The Potential Energy Surface of BH₅ and the Rate of the Hydrogen Scrambling

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The BH₅ molecule, which is suggested as an intermediate of the acidolysis of BH₄⁺, contains a weak two-electron-three-center bond and it requires extremely high-level of theories to calculate the energy and structure correctly. The structures and energies of BH₅ and the transition state for the hydrogen scrambling have been studied using recently developed multi-coefficient correlated quantum mechanical methods (MCCMs). The dissociation energies and the barrier heights agree very well with the previous results at the CCSD(T)/TZ(3d1f1g, 2p1d) level. We have also calculated the potential energy curves for the dissociation of BH₅ to BH₃ and H₂. The lower levels of theory were unable to plot correct potential curves, whereas the MCCM method gives very good potential energy curves and requires much less computation resources than the CCSD(T)/TZ(3d1f1g, 2p1d) level. The potential energy of the BH₅ scrambling has been obtained by the multiconfiguration molecular mechanics algorithm (MCMM), and the rate is calculated using the variational transition state theory including multidimensional tunneling approximation. The rate constant at 300 K is 2.1 × 10⁻⁷ s⁻¹, and tunneling is very important.

Key Words: BH₅, Hydrogen scrambling, MCCM. Rate constant

Introduction

The existence of BH₅ was postulated on the basis of experimental observations of the acidolysis of BH₄⁺ in aqueous solution.¹

H⁺ + BH₄⁺ → 2H₂O → 4H₂ + B(OH)₃

In acidic H₂O, BH₄⁺ accepts a proton to form BH₅, which is dissociated into BH₃ and H₂:

H⁺ + BH₄⁺ → BH₃ + H₂

The first step is slow and the dissociation is known to be very fast. In D₂O, mostly HD molecules are formed from the same mechanism as above, but a small amount of H₂ is also detected. In basic D₂O, the unreacted BH₄⁺ turned into first BH₃D⁺, then BH₂D⁺, etc.² Pitzer et al. have reported that BH₂D was obtained by shaking BH₅ with D₂ at room temperature.³ The possible mechanism is as following:

BH₅ + 2D₂ → [BH₃D₂] → [BH₂DH] → BH₂D + HD

These observations suggest the existence of BH₅ and the scrambling of hydrogens. Later, BH₅ has been detected spectroscopically in a low temperature matrix.⁴

Schreiner et al. have performed extensive ab initio calculations for the BH₅ systems.⁵ They found that geometry and energy of BH₅ depend very much on the level of theory and the size of basis sets. The HF level of theory is inadequate for BH₅, and even CCSD(T) level with the DZP basis sets cannot predict the structure of BH₅ correctly. BH₅ should be considered as a molecule with chemical bonds between BH₃ and H₂.⁶ This is a weak 2-electron-3-center bond, and the correct description for the bond dissociation can be a critical test for theory. Based on the comparison between the dissociation energy of BH₅ into BH₃ and H₂ and the barrier height for the scrambling, Schreiner et al. have concluded that the hydrogen scrambling is not likely. They have also pointed out the possibility of large tunneling effect. Therefore it is necessary to calculate the scrambling rate and the role of tunneling to explain the experimental observations correctly.

Since the reliable ab initio calculations for BH₅ require very high levels of electron correlation with large basis sets, it is almost impractical to generate good potential energy surface for the rate calculation. We have used recently developed multi-coefficient correlated quantum mechanical methods (MCCM) and the multi-configuration molecular mechanics method (MCMM) to generate potential energy surface, and calculated rates using the variational transition state theory including multidimensional tunneling approximations.

Computational Methods

All electronic structure calculations were performed with the Gaussian 98 program packages.⁴ Initial geometries for BH₅ complex were fully optimized at the QCISD level of theory with the TZ2P basis sets, and then the structures of BH₅ complex were partially optimized by fixing the distance between Boron and the center of H₂ along the dissociation coordinate of BH₅ to BH₃ and H₂. The MCCM potential energy curves were calculated using these partially optimized structures. The full geometry optimization was also performed, and frequencies and zero-point energies for H₂, BH₃, and BH₅ were obtained using the optimized structures. The structures optimized at the QCISD/TZ2P level have been used
for the potential energy curve at the G3 level. Although we followed the G3 procedures, it is not the real G3, since the G3 level uses the MP2/6-31G(d) method for the geometry optimization. Therefore we will denote it as G3//QCISD/TZ2P. For the potential energy curve for B1: dissociation, the single-point MCCM calculations were performed using the structures partially optimized at the QCISD/TZ2P level. So these calculations are denoted as MCCM//QCISD/TZ2P.

All of the multi-coefficient correlated quantum mechanical methods have been described elsewhere in detail. Therefore, only a short description of each method employed will be given here. Since all of these methods involve differences between energies at different basis sets and theory levels, a short notation has been used in order to write the equation for a multilevel energy succinctly. In this notation, the pipe (\(\mid\)) is used to represent the energy difference either between two one-electron basis sets B1 and B2 or between two levels of electronic structure theory: L1 and L2. e.g. Möller-Plesset second-order perturbation theory and Hartree-Fock theory. The energy difference between two basis sets is represented as

\[
\Delta E(L/B2|B1) = E(L/B2) - E(L/B1)
\]

where L is a particular electronic structure method, and B1 is smaller than B2. The energy change that occurs upon improving the treatment of the correlation energy is represented by

\[
\Delta E(L2/L1|B) = E(L2/B) - E(L1/B)
\]

where L1 is a lower level of theory than L2, and B is a common one-electron basis set. Finally, the change in energy increment due to increasing the level of the treatment of the correlation energy with one basis set as compared to the increment obtained with a smaller basis set is represented as

\[
\Delta E(L2/L1|B2|B1) = E(L2/B2) - E(L1/B2) - [E(L2/B1) - E(L1/B1)]
\]

The Utah variant of MCCM (MCCM-UT-L) methods are written as

\[
E(\text{MCCM-UT-L}) = c_1 E(\text{HF}/6-31G(d)) + c_2 \Delta E(\text{HF}/6-31G(d)) + c_3 \Delta E(\text{MP2}/6-31G(d)) + c_4 \Delta E(\text{MP4SDQ}/6-31G(d)) + E_{SO} + E_{CC}
\]

The MG3 (modified G3) basis set denotes the G3 large basis set without the core polarization functions. Each of these methods assigns coefficients to each energy difference involved in the linear combination; the coefficients have been optimized to fit the atomization energies of 82 molecules containing first- and second-row elements. In the MCCM-UT, MCC-QCISD, and MG3 methods, the basis set deficiency has been corrected by the linear combination of the energy difference with optimized coefficients.

The multilevel structure, energy, and Hessian are calculated by using the MULTILEVEL 2.1.1 program. This program uses the GAUSSIAN 98 package to obtain the energy, gradient, and Hessian components and then combines the components to calculate the multilevel energy, gradient, and Hessian. Frequencies were calculated from the Hessian. Single-level Hessians were used with the Newton-Raphson step. In most cases, an HF/6-31G(d,p) Hessian was recalculated every three steps, and this matrix was used in the determination of every Newton-Raphson step for all MULTILEVEL optimizations.

Details of the multiconfiguration molecular mechanics (MCMM) algorithm have been described elsewhere in detail. Therefore, only a brief description of each method employed will be given here. In the MCCM formalism, the reactive system can be defined by using several valence bond configurations or, more generally, diabatic configurations corresponding to each of the minima on the potential energy surface. Each configuration can be described by a molecular mechanics potential, \(V_1(q)\) and \(V_2(q)\), which is correct in the vicinity of the well. For a geometry \(q\) far from the minima the energy can be expressed in terms of the two diabatic configurations by solving the secular equation:

\[
\begin{bmatrix}
V_{11} & V_{12} \\
V_{12} & V_{22} - V
\end{bmatrix} = 0
\]

where the term \(V_1(q)\) is called the resonance energy function or resonance integral, and \(V\) denotes the lowest-energy eigenvalue of \(V\). The element \(V_{ij}\) of the matrix \(V\) may be considered to be the representation of the electronic Hamiltonian (including nuclear repulsion) in an electronically diabatic basis, and the eigenvalue \(V\) is the expectation value of the electronic Hamiltonian (including nuclear repulsion) for the lowest-energy electronically adiabatic state. This eigenvalue is given by

\[
V(q) = \frac{1}{2} \left( V_1(q) + V_2(q) - \sqrt{(V_1(q) - V_2(q))^2 + 4V_{12}^2(q)} \right)^{1/2}
\]

the components of its gradient are given by
\[ g_i = \left( \frac{\partial V}{\partial q_i} \right) = \frac{1}{2} \left( \frac{\partial^2 V_{11}}{\partial q_i^2} + \frac{\partial^2 V_{22}}{\partial q_i^2} \right) + \frac{1}{2} \left[ \frac{\partial V_{11}}{\partial q_i} \frac{\partial V_{22}}{\partial q_i} - \frac{\partial^2 V_{12}}{\partial q_i^2} \right] \]

and the elements of its Hessian are given by

\[ f_{ij} = \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right) = \frac{1}{2} \left[ \frac{\partial^2 V_{11}}{\partial q_i \partial q_j} + \frac{\partial^2 V_{22}}{\partial q_i \partial q_j} \right] + \frac{1}{2} \left[ \frac{\partial^2 V_{11}}{\partial q_i \partial q_j} - \frac{\partial^2 V_{22}}{\partial q_i \partial q_j} \right] \]

Now note that \( V \) tends to the energy \( V_1 \) of configuration 1 (reactants) or the energy \( V_2 \) of configuration 2 (products) whenever the value of the resonance integral is negligible.

The critical issue in the MCMM formulation is the calculation of that resonance integral and its derivatives, since the \( V_1 \) and \( V_2 \) terms and their derivatives are extracted from the molecular mechanics force field. Note that \( V_1 \) is generated using the connectivity (valence structure) of reactants, and \( V_2 \) is generated using the connectivity of products.

From Eq. (7), \( V_{12}(q) \) can be expressed as

\[ V_{12}(q) = [V_1(q) - V(q)] [V_2(q) - V(q)] \]

Near the arbitrary geometry \( q^{(k)} \), each quantity on the right hand side of Eq. (11) can be expanded in Taylor’s series. Thus,

\[ V(q,k) \equiv V^{(k)} + g^{(k)} \cdot \Delta q^{(k)} + \frac{1}{2} \Delta q^{(k)} \cdot f^{(k)} \cdot \Delta q^{(k)} \]

where

\[ \Delta q^{(k)} = q - q^{(k)} \]

and \( V^{(k)}, g^{(k)} \) and \( f^{(k)} \) are the target energy, gradient, and Hessian matrix respectively of the reference point (note that if the reference geometry corresponds to a saddle point or local minimum (well) on the potential energy hypersurface, \( g^{(k)} \) is zero). Furthermore we expand the diagonal elements of \( V_{12} \) around the geometry \( q^{(k)} \)

\[ V_{12}(q,k) \equiv V^{(k)} + g^{(k)} \cdot \Delta q + \frac{1}{2} \Delta q^T f^{(k)} \Delta q \]

where

\[ g^{(k)} = \left( \frac{\partial V_{12}}{\partial q_i(q^{(k)})} \right) \]

\[ f^{(k)} = \left( \frac{\partial^2 V_{12}}{\partial q_i \partial q_j(q^{(k)})} \right) \]

for \( n = 1, 2 \). Note that the quantities with superscript \( k \) are constants evaluated at the geometry \( q^{(k)} \) of each reference point \( k \), and therefore are independent of \( q \). The quantities \( V_{12} \) defined in Eq. (14) and \( V_{12}(q,k) \) and its derivatives are functions dependent on the geometry, \( q \), as well as on the geometry of the reference point \( k \). Substituting Eqs. (12) and (14) into (11), we obtain the following general form of the \( V_{12} \) term:

\[ V_{12}(q,k) \equiv V^{(k)} + g^{(k)} \cdot \Delta q + \frac{1}{2} \Delta q^T f^{(k)} \Delta q \]

This expression (16) provides an analytic expression for evaluating the resonance integral in the vicinity of a reference point. However, when dealing with a nuclear configuration far from the reference point \( k \), the value \( V_{12}(q,k) \) given by Eq. (16) is unbounded either positive or negative, and hence the value of \( V(q) \) given by Eq. (8) diverges. In this paper, we applied a modified version of a Shepard interpolation scheme \(^{17}\) previously applied directly to \( V(q) \). This method does not make any assumption, and it allows for systematic improvement as the number \( \mathcal{M} \) of points \( k \) is increased.

The Shepard interpolation algorithm, in internal coordinates \( q \), yields

\[ V_{12}^{\mathcal{M}}(q) = \sum_{k=1}^{\mathcal{M}} W_{j}(q) V_{12}^{\mathcal{M}}(q,k) \]

where the normalized weights \( W_{j}(q) \) are defined as

\[ W_{j}(q) = \frac{\omega_{j}(q)}{\omega(q)} \]

and

\[ \omega(q) = \sum_{j=1}^{\mathcal{M}} \omega_{j}(q) \]

\[ \omega_{j}(q) = \omega_{j}(q) \]

\[ \sum_{j=1}^{\mathcal{M}} \omega_{j}(q) = 1 \]
and $V_{12}(\mathbf{q}; \mathbf{k})$ is a modified quadratic function

$$ [V_{12}(\mathbf{q}; \mathbf{k})]^2 = [V_{12}(\mathbf{q}; \mathbf{k})]^\top \mathbf{u}(\mathbf{q}; \mathbf{k}) $$

where the quadratic part is

$$ [V_{12}(\mathbf{q}; \mathbf{k})]^\top $$

and the modification is

$$ \mathbf{u}(\mathbf{q}; \mathbf{k}) = \begin{cases} \exp(-\Delta/[V_{12}(\mathbf{q}; \mathbf{k})]^2), & [V_{12}(\mathbf{q}; \mathbf{k})]^2 > 0 \\ 0, & [V_{12}(\mathbf{q}; \mathbf{k})]^2 \leq 0 \end{cases} $$

(20)

We use a very small value of $\delta$, $1 \times 10^{-3} E_\text{h}$ (where $1 E_\text{h} = 1$ hartree), so that Eq. (22) converges rapidly to 1 with increasing values of $[V_{12}(\mathbf{q}; \mathbf{k})]^2$. The constants $D^{\mathbf{k}}$, $\mathbf{b}^{\mathbf{k}}$, and $\mathbf{C}^{\mathbf{k}}$ are chosen such that Eq. (20) combined with Eq. (8) reproduces the expansion 12.

The weight should be chosen so that several conditions are fulfilled:

$$ w_\mathbf{k}(\mathbf{q}; \mathbf{k}) = 1, \quad \text{all } \mathbf{k}; $$

$$ w_\mathbf{k}(\mathbf{q}; \mathbf{k}) < 1, \quad \mathbf{k} \neq \mathbf{k}; $$

$$ \frac{\partial^2 w_\mathbf{k}}{\partial \mathbf{q}^2} \bigg|_{\mathbf{q} = \mathbf{q}^{(k)}} \equiv 0, \quad \text{all } \mathbf{k}'; $$

$$ \frac{\partial^2 w_\mathbf{k}}{\partial \mathbf{q}^2} \bigg|_{\mathbf{q} = \mathbf{q}^{(k')}} \equiv 0, \quad \text{all } \mathbf{k}'; $$

(23)

(24)

(25)

(26)

Equations (23) and (24) are required so that Eqs. (8), (17), and (18) essentially reproduce the values of the target Born-Oppenheimer surface at the Shepard points. Eqs. (25) and (26) are required so that Eqs. (8), (17), and (18) reproduce the linear and quadratic terms of Eq. (12) at the Shepard points. In fact, we go to zero as $\mathbf{q}$ approaches $\mathbf{q}^{(k)}$, $\mathbf{k} \neq \mathbf{k}$, and it must do so rapidly enough to preserve these linear and quadratic terms as well. Furthermore, $w_\mathbf{k}(\mathbf{q})$ should be continuous and smooth; as we move from point $\mathbf{k}$ to point $\mathbf{k}'$, the values of $V_{12}(\mathbf{q})$ and its derivatives should go smoothly from their values at $\mathbf{q}^{(k)}$ to their values at $\mathbf{q}^{(k')}$.

The weighting function we are using is

$$ w_\mathbf{k}(\mathbf{q}) = \frac{[d_\mathbf{k}(\mathbf{q})]^{-1}}{\sum_{\mathbf{k}'} [d_\mathbf{k}'(\mathbf{q})]^{-1}} $$

(27)

where $d_\mathbf{k}(\mathbf{q})$ denotes a generalized distance between $\mathbf{q}$ and $\mathbf{q}^{(k)}$ defined as:

$$ d_\mathbf{k}(\mathbf{q}) = \sqrt{\sum_{i=-1}^{N} (q_i - q_i^{(k)})^2} $$

(28)

where $N^*$ is less than or equal to the number $N$ of internal coordinates used in Eqs. (8)-(18).

The reaction rates have been calculated using the variational transition state theory including multidimensional tunneling approximation, which have also been described in many literatures. We have used MC-Tinker that interconnect Polyrate and Tinker program packages for the rate calculations.

Results and Discussion

The optimized structures of BH$_3$ at the QCISD level have $C_3$ symmetry. The MCCM level of theory also predicts the $C_3$ structure and the geometrical parameters are listed in Table 1 along with the previous high-level $ab$ initio results.

The bond lengths for B-H$_2$ and B-H$_3$ at the QCISD level and are longer than the corresponding values from the $ab$ initio study, whereas those from the MCCMs are slightly shorter. The geometrical parameters from the MCCMs show good agreement with those from the CCSD(T)/TZ(3d1f,2p1d) level. In particular, the structure from the MCG3 method agrees very well. Table 2 lists the geometrical parameters for the transition state (TS) of hydrogen scrambling. The QCISD level predict the TS structure with $C_3$ symmetry, which is consistent with the CCSD(T)/TZ(3d1f,2p1d) level. All MCCMs used in this study give the same symmetry for the TS too. The TS structures from the MCG3 and MC-QCISD methods agree almost perfectly with that from CCSD(T)/TZ(3d1f,2p1d) level.

Table 3 lists the dissociation energies of BH$_3$ and barrier heights of hydrogen scrambling calculated at various levels of theory. The $D_b$ values from the QCISD level are 2.14 and 1.89 kcal/mol, respectively, which are too small, and the $V_b^2$ values are 7.52 and 7.57 kcal/mol, respectively. Schreiner et al. have performed various levels of $ab$ initio calculations for the BH$_3$ systems. They found that geometry and energy of BH$_3$ depend very much on the level of theory and the size of basis sets. The $D_b$ values at the CCSD(T) level with TZ2P and DZP basis sets were 3.32 and 0.82 kcal/mol, respectively. They have reported 5.82 and 5.65 kcal/mol for the $D_b$ and $V_b^2$ values, respectively, at the CCSD(T)/TZ(3d1f1g,2p1d)//CCSD(T)/TZ(3d1f2p1d) level, which is the highest level of theory used so far. The $D_b$ and $V_b^2$ values at the CCSD(T)/TZ(3d1f2p1d) level were 5.26 and 6.11 kcal/mol, respectively.

Adding one set of boron g-type function increases the dissociation energy and decreases the barrier height. Considering higher electron correlation and using larger basis sets seem to increase the dissociation energy and decrease the barrier height.

All $D_b$ and $V_b^2$ values from the MCCM agree very well with those from the CCSD(T)/TZ(3d1f1g,2p1d) level. In particular, the G3/QCISD/TZ2P level underestimates the dissociation energy and slightly overestimates the barrier height. The $D_b$ values at the CCSD(T)/TZ(3d1f1g,2p1d) level is 0.92 kcal/mol, which is larger than all the MCCM values. Schreiner et al. have obtained zero-point energies
Table 1. Geometrical parameters of BH$_3$ optimized at the MCCM levels along with the high level ab initio results

| Parameters | QCISD/TZ2P | MC-QCISD | MCCM-UT-CCSD | MCCM-UT-MP4SDQ | MCG3 | CCSD(T)/TZ2P
<table>
<thead>
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<tbody>
<tr>
<td>$r$(B-H1)</td>
<td>1.198</td>
<td>1.203</td>
<td>1.196</td>
<td>1.195</td>
<td>1.204</td>
<td>1.202</td>
</tr>
<tr>
<td>$r$(B-H2)</td>
<td>1.472</td>
<td>1.401</td>
<td>1.401</td>
<td>1.397</td>
<td>1.441</td>
<td>1.422</td>
</tr>
<tr>
<td>$r$(B-H3)</td>
<td>1.484</td>
<td>1.415</td>
<td>1.416</td>
<td>1.411</td>
<td>1.425</td>
<td>1.436</td>
</tr>
<tr>
<td>$r$(B-H4)</td>
<td>1.191</td>
<td>1.194</td>
<td>1.187</td>
<td>1.186</td>
<td>1.195</td>
<td>1.194</td>
</tr>
<tr>
<td>$r$(H2-H3)</td>
<td>0.786</td>
<td>0.808</td>
<td>0.796</td>
<td>0.796</td>
<td>0.805</td>
<td>0.799</td>
</tr>
<tr>
<td>$\theta$(H1-B-H2)</td>
<td>80.2</td>
<td>79.2</td>
<td>79.5</td>
<td>79.5</td>
<td>79.4</td>
<td>79.6</td>
</tr>
<tr>
<td>$\theta$(H2-B-H3)</td>
<td>30.8</td>
<td>33.4</td>
<td>32.8</td>
<td>32.9</td>
<td>33.0</td>
<td>32.5</td>
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<tr>
<td>$\theta$(H4-B-H5)</td>
<td>119.9</td>
<td>120.1</td>
<td>120.0</td>
<td>120.1</td>
<td>120.1</td>
<td>120.1</td>
</tr>
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</table>

Table 2. Geometrical parameters for the transition state of hydrogen scrambling in BH$_3$ optimized at the MCCM levels along with the high level ab initio results

| Parameters | QCISD/TZ2P | MC-QCISD | MCCM-UT-CCSD | MCCM-UT-MP4SDQ | MCG3 | CCSD(T)/TZ2P
<table>
<thead>
<tr>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$r$(B-H1)</td>
<td>1.250</td>
<td>1.250</td>
<td>1.242</td>
<td>1.240</td>
<td>1.253</td>
<td>1.251</td>
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<tr>
<td>$r$(B-H2)</td>
<td>1.180</td>
<td>1.187</td>
<td>1.181</td>
<td>1.178</td>
<td>1.187</td>
<td>1.187</td>
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<tr>
<td>$r$(H1-H2)</td>
<td>1.089</td>
<td>1.189</td>
<td>1.081</td>
<td>1.081</td>
<td>1.088</td>
<td></td>
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<tr>
<td>$\theta$(H1-B-H2)</td>
<td>60.8</td>
<td>51.2</td>
<td>51.2</td>
<td>51.2</td>
<td>51.0</td>
<td></td>
</tr>
<tr>
<td>$\theta$(H4-B-H5)</td>
<td>128.1</td>
<td>128.1</td>
<td>128.1</td>
<td>128.1</td>
<td>128.0</td>
<td>128.1</td>
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Table 3. Dissociation energies of BH$_3$ and barrier height for hydrogen scrambling calculated at various levels of theory

<table>
<thead>
<tr>
<th>Level</th>
<th>$D_s$</th>
<th>$D_b$</th>
<th>$D_r$ (fit)</th>
<th>$V_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCSD(T)/CCSDx(5s4p3d124s2p1d)//MP2/(3s2p1d2s1p)</td>
<td>5.4</td>
<td>0.9</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>CCSD(T)/TZ2P</td>
<td>3.32</td>
<td>0.72</td>
<td>6.79</td>
<td></td>
</tr>
<tr>
<td>CCSD(T)/TP2</td>
<td>0.89</td>
<td>0.19</td>
<td>6.38</td>
<td></td>
</tr>
<tr>
<td>CCSD(T)/TP2</td>
<td>5.26</td>
<td>0.36</td>
<td>6.11</td>
<td></td>
</tr>
<tr>
<td>CCSD(T)/TP2</td>
<td>5.82</td>
<td>0.92</td>
<td>5.65</td>
<td></td>
</tr>
<tr>
<td>CCSD(T)/TP2</td>
<td>2.14</td>
<td>-2.09</td>
<td>7.52</td>
<td></td>
</tr>
<tr>
<td>G3/QCISD/TZ2P</td>
<td>4.95</td>
<td>5.13</td>
<td>6.10</td>
<td></td>
</tr>
<tr>
<td>CCSD(T)/cc-pVQZ/QCISD/TZ2P</td>
<td>5.58</td>
<td>5.74</td>
<td>5.96</td>
<td></td>
</tr>
<tr>
<td>MC-QCISD</td>
<td>6.15</td>
<td>0.83</td>
<td>6.12</td>
<td>5.44</td>
</tr>
<tr>
<td>MCCM-UT-CCSD</td>
<td>5.76</td>
<td>0.37</td>
<td>5.76</td>
<td>5.71</td>
</tr>
<tr>
<td>MCCM-UT-MP4SDQ</td>
<td>6.11</td>
<td>0.73</td>
<td>6.09</td>
<td>5.59</td>
</tr>
<tr>
<td>MCG3</td>
<td>5.95</td>
<td>0.65</td>
<td>5.92</td>
<td>5.83</td>
</tr>
</tbody>
</table>

Energies are in kcal/mol. $D_s$ and $D_b$ are dissociation energies from the equilibrium structure and from the zero-point energy level, respectively. $V_0$ is the barrier height for the hydrogen scrambling of BH$_3$. The TS structure has C$_2v$ symmetry. Lengths are in Å and angles in degree. Reference 5.

The potential energy curve where $R_c$ is between 1.6 and 2.4 Å. Using higher level of electron correlation increases the well depth and improves the shape of the curve, as shown in the curve at the QCISD(T)/QCISD/TZ2P level, but this curve is still far from the standard Morse type potential curve. At the CCSD(T)/cc-pVQZ/QCISD/TZ2P level, the potential curve is very smooth without the flat region. Not only high correlation level but also larger basis sets seems mandatory for the high quality potential energy surface. The potential energy curves plotted at the MCCM levels are shown in Figure 2. These potential curves are quite consistent with each other, and no flat region is appeared. However, these curves cannot be fitted into a single Morse type function either. It is not
The potential energy curves along the dissociation coordinate of BH$_3$. The partially optimized structures at the QCISD/TZ2P level were used. The open circles, closed triangles, open triangles, and closed squares are obtained at the QCISD/TZ2P, QCISD(T)/QCISD/TZ2P, G3/QCISD/TZ2P, and CCSD(T)/cc-pVQZ level, respectively.

Figure 1. The potential energy curves along the dissociation coordinate of BH$_3$. Potential energies were calculated by using the partially optimized structure at the QCISD/TZ2P level. The closed circles, open circles, closed triangles, and open inverted triangles are from the MC-QCISD, MCCM-UT-QCISD, MCCM-UT-MP4SDQ, and MCG3 methods, respectively. The lines passing through the point are from the best fit of Eq. (29).

Figure 2. The potential energy curves along the dissociation coordinate of BH$_3$. The minimum of the potential energy curve, and $\alpha$ and $(1-\alpha)$ controls the relative importance of two terms with range parameters. The estimated $D_e$ values from Eq. (29) are listed in Table 3, and these values at the MCCM levels are almost identical to the optimized $D_e$ values. The $R_e$ values are 1.351, 1.351, 1.348, and 1.360 A at the MC-QCISD, MCCM-UT-CCSD, MCCM-UT-MP4SDQ, and MCG3 levels, respectively.

Although the G3 method cannot be used to calculate the potential energy for the dissociation of a molecular to atomic species because of the HLC term, it is okay for BH$_3$ dissociation since it dissociates into two molecular species, BH$_3$ and H$_2$. The potential curve from the G3/QCISD/TZ2P method is shown in Figure 1. This curve is better in shape than those at the QCISD or QCISD(T) levels. We have fitted the G3 potential curve to Eq. (29), and obtained 5.13 kcal/mol and 1.360 A for the $D_e$ and $R_e$ values, respectively. The $R_e$ value is the same as that from the MCQ method, however, the $D_e$ value is smaller than the MCCM and the CCSD(T)/TZ(3d1f1g2p1d) values. The potential curve at the CCSD(T)/cc-pVQZ/QCISD/TZ2P level was also fitted to Eq. (29). This curve is lower in energy than the G3 curve. The well depth from the curve fitting is increased to about 5.74 kcal/mol and the $R_e$ value is 1.366 A. This well depth is almost identical to the $D_e$ value at the CCSD(T)/TZ(3d1f1g2p1d) level. These results suggest that at least the CCSD(T)/cc-pVQZ level of theory is required to generate reasonably accurate potential energy surface of the BH$_3$ dissociation.

Figure 1 and Figure 2 shows quite clearly that the MCCM can correct the incompleteness of the QCISD level with TZ2P basis sets for the potential energy surface of BH$_3$ dissociation. This method is even superior to the QCISD(T)/TZ2P and G3 methods. It is interesting to note that only experimental atomization energies are used to adjust the coefficients of the MCCM. No experimental data for weak chemical interactions are used. The MCCM can be tested successfully to reproduce the structures and energies of hydrogen-bonded dimers and hydrated proton clusters and proton affinities of molecules. In this study and previous results suggest that the MCCM could be applied to reproduce many other chemical properties than the atomization energy. Another important observation is that the most accurate method among the MCCMs for the atomization energy is not necessarily the case for other chemical properties. In this study, all four MCCMs give almost the same results in the dissociation energy and barrier height. The Maximum deviation within these four methods is only 0.4 kcal/mol for both dissociation energy and barrier height. The MCCM-UT-CCSD agrees the best with the CCSD(T)/TZ(3d1f1g2p1d) level.

We used the MM3 force field for the $V_{13}$ and $V_{22}$ terms in Eq. (7), and the MCCM-UT-CCSD method was used for energies, gradients, and Hessians for the high-level Shepard points. We defined several force field parameters for BH$_3$ that are missing. The potential and vibrationally adiabatic energies along the reaction coordinate are shown in Figure 3. We have used 15 high-level Shepard points step by step to generate the potential surfaces. The potential energy, $V_{rep}$ is very smooth, however, the vibrationally adiabatic potential energy, $V_T$, runs in and out slightly, along the reaction.
coordinate. It occurs in the interpolated region between high-level Shepard points, and in principle, it will be disappeared when we use infinite number of Shepard points. The tunneling coefficients and rate constants are listed in Tables 4 and 5. The microcanonically optimized tunneling coefficient is 7.2 at 300 K, which is large compared with the tunneling coefficient of general proton transfer reactions. The Arrhenius plots for the rate constants are shown in Figure 4. The plot for the rate constants including tunneling correction is curved, it becomes flat at a very low temperature, which indicates large tunneling effect. The rate constant at 300 K with this tunneling coefficient is 2.1 \times 10^{7} s^{-1}, which is very fast. This suggests that the hydrogen scrambling might compete with the fast dissociation of BH$_{3}$ into BH$_{2}$ and H$_{2}$.

Figure 3. The potential energy and vibrationally adiabatic potential energy curves along the reaction coordinate of hydrogen scrambling in BH$_{3}$. The vertical lines show the position of the high-level Shepard points at the transition state (s=0) and in the reactant channel (s=0). The same points are in the product channel (s>0).

Table 4. Small curvature, large curvature, and microcanonically optimized tunneling coefficients at various temperatures

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Figure 4. The Arrhenius plots for the rate constants with and without tunneling correction.

Conclusions

We have calculated structures and energies of BH$_{3}$ and the TS for the hydrogen scrambling using recently developed multi-coefficient correlated quantum mechanical methods. Our results agree very well with those from the CCSD(T)/TZ(3d1f1g,2p1d) level. We have also calculated the potential energy curves for the dissociation of BH$_{3}$ into BH$_{2}$ and H$_{2}$. The QCISD level with TZ2P basis sets produce a flat region on the potential curves, where reaction coordinate parameter, R$_{c}$, is around 1.6 and 2.4 A. It would be necessary to use the CCSD(T)/TZ(3d1f1g,2p1d) level of theory to generate the reasonable potential energy curve for the BH$_{3}$ dissociation. The lower levels of theory were unable to give correct potential curves, whereas the MCCM generates very good potential energy curves and requires much less computing resources than the CCSD(T)/TZ(3d1f1g,2p1d) and CCSD(T)/cc-pVQZ levels.

The MCCM-UT-CCSD level of theory was used for the energy, gradients, and Hessians of high-level Shepard points to generate the potential energy surface using the MCCM algorithm. Tunneling is very important and the rate constant for the BH$_{3}$ scrambling is 2.1 \times 10^{7} s^{-1}, which is very large. This suggests that the hydrogen scrambling might compete with the fast dissociation of BH$_{3}$ into BH$_{2}$ and H$_{2}$.

Acknowledgment. This study is supported by a grant from the Korea Research Foundation (KRF-2002-070-C00048).

Table 5. Rate constants without and with tunneling corrections

<table>
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<th>k (H)$^{C^{T}}$</th>
<th>k (H)$^{C^{T^{M^{CT}}}}$</th>
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References