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Beyond Hydrolysis: Scalable, On-Demand Dihydrogen Release from NaBH₄ enables Circular and Sustainable Process Design

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Abstract:

Hydrogen storage in its elemental form poses significant safety and economic challenges. Metal hydrides, particularly sodium borohydride, offer a promising alternative because of their superior safety profiles and enhanced transportability. This study presents a scalable hydrogen release system based on sodium borohydride and commercially available alcohols and acids. The system enables rapid, controlled hydrogen generation achieving quantitative yields. Quantum chemical calculations were performed to propose a mechanism for the alcoholysis of NaBH₄ with isopropyl alcohol (IPA) and acid present. It was demonstrated that the reaction proceeds via isopropoxy substituted borane derivatives BH(3-n)OiPr_n (for n = 0, 1, 2, 3), which can form Lewis acid-base adducts with IPA. These Lewis acid-base adducts serve as reaction complexes for B-H bond metathesis, upon which an equivalent of hydrogen gas is released. Notably, the spent fuel can be regenerated to sodium borohydride using established chemical reactions, ensuring the system's sustainability and applicability for larger-scale hydrogen production

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Contributors' Statement: J. C. Sootweg devised the project, the main conceptual ideas and proof outline. P. W. Wessels, T. Wesselingh and P. Germanacos carried out the experiments. C. J. Verhoef planned and carried out the simulations. G. B. De Jong aided in interpretation of results and design of experiments. F. Buß supervised the project and made contributions to the manuscript. V.J. Geiger supervised the project and processed the analytical data. All authors discussed the results and commented on the manuscript.

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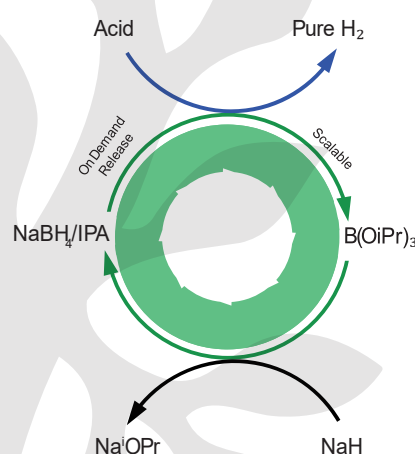
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SIGNIFICANCE (max 590 characters)

The study presents a novel hydrogen release system using NaBH₄ and isopropanol, enabling rapid, controlled hydrogen generation. This system addresses limitations in existing hydrogen technologies, by allowing easy storage, transport, and on-demand hydrogen release. The spent fuel is regenerated to NaBH₄ using established reactions, making it a sustainable and scalable solution for hydrogen economy applications. Mechanistic studies shed light on the physical organic interactions driving the alcoholysis of organo-boron compounds, expanding fundamentals of Lewis acid-base chemistry.



Keywords

Hydrogen Storage, NaBH₄, Energy Transition, Alcoholysis, Semi-Alcoholysis

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ABSTRACT

Hydrogen storage in its elemental form poses significant safety and economic challenges. Metal hydrides, particularly sodium borohydride, offer a promising alternative because of their superior safety profiles and enhanced transportability. This study presents a scalable hydrogen release system based on sodium borohydride and commercially available alcohols and acids. The system enables rapid, controlled hydrogen generation achieving quantitative yields. Quantum chemical calculations were performed to propose a mechanism for the alcoholysis of NaBH₄ with isopropyl alcohol (IPA) and acid present. It was demonstrated that the reaction proceeds via isopropoxy substituted borane derivatives BH₃-nO'Pr_n (for n = 0, 1, 2, 3), which can form Lewis acid-base adducts with IPA. These Lewis acid-base adducts serve as reaction complexes for σ-bond

metathesis, upon which an equivalent of hydrogen gas is released. Notably, the spent fuel can be regenerated to sodium borohydride using established chemical reactions, ensuring the system's sustainability and applicability for larger-scale hydrogen production.

Introduction

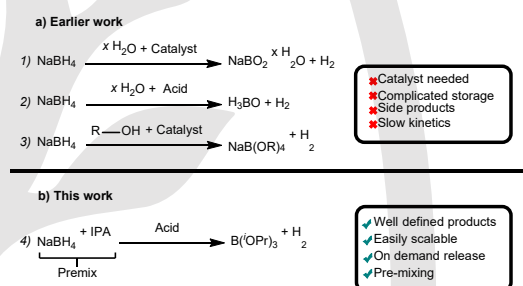
The transition from fossil fuel-based energy systems to a hydrogen economy has been significantly impeded by insufficient storage capacity.¹ Hydrogen gas exhibits low volumetric density, and its liquefaction demands substantial energy input.² Moreover, safety considerations, transportation challenges, and boil-off losses hinder the widespread adoption of hydrogen as an energy storage medium.³⁻⁵ To address these limitations, various chemical based hydrogen storage methods have been proposed, including ammonia, liquid organic hydrogen carriers (LOHC's) and metal hydrides.⁶⁻⁹

Ammonia exhibits several advantages, including a relatively high volumetric energy density (~13.5 MJ/L) as opposed to liquefied hydrogen gas (~8 MJ/L), along with well-established large-scale commercial production processes.⁸ Nevertheless, concerns related to safety, environmental impact, and toxicity significantly constrain its potential as a widely adopted hydrogen storage method.^{10,11} Conversely, most LOHCs are regarded as relatively safe and non-toxic. However, their development remains in its infancy due to challenges such as high dehydrogenation temperatures and severely limited large-scale synthesis.^{12,13}

Metal hydrides are well studied, offer superior safety profiles, enhanced transportability, and mitigate hydrogen loss during storage.¹⁴ However, the liberation of dihydrogen from these compounds typically necessitates elevated temperatures and pressures.^{15,16} Additionally, the synthesis of these materials often requires critical raw materials, which present potential resource constraints. These factors collectively impact the practical implementation and scalability of metal hydride-based hydrogen storage systems.¹⁷

NaBH₄ has been a promising candidate among metal hydrides for hydrogen storage, exhibiting favorable characteristics that alleviate several of the limitations mentioned above, due to the high gravimetric and volumetric energy density (21.4 wt% H₂ and 137 kg/m³ respectively, based on the reaction with acid and isopropanol), low toxicity and superior safety.^{18,19} Despite the U.S. Department of Energy's decision in 2007 to discontinue research on NaBH₄ as a vehicular hydrogen energy carrier, recent advancements have demonstrated NaBH₄'s potential for portable and remote fuel cell applications.²⁰⁻²⁴

Initial investigations into the utilization of NaBH₄ as a solid-state hydrogen storage vector, primarily centered on its hydrolysis reaction, resulting in the liberation of dihydrogen gas and the formation of sodium metaborate as a byproduct. However, this reaction is characterized by notoriously slow kinetics and produces a variety of hydrated metaborate species, significantly reducing the effective gravimetric hydrogen storage capacity.^{25,26,27} The incorporation of catalysts can enhance the reaction kinetics and provide greater control over byproduct formation of the hydrolysis of NaBH₄ (Scheme 1).^{28,29} Nevertheless, this approach compromises the system's recyclability and circularity, presenting challenges for sustainable long-term use. Addition of an acid also improves kinetics, but large-scale applications necessitate complex transportation and storage systems for the reagents, which presents logistical challenges (Scheme 1).³⁰



Scheme 1: Different reaction routes of releasing hydrogen from NaBH₄. 1. Catalytic hydrolysis with sodium metaborate as side product. 2. Acid-mediated hydrolysis with boric acid as side product. 3. Alcoholysis with tetraalkoxy borate as side product. 4. Acid-mediated alcoholysis with isopropanol.

An alternative and potentially more effective method for the liberation of dihydrogen from NaBH₄ is through alcoholysis reactions, particularly using methanol or other small alcohols (Scheme 1).³¹ These reactions are generally exothermic and have well defined spent fuels. However, the difficulties in transport and storage remain. Moreover, in the absence of catalysts, these reactions still exhibit slow kinetics, and precise control over dihydrogen release becomes problematic.³²

As an important matter in this respect, the balance between the costs of the required time, energy input and the created value of the produced hydrogen has to be economically feasible. In this context, a system that allows the premixing of alcohols and borohydrides, combined with a chemical trigger, to initiate the dihydrogen release would be an incredibly valuable tool.

The method herein described uses a cheap and commercially available acid to modulate the production of hydrogen gas out of a premixed borohydride alcohol solution, allowing its release on demand in one step with fast reaction kinetics. This system could give rise to a highly tuneable and controllable industrial application allowing the direct feed of the resulting spent fuel in existing industrial processes.

Results and Discussion

The study was initiated by mixing commercially available alcohols with NaBH_4 . For a selection of alcohols, various steric and electronic properties were examined, along with considerations of economic feasibility. The ^{11}B -, ^1H - and ^{13}C -NMR spectra indicated complete conversion of NaBH_4 to tetraalkoxy borates upon mixing of NaBH_4 with methanol (Figure S1-S3), ethanol (Figure S4-S6), propanol (Figure S7-S9), and butanol (Figure S10-S12), respectively.^{33–35} Meanwhile, the ^{11}B - and ^1H -NMR spectra of a mixture of isopropanol and NaBH_4 , as well as *tert*-butanol and NaBH_4 , were identical to those recorded initially after mixing both components with no line broadening and no solvation, even when heated to reflux for multiple days. Collectively, these experiments indicate that both isopropanol and *tert*-butanol can be used for a premixed formulation with NaBH_4 creating a suitable fuel for on-demand hydrogen release. However, due to the instability and poor reaction kinetics of *tert*-butanol, this manuscript will focus on the premixed isopropanol/ NaBH_4 system.

Inspired by these initial results and the work of Paskevicius et al.,¹⁹ in which they synthesized tetraalkoxy borates from alcohols and NaBH_4 , an investigation was conducted to determine if a premixed isopropanol/ NaBH_4 suspension allows the clean formation of dihydrogen gas after addition of an acid concomitant with the selective formation of trialkyl borates as a recyclable spent fuel.

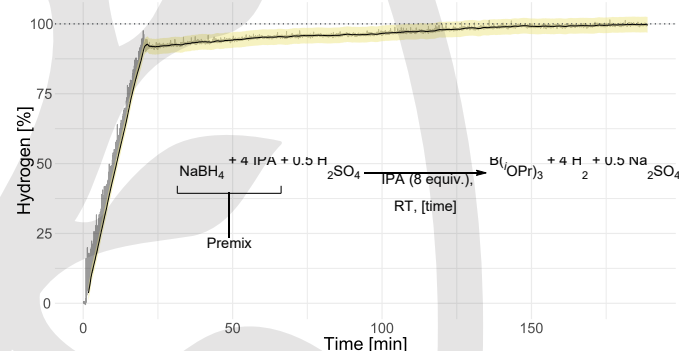
A reaction system consisting of a pre-mixed suspension of NaBH_4 and isopropanol was subjected to the addition of various commercially available acids (SI, 3). The progress of the reaction was monitored using ^{11}B - and ^1H -NMR spectroscopy. Among the acids tested, only H_2SO_4 displayed sharp, well-defined peaks, during and after the reaction. In contrast, all other acids examined resulted in extreme line broadening, likely due to the coordination of the respective anions, significantly hindering the ability to effectively monitor the reaction progress. Therefore, H_2SO_4 was deemed the most suitable acid for this system.

With the use of H_2SO_4 as an acid concomitant, the formation of Na_2SO_4 as an unwanted byproduct was acknowledged as a potential limitation for large-scale applications. Na_2SO_4 is already abundant as it is not widely used as a resource chemical and therefore generally regarded as a waste product in chemical industry.³⁶ Consequently, alternative acids may warrant consideration for bigger scale reactions.

Full conversion of NaBH_4 , isopropanol and acid to triisopropyl borate was observed at room temperature, monitored via ^{11}B -

and ^1H -NMR recorded from the reaction mixture, and no distinguishable side products were detected in the recorded NMR spectra.³⁷ To confirm the high purity of the released dihydrogen, the evolved gas was passed through a D_2O -filled bubbler, in order to trap any released volatiles from the reaction mixture. Subsequent analysis of the D_2O by ^1H - and ^{11}B -NMR spectroscopy confirmed the absence of other volatile species in the developed gas.

Further evidence for the formation of dihydrogen gas from the system was gained by volumetric hydrogen gas measurement using a modified set-up from Zheng *et al.*³⁸ Indeed, quantitative dihydrogen gas formation was observed for the reaction based on an isopropanol/ NaBH_4 pre-mix within the error margin of our setup (Scheme 2).



Scheme 2: Gas displacement measurement of the one step release of dihydrogen gas from premixed NaBH_4 and IPA with a 20 minute acid addition time. Relatively slow hydrogen gas release was still measured 2 hours after acid addition was completed. The black line is the corresponding moving average of the measured displacement, whereas the yellow area indicates the error margin. 100% corresponds to the maximum expected yield.

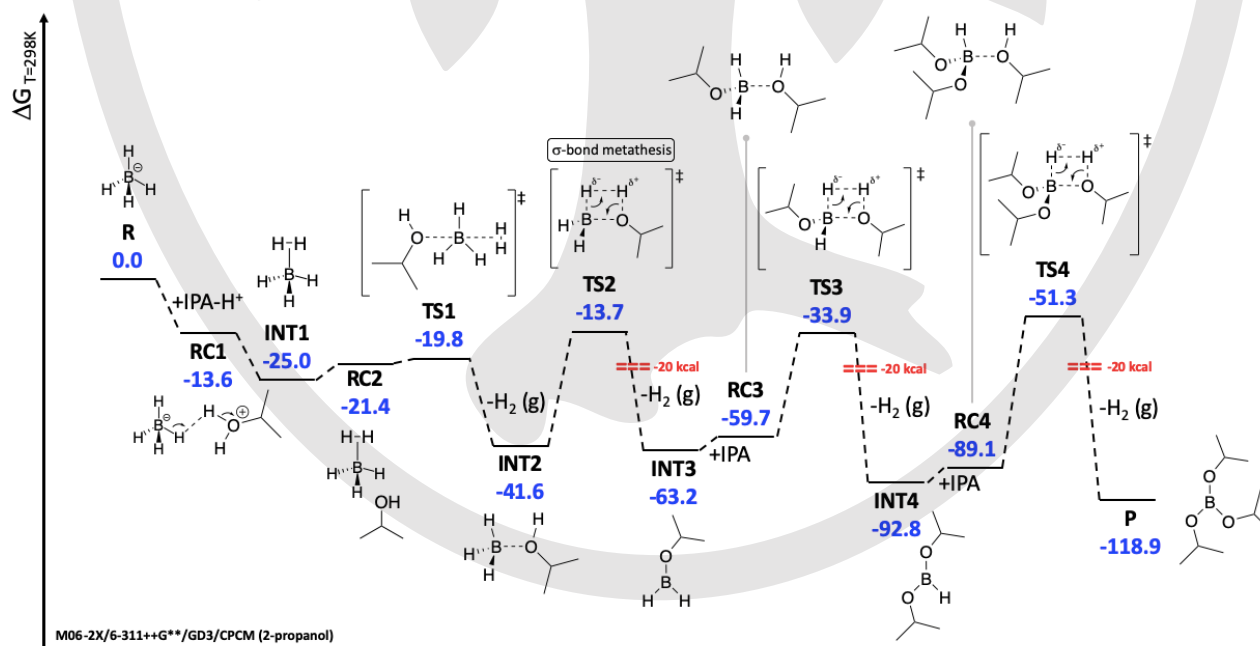
A sub-stoichiometric 0.25:1 ratio of H_2SO_4 to NaBH_4 facilitated the release of the theoretically predicted volume of gas and resulted exclusively in the formation of the desired product. In line with expectations, after subsequent addition of the remaining 0.25 equivalence of H_2SO_4 , full conversion was achieved, and the residual amount of dihydrogen gas was released. It is the modularity of our approach, combined with the initial option of preparing a stable pre-mix system, which distinguishes this approach from previous reported ones.^{39–41}

Gifted with the simple design of the premix isopropanol/ NaBH_4 system, which demonstrated efficient and quantitative on-demand dihydrogen release, we proceeded to evaluate the scalability of our approach. A 20-gram batch reaction was conducted under similar conditions in previously described fashion. Upon the addition of sulfuric acid, a quantitative conversion to triisopropoxy borate was achieved, resulting in the release of 53 liters of pure dihydrogen gas over a total reaction time of 40. The resulting azeotropic mixture was separated by distillation from the excess of alcohol and Na_2SO_4 . Separation of this azeotropic mixture via distillation

requires significant separation power or expensive membranes, not achievable on our lab scale. However, separation of azeotropic mixtures by pressure-swing distillation on industrial scale are well-established, therefore not hindering the intended application.⁴² Hence, this premixed NaBH₄ based fuel system demonstrates potential for scalable, controlled dihydrogen generation with efficient separation of the spent fuel.

To elucidate the reactivity trends of the alcohol/NaBH₄ system, particularly the stability of the isopropanol/NaBH₄ premixed fuel, and to further comprehend the reaction kinetics of the acid-mediated hydrogen release in this premixed system, extensive mechanistic studies were conducted. Quantum chemical density functional theory (DFT) calculations were performed to propose a mechanism for the alcoholysis of NaBH₄ with IPA and acid present. All computational details are available in the Supporting Information. The proposed pathway (M06-2X/6-311++G**/GD3/CPCM (2-propanol) level of theory, (SI.1) describes NaBH₄ alcoholysis with isopropanol (3 equiv.) and protonated isopropanol ('PrOH₂⁺, 1 equiv., serving as model compound for the isopropanol/H₂SO₄ mixture) in stoichiometric amounts (Scheme 1b). Alcoholysis is initiated with the formation of a thermodynamically stable complex between BH₄⁻ and 'PrOH₂⁺ (R to RC1, -13.6 kcal/mol), followed by a barrierless proton transfer from the protonated alcohol to BH₄⁻ (RC1 to INT1, -11.4 kcal/mol), generating a BH₃-H₂ Lewis acid-base type adduct (SI.7.2). Subsequently, the BH₃-H₂ adduct can undergo a thermodynamically favourable exchange of H₂ with IPA (INT1 to

INT2, -16.6 kcal/mol) via TS1 with a reaction barrier of +5.2 kcal/mol, releasing the first equivalent of hydrogen gas. The formed BH₃-IPA adduct, again characterized by Lewis acid-base type HOMO/LUMO interactions (SI.7.3), reacts via σ -bond metathesis (TS2, +27.9 kcal/mol) to mono-isopropoxy borane (INT3, BH₂O'Pr) releasing the second equivalent of H₂ gas. Thereafter, BH₂O'Pr (INT3) forms a Lewis acid-base adduct with IPA (RC3). The formation of this adduct was found to be slightly uphill (+3.5 kcal/mol), predicted due to steric shielding and increasing occupation of the isopropyl substituted borane LUMO (Scheme S8). The resulting BH₂O'Pr-isopropanol complex can again undergo σ -bond metathesis to form BH(O'Pr)₂ (INT4) via TS3 (+29.3). This two-step process of complex formation with subsequent σ -bond metathesis is repeated once more (INT4 to RC4, then RC4 to P via TS4). The third σ -bond metathesis (INT4 to P) has a barrier of +41.5 kcal/mol (TS4) and is rate determining. This relatively high barrier for the release of the fourth equivalent of hydrogen gas can be overcome by heat evolution due to the extremely exergonic nature of the overall reaction (-118.9 kcal/mol) and aligns with experimental findings showing that active cooling of the reaction generates B-NMR visibility of the BH(O'Pr)₂ intermediate (Figure S16). To conclude, the alcoholysis of NaBH₄ with IPA and acid present can proceed via isopropoxy-substituted borane derivatives BH_(3-n)O'Pr_n (for n = 1, 2, 3), which can form Lewis acid-base adducts with IPA. These Lewis acid-base adducts serve as reaction complexes for σ -bond metathesis, upon which an equivalent of hydrogen gas is released. After three consecutive cycles of σ -bond metathesis the

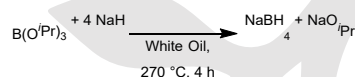


Scheme 3: proposed mechanism for NaBH₄ alcoholysis with isopropyl alcohol and sulfuric acid in isopropyl alcohol as solvent. Free energies (ΔG 298K°, in kcal mol⁻¹) calculated with DFT at the M062X/6-311++G**/disp-3/CPCM, 2-propanol (ultrafine grid) level of theory.

triisopropyl borate product has formed.

Despite the clean acid-initiated on-demand release of dihydrogen from pre-mixed alcohol/ NaBH_4 , it is undeniable that an economically favorable hydrogen production on a larger scale requires the spent fuel to be recovered in cheap and accessible manner. Challenging aspects in this context are the separation of the excess of alcohol from the respective trialkoxy borates and reconversion of borates to NaBH_4 to close the loop. Notably, there are numerous literature procedures available describing the recycling of a variety of trialkoxy borates to NaBH_4 .^{43,44} However, the recycling of triisopropyl borate to NaBH_4 has not been previously demonstrated. In order to close that gap, we conducted a small-scale reaction using the established Brown-Schlesinger conditions for the recycling of triisopropyl borate to NaBH_4 .

Indeed, full conversion to NaBH_4 , as confirmed by ^1H - and ^{11}B -NMR analyses with moderate isolated yield (48%) was achieved in 4 hours at the applied scale, and work-up (Scheme 4).⁴⁵ The observed compatibility of triisopropyl borate with the Brown-Schlesinger reaction indicates that its integration into existing industrial processes would require only minor modifications to current infrastructure.



Scheme 4: Recycle reactions of triisopropyl borate to sodium borohydride with sodium hydride.

Conclusions

In conclusion, the novel approach of a premixed system of the widely available hydrogen carrier sodium borohydride with isopropanol exhibits major advantages such as long-term storage, on-demand hydrogen release and scalability. It was demonstrated that NaBH_4 alcoholysis with IPA and acid via $\text{BH}_3\text{-n}(\text{O}^i\text{Pr})_n$ ($n = 0, 1, 2, 3$) species is thermodynamically feasible and highly exergonic. After proton transfer and H_2 elimination at the B-centre by the protonated alcohol, the reaction proceeds via consecutive σ -bond metathesis with IPA, with Lewis acid-base type orbital interactions as a driving force for the formation of the reaction complexes. The spent fuel can be readily separated and recycled back into NaBH_4 in one step, using well-established chemical reactions.

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Primary Data

Is there Primary Data associated with this article? If so upload them on Zenodo.org and add here the corresponding DOI.

If no Primary Data are associated to the article simply write NO in this section.

Conflict of Interest

The authors declare no conflict of interest.

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- (45) In a glovebox a Schlenk tube was filled with a suspension of white oil (3 mL) and NaH (0.140 g, 5.85 mmol, 4.40 equiv.), triisopropyl borate (0.250 g, 1.33 mmol, 0.30 mL) was added. The Schlenk was buried in a sand bath and stirred at 270 °C for 4 h. The reaction was cooled to room temperature and extracted with isopropanol (3 × 10 mL). A second extraction with isopropylamine (3 × 3 mL) was performed, and the resulting solution was evaporated in vacuo. The residue was dried in a vacuum oven at 80 °C for 24 h and NaBH₄ was obtained as a colorless solid (0.03 mg, 0.64 mmol, 48%). The analytical data is in accordance with previous publications.⁴⁸
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