)_4]NH_4$. Recent efforts in the center and elsewhere on AB systems have provided plentiful information on the potential of similar materials for hydrogen storage.

Results

Catalytic Hydrolysis of $NaB_{11}H_{14}$, *Closo*- $B_{10}H_{10}^{2-}$ and *Closo*- $B_{12}H_{12}^{2-}$

Earlier we reported that among various metal catalysts investigated, rhodium was most active catalyst in the hydrolysis of these polyhedral borane anions. During the past year the main focus was to optimize the hydrolysis process, study the kinetics and explore the mechanism of the hydrolysis reaction. A rhodium

carborane complex L_2RhH -carborane ($L=PPh_3$) was synthesized and investigated for the hydrolysis process. However it was found to be inactive.

Kinetic Studies on the Rh Metal Catalyzed Hydrolysis of Borane Anions

The kinetic studies on the boranes anion hydrolysis showed that: a) the rate of hydrolysis is first-order with respect to the concentration of borane anion salts and with respect to the concentration of Rh catalyst; b) the change in hydrogen ion concentration doesn't affect the rate of hydrolysis; and c) the cation accompanying the borane anions does not have any appreciable effect on the rate of hydrolysis.

Activation Energy of the Hydrolysis Reaction

The rate of hydrolysis increases with the raise in temperature. This indicates first order reaction kinetics for all the polyhedral anions investigated. The rate equation can be written as follows:

$$k = A e^{-E_a/RT} \text{ or } \ln(k) = -E_a/RT + \ln(A)$$

where k is the reaction rate (mol s⁻¹), A the reaction constant (mol s⁻¹), E_a the activation energy for the reaction, R the gas constant and T is the reaction temperature (K). An Arrhenius plot, in which $\ln(k)$ is plotted against the reciprocal of absolute temperature ($1/T$), is shown in Figure 1 and summarized in Table 1. Similarly, the enthalpy of activation ΔH^\ddagger and entropy of activation ΔS^\ddagger for $NaB_{11}H_{14}$, *Closo*- $B_{10}H_{10}^{2-}$ and *Closo*- $B_{12}H_{12}^{2-}$ anions were calculated using the Eyring equation. These values are also summarized in Table 1.

Mechanism of the Hydrolysis Reaction

For this study we synthesized various derivatives of $B_nH_n^{2-}$ ($n = 10$ and 12), particularly $B_{12}(OH)_{12}^{2-}$, $B_{12}Cl_{12}^{2-}$,

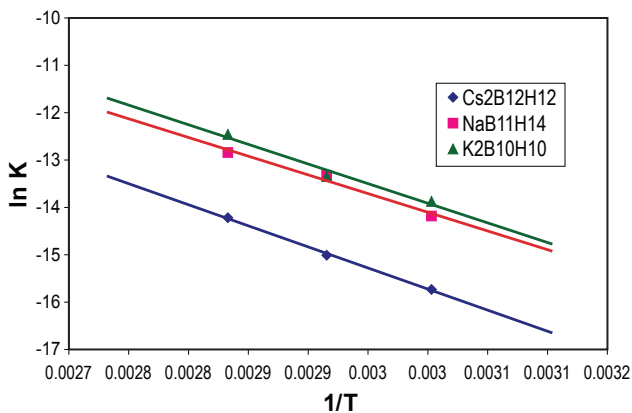


FIGURE 1. Arrhenius Plot of Rh (5 mol%) Catalysed Hydrolysis of $B_{10}H_{14}^-$, $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ (0.013 M)

TABLE 1. Calculated Activation Energy E_a , Enthalpy of Activation ΔH^\ddagger and Entropy of Activation ΔS^\ddagger for the Hydrolysis of Polyhedral Borane Anions

Borane Anions	E_a kJ/mol	ΔS^\ddagger , J/(mol K)	ΔH^\ddagger kJ/mol
$K_2B_{10}H_{10}$	68.95	-220.05	66.06
$NaB_{11}H_{14}$	65.70	-231.80	62.82
$Cs_2B_{12}H_{12}$	73.99	-220.50	71.11

$B_{10}Cl_{10}^{2-}$ and a partially chlorinated species $B_{10}Cl_8H_2^{2-}$. These derivatives were subjected to the same hydrolysis conditions as in case of $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ anions. The results showed that only $B_{10}Cl_8H_2^{2-}$ hydrolyzed under these conditions. This indicates that presence of the B-H bond is necessary for the hydrolysis process.

Conclusions and Future Directions

- The hydrolysis process follows first-order kinetics with respect to borane anion and Rh catalyst concentration.
- The hydrolysis of borane anions are in order of $B_{11}H_{14}^- > B_{10}H_{10}^{2-} > B_{12}H_{12}^{2-}$.
- Presence of the B-H bond is necessary for the catalytic hydrolysis.

For phase II of the project, we will investigate dehydrogenation of the Al-AB system.