THEORETICAL STUDY OF POSSIBLE REACTION PATHWAYS FROM BH_4^- TO $B_{12}H_{12}^{2-}$

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Borohydrides have seen renewed interest due to their ability to store and carry a high weight percentage of hydrogen making them desirable materials in large scale and long-duration energy storage applications. In this work we present a systematic computational study of the thermochemical feasibility of a series of mechanistic pathways that can lead to formation of the observed boron clusters. This allowed us to identify predominant pathways for buildup, following a complex network of pathways. We find that the preferred mechanisms are different for smaller and larger clusters. The primary mechanism for buildup in clusters up to ~5 boron atoms is by addition of BH_4^- / BH_3 species followed by loss of H_2 or H^-. For larger clusters, fusion reactions dominate, again followed by loss of H_2 or H^-. Few species were identified as possible branching points, where the trends for favorability change; $B_2H_7^-$ as an initiation step and $B_4H_7^-$, $B_3H_8^-$, and $B_9H_{13}^{2-}$ as minima on the potential energy surface are most notable. This work demonstrates that borohydride clusters feature a wealth of pathways for reaching the desired products ($B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$), the redundancy of which may help avoid energetic sinks or kinetic bottlenecks. This robustness in reactivity has the potential to make them a versatile H_2 storage material.

References

H. Hagemann obtained his PhD in 1984 at the University of Geneva. After a postdoctoral stay at UC Berkeley, he returned to the University of Geneva. His research interests are solid state chemistry, lanthanide spectroscopy, hydrogen storage materials and more recently also new battery materials. He was scientific supervisor of the chemistry outreach platform “Chimiscope” (https://scienscope.unige.ch/chimiscope/) from 2011 to 2021.