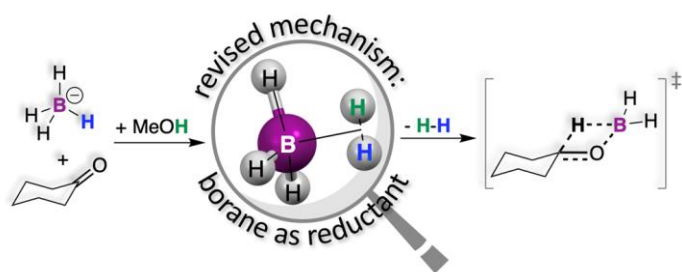


# RESEARCH CONNECTION

## Unifying orthogonal reactivity of borohydride: A ubiquitous chemical

By Shrinwantu Pal, PhD



### Why this research is important

Chemical reductions are an important class of reactions where reducing agents push electrons or other electron-rich fragments into substrates undergoing reduction. One such fragment is hydride ( $\text{H}^-$ ). A hydrogen atom ( $\text{H}$ ) is the smallest chemical species imaginable, and therefore, it is no surprise that  $\text{H}^-$  is an electron-rich species. The small size and the large electron density together make  $\text{H}^-$  a very reactive and unstable species. Sodium borohydride ( $\text{NaBH}_4$ ) is a molecule that has four such hydrides, which are stabilized by robust chemical bonds to the central B atom in the  $\text{BH}_4^-$  anion. The sodium cation serves to make  $\text{NaBH}_4$  a crystalline solid. These make  $\text{NaBH}_4$  a bench-stable reducing agent that, pending the right conditions, is ready to transfer  $\text{H}^-$  fragments to substrates such as ketones. However, like other hydrides, the  $\text{BH}_4^-$  anion also undergoes reactions with protic solvents (i.e., solvents that

### What you need to know

Discovered in the 1940s, sodium borohydride ( $\text{NaBH}_4$ ) is a ubiquitous chemical that is not only available in every chemistry research group but also forms the basis for standard undergraduate organic chemistry experiments.  $\text{NaBH}_4$  is widely used in chemical reductions and has recently also been exploited as a potential hydrogen storage medium.

can supply protons,  $\text{H}^+$ ) such as water or alcohol to form  $\text{H}_2$  according to the simple equation:  $\text{H}^- + \text{H}^+ \rightarrow \text{H}_2$ . This is a side reaction that serves to deplete the number of hydrides in  $\text{BH}_4^-$  available for reduction. Still, surprisingly, reductions with  $\text{BH}_4^-$  are performed in alcohols! This is an unsustainable choice that requires excess  $\text{BH}_4^-$  to compensate for the loss of  $\text{H}_2$ . On the other hand, reductions performed in aprotic solvents simply do not work! Is it possible that this loss is a necessary evil? This conundrum had not been explained in the 80 years that have passed since the discovery of  $\text{NaBH}_4$ .

### How the research was conducted

Firstly, the reaction between the  $\text{BH}_4^-$  anion and the protons in solvents like water or alcohol was examined with microscopic precision through density functional theory (DFT) calculations. These calculations indicated that the  $\text{BH}_4^-$  anion does not actually transfer hydride fragments as

previously thought; rather, it preferentially undergoes a reaction with protons to form an elusive intermediate  $\text{BH}_3(\text{H}_2)$  that loses  $\text{H}_2$  to afford the reduction. As a testament to the ability of modern computational methods to predict experimental outcomes, this proposed intermediate was ascertained experimentally by isotope scrambling and nuclear magnetic resonance spectroscopy. A multitude of experimental data from the literature that had not been mechanistically corroborated were assessed and benchmarked against this new mechanism.

### What the researcher found

Although reaction mechanisms can never be proven, they can be supported by looking at the rates at which reactions occur, by isotopic substitutions that allow us to track specific atoms in the transformations, or by looking at stereoselectivity, which allows us to compare the geometries of reaction products. For the first time, the intermediacy of  $\text{BH}_3(\text{H}_2)$  in this work unified two reactions that have remained orthogonal for over 80 years, explaining that the loss of  $\text{H}_2$  and the need for alcohol as a solvent are actually necessary. This new mechanistic model was benchmarked against these indicators and found to be consistent with experimental rate constants, isotope effects and stereoselectivity data published in over 20 articles since the 1940s.

### How this research can be used

The mechanistic insights in this work might promote the exploration of new avenues for reductions of substrates inert to  $\text{BH}_4^-$  (such as alkenes, esters, and carboxylic acids). It is anticipated that these mechanistic insights will further our understanding of the reactions of borohydride and its use in hydrogen storage applications.

### About the researcher

Dr. Shrin Pal is an assistant professor at Brandon University specializing in inorganic and organometallic chemistry.

Prior to joining Brandon University, he was involved in researching organometallic chemistry and catalysis at University of Calgary, University of Tokyo, University of British Columbia - Vancouver, University of Maryland and JNCASR, Bangalore.

When not doing chemistry, Shrin enjoys cooking (ok, sorry, that's kind of chemistry, too) and dabbling in photography.

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### Publication based on this research

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