Energy barrier of structure transition from icosahedral
B_{12}H_{6}^{+} to planar B_{12}H_{5}^{+} and B_{12}H_{4}^{+} clusters

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Abstract. Ab initio calculations indicated that icosahedral structure is more stable for B_{12}H_{n}^{+} clusters with
\( n = 6-12 \), but planar configuration is more stable for B_{12}H_{n}^{+} with \( n = 0-5 \). Here, we report the energy barriers of structure transition by detaching H atoms from icosahedral B_{12}H_{6}^{+} to planar B_{12}H_{5}^{+}, planar B_{12}H_{4}^{+}, icosahedral B_{12}H_{5}^{+} or icosahedral B_{12}H_{4}^{+} cluster. We performed density functional theory calculations to explore the energy barriers and the reaction path of the structure transition. The resultant energy barriers are almost the same, enabling the transition to proceed and suggesting that the structure of B_{12}H_{n}^{+} clusters is controlled by the number of hydrogen atoms \( n \).

1. Introduction

There is much interest in utilizing small atomic clusters to build well-controlled nanostructures. Boron has rich chemistry [1-2] and forms cluster solids, where structural units are icosahedra containing 12 boron atoms [3-6]. On the other hand, it has been proved theoretically and experimentally that all small boron clusters known so far have planar or quasiplanar structures [7-11]. These features make boron clusters an attractive unit for building nanostructures.

Hydrogen-terminated icosahedral (I\textsubscript{h}) B_{12}H_{12}^{2-} cluster is the most stable among the various polyhedral boranes synthesized thus far. The three-dimensional aromaticity of its highly symmetrical structure [1] and the perfect matching of its electron number with that required by the Wade’s rule [12, 13] accounts for its stability. On the other hand, the B\textsubscript{12} cluster (without hydrogen) has quasi-planar structure with six delocalized \( \pi \)-electrons, similar to C\textsubscript{6}H\textsubscript{6} (benzene) [7-11]. Compared with clusters of carbon or the other elements neighboring boron in the periodic table, elemental boron clusters have received relatively little experimental and theoretical attention. In particular, few reports are known on the gas-phase reactions of boron clusters [14, 15].

In a recent article, we produced B_{12}H_{8}^{+} cluster cations experimentally [16] using an external quadrupole static attraction ion trap (EQSIT) [17-20]. In that article [16], we reported the stability of B_{12}H_{n}^{+} clusters calculated at B3LYP/6-31G(d). Comparison of the energies of icosahedral B_{12}H_{n}^{+} and planar B_{12}H_{n}^{+} clusters reveals that they are planar for \( n = 0-5 \) and icosahedral for \( n = 6-12 \) [16].
Calculations of the energies of formation reactions and detachment pathways of H₂ molecules and H atoms from the produced cluster ions indicate that the B_{12}H₆⁺ cluster, produced in the EQSIT, is icosahedral. Assuming that the energy barrier of the structure transition is not high compared to that of hydrogen detachment, one can expect that planar B_{12}H₆⁺ is produced by the detachment of hydrogen atoms. This suggests that the structure of B_{12}H₆⁺ is controlled by the number of H atoms. In this study, we calculated the pathway by which hydrogen molecules and atoms are eliminated from icosahedral B_{12}H₆⁺, thus forming icosahedral and planar B_{12}Hₙ⁺ (n = 5,4) clusters. The objective was to predict the possibility of transition from icosahedral to planar structure through the calculation of the energy barriers.

2. Quantum chemical calculations
The geometries of low-lying minima and transition states for B_{12}Hₙ⁺ are determined at the B3LYP/6-31G(d) level of the density functional theory. For all the species considered in this study, the natures of the calculated stationary points are determined by frequency calculation at the B3LYP/6-31G(d) level. The potential energy surfaces are calculated to investigate the reaction energy, following previous studies on the mechanism of gas-phase reactions [21-23]. All minima are characterized by the presence of all positive vibration frequencies. All transition states are characterized by the presence of one imaginary vibration frequency. The intrinsic reaction coordinate [24-26] calculations are further carried out at the B3LYP level to confirm that the transition states connect the right minima. Zero-point energies are calculated, scaled by a factor of 0.9804, and included in the calculation of relative energies. All calculations are carried out using the GAUSSIAN 03 program package [27].

3. Results and discussion
To find the transition state which connects icosahedral and planar structures, first, the most stable planar structure of B_{12}H₆⁺ (figure 1(a)) is chosen as a starting geometry. As shown in figure 1(a), hydrogen atoms are bonded with peripheral boron atoms, and the structure is completely planar. Because the hydrogen-bonded boron atom is pulled toward the direction of hydrogen atom, spherical structure (figure 1(b)) is produced by moving hydrogen atoms to the inner boron atom. As the movement of one hydrogen atom to the inner boron atom is insufficient to obtain closed structure, one more hydrogen atom is moved to the inner boron atom. Three structures shown in figures 1(b), (c) and (d) are chosen as a starting geometry; (c) and (d) are obtained from (b) by moving the hydrogen atom bonded with the inner boron atom to the neighboring other inner boron atoms. We calculated all possible structural isomers of B_{12}H₆⁺, which are obtained by moving one more peripheral hydrogen atom to the inner boron atom, starting from (b), (c) and (d). Among these trials, the optimization of (e), which is obtained from (c), results in the most spherical structure (f). The transition state between (c) and (e) is calculated, leading to the structure (g).

Figure 1. Procedure for determining the transition state between planar and icosahedral structures. The black filled circles indicate the moved hydrogen atoms.
To examine whether the structure (g) is the transition state which connects icosahedral and planar structures, we calculated the geometrical structures (see figure 2) and relative energies of each state in the reaction path which connect the most stable structure of icosahedral B$_{12}$H$_{6}^+$ and planar B$_{12}$H$_{5}^+$, B$_{12}$H$_{4}^+$ clusters. In figure 2, structure (6) is same as structure (g) in figure 1. At first, intrinsic reaction coordinate calculation is conducted for structure (6) to obtain the local minimum structures, which are connected by structure (6). This means that the structure transition is bidirectional. The calculation results in the closed structure (5) and planar structure (7) as shown in figure 2. Icosahedral structure (3) is obtained from (5) through the transition state (4). The most stable isomer of icosahedral B$_{12}$H$_{6}^+$ (1) is obtained from (3) by migration of a hydrogen atom through transition state (2). In a similar way, the most stable isomer of planar B$_{12}$H$_{6}^+$ (15) is obtained from (7) by migration of a hydrogen atom through (8) to (14) structures. The hydrogen atom detaches from planar B$_{12}$H$_{6}^+$ (15) without transition state, leading to the planar B$_{12}$H$_{5}^+$ configuration (16), which is the most stable isomer of B$_{12}$H$_{5}^+$. The hydrogen molecule detaches from the planar B$_{12}$H$_{6}^+$ (15) through transition state (17), leading to the planar B$_{12}$H$_{4}^+$ (18), which is the most stable isomer of B$_{12}$H$_{4}^+$. The relative energies of each state are shown in figure 3. The resultant relative energies indicate that the energy barriers of the structure transition and of the following detachment of hydrogen atom and molecule are both equal to 3.67 eV.

Figure 2. Geometrical structures of each state in the reaction path which connect the most stable configuration of icosahedral B$_{12}$H$_{6}^+$ (1) and planar B$_{12}$H$_{5}^+$ (16), B$_{12}$H$_{4}^+$ (18) clusters with their relative energies in eV. The structures (2-15, 17) correspond to the locally stable or transition states of B$_{12}$H$_{6}^+$ in the reaction path. The circled numbers indicate transition states.
Figure 3. The relative energies of each state in figure 2. The dashed line shows the detachment of H atoms. The filled circle shows the local minima and open circle shows the transition state.

We have also calculated hydrogen detachment without changing the structure of the cluster. The geometrical structures and energies of each state are shown in figures 4 and 5, respectively. The energy of icosahedral B\(_{12}\)H\(_6^+\) (1) is chosen as the reference, and it is the same as in figures 2 and 3. The structure of icosahedral B\(_{12}\)H\(_6^+\) cluster (20) is obtained by moving the hydrogen atom of starting structure (1) to the neighboring bare boron atom through a transition form (19). A hydrogen atom is detached from (20) without a transition state, leading to the most stable isomer of B\(_{12}\)H\(_5^+\) (21). In case of the detachment of a hydrogen molecule, a hydrogen atom approaches the neighboring hydrogen atom, forming a B\(_{12}\)H\(_4^+\)・H\(_2\) complex (23) through a transition state (22). The hydrogen molecule detaches from the complex with zero activation energy, resulting in icosahedral B\(_{12}\)H\(_4^+\) (24). The resultant relative energies indicate that the energy barrier for transition from icosahedral B\(_{12}\)H\(_6^+\) to icosahedral B\(_{12}\)H\(_5^+\) and H atom is 3.82 eV and the barrier for transition from icosahedral B\(_{12}\)H\(_6^+\) to icosahedral B\(_{12}\)H\(_4^+\) and H\(_2\) molecule is 3.59 eV.

Figure 4. The geometrical structures of each state in the reaction path from icosahedral B\(_{12}\)H\(_6^+\) (1) to icosahedral B\(_{12}\)H\(_5^+\) (21) and icosahedral B\(_{12}\)H\(_4^+\) (24) with their relative energies in eV. The structures 19, 20, 22 and 23 correspond to the local stable or transition states of B\(_{12}\)H\(_6^+\) in the reaction path. The circled numbers indicate transition states.
The calculated reaction processes and the corresponding energy barriers are summarized in table 1. When one hydrogen atom is detached from icosahedral $\text{B}_{12}\text{H}_6^+$, the formation of planar $\text{B}_{12}\text{H}_5^+$ with H atom needs 0.152 eV less energy. On the other hand, when one hydrogen molecule is detached from icosahedral $\text{B}_{12}\text{H}_6^+$, the icosahedral $\text{B}_{12}\text{H}_4^+$ is favored by 0.08 eV. Because these differences are 4.14% and 2.23% of the energy barriers, energetically favorable structure should be produced by the detachment of hydrogen atoms or molecules.

Figure 5. The relative energies of each state in figure 4. The dashed line shows the detachment of H atom. The filled triangle shows the local minima and open triangle shows the transition state.

Table 1. The reaction processes and the corresponding energy barriers.

| Reaction process                                              | Barrier (eV) |
|---------------------------------------------------------------|--------------|
| $\text{B}_{12}\text{H}_6^+$ (icosahedral) $\rightarrow$ $\text{B}_{12}\text{H}_5^+$ (planar) + H | 3.669        |
| $\text{B}_{12}\text{H}_6^+$ (icosahedral) $\rightarrow$ $\text{B}_{12}\text{H}_4^+$ (planar) + H | 3.669        |
| $\text{B}_{12}\text{H}_6^+$ (icosahedral) $\rightarrow$ $\text{B}_{12}\text{H}_5^+$ (icosahedral) + H | 3.821        |
| $\text{B}_{12}\text{H}_6^+$ (icosahedral) $\rightarrow$ $\text{B}_{12}\text{H}_4^+$ (icosahedral) + H | 3.589        |

4. Conclusion
The energy of each state in the reaction path from icosahedral $\text{B}_{12}\text{H}_6^+$ to planar $\text{B}_{12}\text{H}_5^+$, planar $\text{B}_{12}\text{H}_4^+$, icosahedral $\text{B}_{12}\text{H}_5^+$ or icosahedral $\text{B}_{12}\text{H}_4^+$ cluster is calculated. The resultant energy barriers are 3.67, 3.67, 3.82 and 3.59 eV, respectively. Because their differences are within 5% of the energy barriers, energetically favorable structure should be produced by the detachment of hydrogen atoms or molecules. This implies that the structure of $\text{B}_{12}\text{H}_n^+$ clusters is controlled by the number of H atoms.

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