

## Global Search for the Dehydrogenation Pathway of Amine-Borane Adduct: An Application of Scaled Hypersphere Search (SHS) Method

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Mechanism is an essential aspect of chemistry in general and of catalytic process in particular. The transition-metal-catalyzed dehydrocoupling of amineboranes has attracted considerable attention because of not only its application in organic synthesis and importance in the development of hydrogen storage materials, but also the advantage of mild temperature over the thermal conditions. In this framework, many experimental studies have been done for exploring the mechanistic aspect and the hetero- vs homogenous mechanism has been well characterized for such kind of reactions. Although a concerted mechanism was proposed for the dehydrogenations of amonia-borane and hydrocarbon-borane, it still remains unknown whether the transition-metal-catalyzed hydrogen releases from amineborane or aminoborane, such as  $\text{H}_3\text{N}-\text{BH}_3$  and  $\text{H}_2\text{N}=\text{BH}_2$ , are stepwise or concerted processes. Moreover, the global dehydrogenation pathway of these compounds remains unknown to date. In this connection, our group has successfully developed the scaled hypersphere search (SHS) method [1] for global reaction route mapping [2,3]. In this study, we applied the SHS method to global search for both thermal and catalytic dehydrogenation pathways of these substrates.

The SHS method is an uphill walking technique on a potential energy surface (PES) starting from an equilibrium structure (EQ) toward transition state structures (TS) or dissociation channels [1]. The SHS method can follow approximate reaction pathways from an EQ based on a simple principle of chemical reactions “*reaction pathways can be followed starting from an EQ by noting anharmonic downward distortions (ADD) as symptoms of chemical reactions*”. The ADD following by the SHS method can be used for finding many reaction pathways around an EQ, and a one-after-another algorithm has been established for global reaction route mapping (GRRM) on a quantum chemical PES by combining a downhill walking technique with uphill walking by the SHS method [2,3].

Fig. 1 shows global topographies of PESs for  $\text{H}_6\text{BN}$ ,  $\text{H}_4\text{BN}$ , and  $\text{H}_2\text{BN}$  connected via thermal dehydrogenation pathways. Fig. 1 is based on the UCCSD(T) energies calculated at B3LYP geometries located by applications of the SHS method. Although some important parts have already been reported by other groups [4,5], global topographies of these PESs with many supplements to previous studies have been disclosed by the SHS method in an automatic way. To further investigate on catalytic dehydrogenation pathways, global reaction route mapping of PESs for metal including systems (i.e.  $\text{H}_6\text{BNM}$ ) are in progress, and will be presented in the symposium.

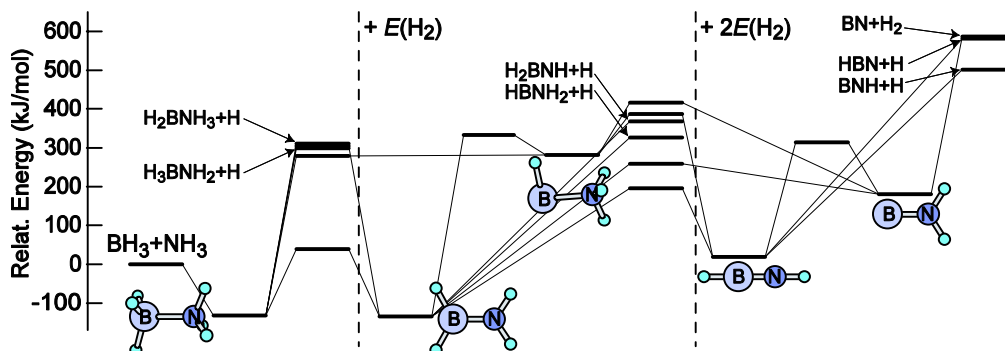


Fig. 1. Global Topographies of PESs for  $\text{H}_6\text{BN}$ ,  $\text{H}_4\text{BN}$ , and  $\text{H}_2\text{BN}$  linked by Dehydrogenation Pathways.

**References:** [1] Ohno, K.; Maeda, S. *Chem. Phys. Lett.* **2004**, *384*, 277. [2] Maeda, S.; Ohno, K. *J. Phys. Chem. A* **2005**, *109*, 5742. [3] Ohno, K.; Maeda, S. *J. Phys. Chem. A* **2006**, *110*, 8933. [4] Li, Q. S.; et al. *Chem. Phys. Lett.* **2005**, *404*, 101. [5] Zhang, J.; et al. *J. Mol. Struct. (Theochem)* **2005**, *717*, 33.