Mechanistic Study of Pyrolysis of Small Boron Hydrides

by

Baili Sun

A thesis submitted to the Graduate Faculty of
Auburn University
in partial fulfillment of the
requirements for the Degree of
Master of Science

Auburn, Alabama
August 3, 2013

Keywords: Mechanism, Boron Hydrides, Kinetics

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Approved by
Michael L. McKee, Chair, Professor, Department of Chemistry and Biochemistry
David M. Stanbury, Professor, Department of Chemistry and Biochemistry
German Mills, Associate Professor, Department of Chemistry and Biochemistry
Abstract

Theoretical background and computational methods are introduced in Chapter 1. In Chapter 2 the rate constant for the association of two boranes to form diborane is investigated using several methods. The most sophisticated method is variable reaction coordinate - variation transition state theory (VRC-VTST) which has been developed to handle reactions with no enthalpic barriers. The rate constant was computed using conventional VTST with the IRC from the G4 and W1DB methods. Two variations of the multi-step mechanisms for diborane pyrolysis are presented.

The initial steps in the B₄H₁₀ pyrolysis mechanism have been elucidated in Chapter 3. The mechanism can be divided into three stages: initial formation of B₄H₈, production of volatile boranes with B₃H₇ acting as a catalyst, and formation of nonvolatile products. The first step is B₄H₁₀ decomposition to either B₄H₈/H₂ or B₃H₇/BH₃ where the free energy barrier for the first pathway is 5.6 kcal/mol higher (G4, 333 K) than the second pathway when transition state theory (TST) is used. We suggest that the rate-determining step is B₄H₁₀ + B₃H₇ → B₄H₈ + H₂ + B₃H₇ where B₃H₇ acts as a catalyst. The role of reactive boron hydrides such as B₃H₇ and B₄H₈ as catalysts in the build-up of larger boron hydrides may be more common than that previously considered.
Acknowledgments

I would like to acknowledge Prof Michael L. McKee. This thesis would not have been possible without his support and guidance. He continually conveyed a spirit of excellence to me in regard to research and study. I am also very grateful to Dr. Nida McKee for her help in my graduate life in Auburn.

I also thank my committee members, Prof. David M. Stanbury and Prof. German Mills for their persistent help towards my thesis.

Finally, I would like to thank my father Chuanlin Sun and my mother Shuhua Yang for their endless love and full support.
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<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>Hartree-Fock</td>
</tr>
<tr>
<td>STO</td>
<td>Slater-type Orbital</td>
</tr>
<tr>
<td>GTO</td>
<td>Gaussian-type Orbital</td>
</tr>
<tr>
<td>CBS</td>
<td>Complete Basis Set</td>
</tr>
<tr>
<td>TST</td>
<td>Transition State Theory</td>
</tr>
<tr>
<td>VTST</td>
<td>Variational Transition State Theory</td>
</tr>
<tr>
<td>GTST</td>
<td>Generalized Transition State Theory</td>
</tr>
<tr>
<td>IRC</td>
<td>Intrinsic Reaction Coordinate</td>
</tr>
<tr>
<td>MEP</td>
<td>Minimum-energy Path</td>
</tr>
<tr>
<td>VRC</td>
<td>Variable Reaction Coordinate</td>
</tr>
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</table>
Chapter 1

General Introduction

Computational chemistry has developed into a standard tool to understand chemical phenomena at the electronic and molecular levels. Its application has spread to almost all areas of science and engineering such as quantum chemistry, molecular modeling, drug delivery, and hydrogen storage. Through investigating the structures and properties of intermediates and transition structures, reaction mechanisms can be elucidated.

1.1 Schrödinger equation

The Schrödinger equation is the essential equation of quantum mechanics.\(^1\,^2\) This second order partial differential equation determines how a physical system evolves in time. The Schrödinger equation in quantum mechanics is an analogy of Newton’s law in classical mechanics.

The Schrödinger equation can be divided into two general subcategories: time-dependent and time-independent.

Time-dependent Schrödinger equation:

\[
i\hbar \frac{\partial}{\partial t} \psi = \hat{H} \psi
\]  
(1)

Time-independent Schrödinger equation:

\[
E \psi = \hat{H} \psi
\]  
(2)
1.2 The Born-Oppenheimer Approximation

The Born-Oppenheimer (BO) Approximation is indispensable in quantum chemistry. It originates from the significant mass difference between nuclei and electrons. Since the nuclei are much heavier, their velocities are much smaller. Therefore, intuitively, the motion of electrons can be considered as circling mass points around the fixed nuclei. The Schrödinger equation is composed of two components. The electronic part describes the electronic wave function ($\psi_{\text{electronic}}$) depending only on electrons with fixed nuclei configuration. The nuclear part (vibrational, rotational) describes the nuclear wave function. For the general molecular system, the Schrödinger equation without electron effects can be drawn:

\[
(T_{\text{elec}} + T_{\text{nuc}} + V_{\text{nuc} - \text{elec}} + V_{\text{elec}} + V_{\text{nuc}}) \psi = E\psi
\]  

(3)

T and V terms present kinetic and potential energies terms, respectively. The key point of the Born-Oppenheimer (BO) approximation is that it treats the two parts of the problem separately. Therefore, an electronic Schrödinger equation can be constructed:

\[
\hat{H}_{\text{elec}} \psi_{\text{elec}} = E_{\text{elec}} \psi_{\text{elec}}
\]  

(4)

\[
\hat{H}_{\text{elec}} = T_{\text{elec}} + V_{\text{nuc} - \text{elec}} + V_{\text{elec}} + V_{\text{nuc}}
\]  

(5)

$E_{\text{elec}}$ represents the potential energy surface which depends on the nuclear configuration. The Born-Oppenheimer approximation is ubiquitous. Only the eigenfunctions of $H_2$ can
be solved accurately without it. One limitation of Born-Oppenheimer approximation is that relativistic effects are ignored which is important for heavy atoms.

1.3 Hartree-Fock Theory (HF theory)

As one of the basic fundamental theories of quantum chemistry, the solution of the Hartree-Fock equation is the root for most advanced *ab-initio* methods which provide more accurate description for many electrons system. One problem with HF theory is that electron correlation is ignored in multi-electron systems. Electron correlation is treated in an average way, in other words, each electron only interacts with a static electron cloud of all the other electrons. Therefore, the lowest energy from HF theory will be always greater than the true energy of the system on the basis of the variational principle.

The self-consistent field method is proposed to solve HF theory. The key idea is as follows: first, an initial electronic configuration of the wavefunction (typically the ground state) will be guessed, which is a product of single electron-electron wave function. Second, the effect of all the other electrons have been included in the effective potential which will be solved for a new one-electron wavefunction for atom i. The same procedure will be applied for the next electron. After all the electrons have been scanned, the above procedure is iterated until the one-electron wavefunctions reach convergence.

1.4 Basis set

Mathematically, any set of functions can be used as a basis set. The definition of basis set in theoretical and computational chemistry is as follows: a basis set is a set of
functions (called basis functions) which are linear combinations used to create molecular orbitals ($\psi_j$),

$$\psi_j = \sum_{i=1}^{n} c_{ij} \chi_i$$

where the coefficients $c_{ij}$ are also called the molecular orbital expansion coefficients, which can be determined numerically using the variational principle. $\chi_i$ refers to an arbitrary function. Larger basis sets more accurately approximate the orbitals by imposing fewer restrictions on the locations of the electrons in space. Meanwhile, the energy converges towards the HF limit of the method more closely.

Slater-type orbitals (STOs)$^6$ and Gaussian-type orbitals (GTOs)$^4$ are the two types of orbitals in quantum chemistry. Historically, STOs are important. Their application is now limited since integrals of STOs are difficult to evaluate. GTOs are dominant orbitals in modern chemistry calculations. GTOs are based on STOs but have a radial term following the function $e^{-r^2}$, thus they are more efficient for computation than STOs. However, GTOs also exhibit a deficiency which can be summarized as: "No cusp at nucleus". The solution to this deficiency is to typically replace each STO with 3 or 6 GTOs.

There are several terms used to describe basis sets. The definition of minimal basis set is that one basis function is employed per atomic orbital. For example, for CH$_4$, a 1s orbital is used for each H while 1s, 2s, 2px, 2py and 2pz orbital are employed for the atom C. Minimal basis sets can not describe the wavefunction sufficiently since the number and size of the orbitals are fixed for all systems. To improve the performance of
the minimal basis set, the number of basis functions for each orbital with different orbital exponents has been doubled and tripled, called Double-Zeta and Triple-Zeta, respectively. Usually, it is time-consuming to calculate a double-zeta basis set for every orbital. In chemical bonding, the core orbitals only weakly affect bonding properties while valence orbitals are very important. Split valence basis add additional flexibility for describing valence orbitals. Diffuse basis sets are applied to deal with systems that allow electrons to flow away from the nucleus, for instance, excited states and anions. Another modification of basis sets is to make the atomic orbitals polarized by the influence of their surroundings. Polarization basis set are usually presented as * or (d), for example, 6-31G(d) which is important for heavy atoms.

1.5 Composite method

The goal of the composite method is to model the thermochemical quantities accurately. Through combination of a series of different calculations an approximation to a higher level computation is made that would be very expensive in actual calculation, and high accuracy can be obtained. There are several families of the method: the Gaussian-n methods,\textsuperscript{7-9} the Complete Basis Set (CBS) methods\textsuperscript{10} and the W1 method.\textsuperscript{11}

1.6 Fundamentals of kinetics

1.6.A Reaction Rates

For a general chemical reaction,\textsuperscript{12}

\[ aA + bB \rightarrow pP + qQ \]  

\textsuperscript{(8)}
the change of the reaction mixture with time is the reaction rate which is defined as.\textsuperscript{12,13}

\[
r = -\frac{1}{a} \frac{dA}{dt} = -\frac{1}{b} \frac{dB}{dt} = -\frac{1}{p} \frac{dQ}{dt} = -\frac{1}{q} \frac{dP}{dt}
\]  \hspace{1cm} (9)

The negative sign means the reactants are consumed; conversely, a positive sign indicates the concentrations of products are increasing.

1.6.B Reaction Laws and Reaction Order

For most reactions, the rates depend on the concentrations of one or more reactants or products. The exponents \(a, b, p\) and \(q\) may be integer, fractional, or negative while \(k\) is the rate constant. The equation is the rate equation or rate expression. The overall order of the reaction is simply the sum of exponents \((a+b+p+q)\).

\[
\]  \hspace{1cm} (10)

1.6.C Unimolecular Reactions

The elementary reaction step,

\[
k_1 \hspace{1cm} A \rightarrow B
\]  \hspace{1cm} (11)

is unimolecular since there is only one reactant while the rate law is
Another simple unimolecular reaction may be described in fast equilibrium:

\[
\frac{dB}{dt} = k_1[A] \tag{12}
\]

where A and B are isomers, for example, conformational or constitutional isomer. This reversible unimolecular step implies the following rate law,

\[
\frac{dB}{dt} = k_1[A] - k_{-1}[B] \tag{14}
\]

The system is in equilibrium, in other words, the reactant concentration is stationary, thus

\[
\frac{k_1}{k_{-1}} = \frac{[B]_{eq}}{[A]_{eq}} = K_{eq} \tag{15}
\]

A unimolecular reaction step can have more than one product such as in fragmentation.

\[
A \xrightarrow{k_2} B + C \tag{16}
\]
1.6.C Bimolecular Reactions

The bimolecular reaction

\[ A + B \xrightarrow{k_1} C \] \hspace{1cm} (17)

implies the rate law

\[ \frac{dc}{dt} = k_2[A][B] - k_{-2}[C] \] \hspace{1cm} (18)

or it could be written as a rate of loss of A or B as we have seen above. The reversible bimolecular reaction,

\[ A + B \xrightarrow{k_1} C + D \] \hspace{1cm} (19)

implies the rate law

\[ \frac{dc}{dt} = k_2[A][B] - k_{-2}[C][D] \] \hspace{1cm} (20)

1.7 Transition State Theory

Initiated by Wigner and Pilzer and extended by Eyring, transition state theory has become one of the most important theories in physical chemistry, which unveils the a
fundamental relation between the rate constant for a reaction and the enthalpy and entropy of activation for that reaction.

The essential assumption of transition state theory is that a quasi-equilibrium has been built up between the reactants and the activated complex at the saddle point. The rate is then directly proportional to the concentration of these complexes multiplied by the frequency \( \frac{k_n}{\hbar} T \) with which they are converted into products.\(^{14}\)

1.7.A Eyring equation

The derivation of Eyring equation can be illustrated through a bimolecular reaction as follows, and also can be generalized to unimolecular reactions.

\[
A + B \xrightarrow[k]{\ } P
\]  

(21)

The objective is to compute the forward rate constant \( k \). For the same bimolecular reaction sequence, transition state theory assumes that A and B reversibly react to form an intermediate complex (AB)\(^\dagger\), which irreversibly decomposes to form final product P. The species (AB)\(^\dagger\) is a so-called transition state (or a activated complex) whose lifetime is less than \( 10^{-13} \) sec. This can be shown schematically in Figure 1.

\[
A + B \rightleftharpoons [AB]^\ne \rightarrow P
\]  

(22)
The rate of product p formation is proportional to the concentration of the activated complex.

\[
\frac{dP}{dt} = k[A][B] = k'[AB]^* \tag{23}
\]

where \( k \) is the bimolecular rate constant for the reaction of A and B to P and \( k' \) is the unimolecular rate constant for formation of product P from the activated complex \([AB]^*\). Under the transition state theory, there is a thermodynamic quasi-equilibrium existing between A, B and \([AB]^*\).

\[
K^* = \frac{[AB]^*}{[A][B]} \tag{24}
\]
So, the concentration of the transition state $[AB]^\dagger$ is

$$[AB]^* = K^*[A][B]$$  \hspace{1cm} (25)

Therefore the rate equation for the production of product is

$$\frac{dP}{dt} = k' [AB]^* = k^* K^*[A][B] = k[A][B]$$  \hspace{1cm} (26)

where the rate constant $k$ is given by

$$k = k^* K^*$$  \hspace{1cm} (27)

During the activated complex formation, one bond is breaking while a vibration is being transformed into a translation as the bond breaks. $k^*$ is proportional to the frequency ($\nu$) of the imaginary vibrational mode. A proportionality constant $\kappa$, also called transmission coefficient is introduced. So $k^*$ can be rewritten as

$$k^* = \kappa \nu$$  \hspace{1cm} (28)

A temperature dependent expression of $K^\dagger$ is brought from statistical mechanics as follows:
\[ K^* = \frac{k_B T K^*}{h} \]  

(29)

where

\[ K^* = e^{-\frac{\Delta G^*}{RT}} \]  

(30)

From above equations, the new rate constant expression can be re-written, which is given as

\[ k = k^* K^* = \kappa \frac{k_B T}{h} e^{-\frac{\Delta G^*}{RT}} \]  

(31)

The rate constant expression can be divided into two parts according to

\[ \Delta G = \Delta H - T\Delta S. \]  

The final Eying equation is

\[ k = \kappa \frac{k_B T}{h} e^{\frac{\Delta S^*}{R}} e^{-\frac{\Delta H^*}{RT}} \]  

(32)

1.7.B Relation between theory and experiment

Experimentally two types of analysis are usually applied to measure the reaction physical quantities. Rate constants have been measured along a series of temperatures. The relationship between \( \ln(k/T) \) versus \( 1/T \) can be plotted. The activation energy can be
readily obtained from this analysis during the range of data points. Application of the Arrhenius equation is an alternative choice.\textsuperscript{4}

\[ k = Ae^{-Ea/(RT)} \]  \hspace{1cm} (33)

The Arrhenius activation energy is an important term that experimental scientists often refer to in the literature. It can be connected with calculated activation enthalpy as follows:\textsuperscript{12}

\[ E_a = \Delta H^\# + RT - P\Delta V^\# \]  \hspace{1cm} (34)

where $\Delta V^\#$ is the standard volume of activation. For a unimolecular reaction, from the reactions to the transition state, $\Delta V^\#$ does not change. Thus,

\[ E_a = \Delta H^\# + RT \]  \hspace{1cm} (35)

1.7.C Lindemann-Hinshelwood theory

Lindemann-Hinshelwood theory was first proposed by Lindemann in 1922 which built up the basis for the modern theory of thermal unimolecular rates. The essential idea can be summarized as follows: the reaction molecules will be activated by bimolecular collisions first, which could then undergo deactivating collisions. One of the achievements of Lindemann-Hinshelwood theory is that it provides reasonable
explanations to the experimental observation that the reaction order is different at high- and low-pressure limit.

For example, the mechanism of the unimolecular reaction might be proposed:

\[ X + M \xrightarrow{k_1} A^* + M \]  
\[ A^* + M \xrightarrow{k_{12}} A + M \]  
\[ A^* \xrightarrow{k_2} \text{Products} \]

In this scheme, \( A^* \) represents the energized molecule and \( M \) is the third-body molecule, also called collision partner. Steady-state approximation is used to deduce the rate expression,

\[ \text{rate} = k_{\text{uni}}[A] = k_2[A^*] = \frac{k_1k_2[A][M]}{k_1[M]+k_2} \]  
\[ \text{rate} = \frac{k_1k_2}{k_1} \]

The high pressure and low pressure have been defined at \([M] \to \infty\) and \([M] \to 0\), respectively. Therefore, the high- and low-pressure rate constant expressions are

\[ k_\infty = \frac{k_1k_2}{k_1} \]

and

\[ k_0 = k_1[M]. \]
1.8 Variational Transition State Theory (VTST) and Generalized Transition State Theory

Transition state theory determines the reaction activation free energy from the activated complex based on the transition structure. TST can usually provide reasonable results for reactions with a tight reaction barrier, but it can not effectively handle reactions without a transition structure or with a loose transition state. Generalized transition state theory (GTST) was developed to deal with this deficiency of transition state theory.\textsuperscript{15,16} The definition of GTST from IUPAC is "Any form of transition-state theory (TST), such as microcanonical variational TST, canonical variational TST, and improved canonical variational TST, in which the transition state is not necessarily located at the saddle point, is referred to as "generalized transition-state theory."\textsuperscript{17} Variational transition state theory (VTST) is one of the common methods of GTST.

Conceptually, the procedure of VTST involves two steps. First the minimum-energy path (MEP) or the intrinsic reaction coordinate (IRC) is constructed. Second, the activation free energy will be calculated until the minimal rate constant is approached.

\[
k^{VTST}(T, s) = \min_s \frac{k_B T Q^\circ(TS)}{Q_R} \frac{Q^\circ_R}{Q^\circ_o} e^{-\Delta V^\circ(s)/k_B T}
\]

By definition, \(s = 0\) is the position of the saddle point, and positive and negative values represent the product and reactant sides relative to the saddle point, respectively.

1.9 Variable Reaction Coordinate - Variational Transition State Theory (VRC-VTST)
The accurate calculation of rate constants for reactions without a barrier or with a loose barrier is always challenging, for instance, in the case of radical-radical associations. First of all, the dividing surface should be flexible and second, the calculated potential energy surfaces should be calculated with high-level electronic structure theory. For barrierless association reaction, the two reactants separated at infinite distance come to each other. The region beyond the transition-state region does not play a vital role since there is no interaction. In the transition-state region, free rotation modes of the individual reactants are gradually transformed into hindered rotations which are eventually converted into rigid bending vibrations. This significantly differs from the reactions with a tight barrier. The rigid-rotor harmonic-oscillator approximation can provide good results for tight barrier reaction. All orientations of the approaching fragments are crucial in the bond-forming range which is usually 1.5-6.0 Å.

In variable Reaction Coordinate - Variational Transition State Theory (VRC-VTST):\textsuperscript{18,19} as it implies, a new reaction coordinate is proposed as follows in Figure 2.

![Figure 2. Schematic description of variable reaction coordinate.](image)
The two ellipses represent reactant 1 and reactant 2, respectively. Center of mass is abbreviated as COM. P1 and P2 are pivot points associated with reactant 1 and reactant 2, respectively. Their positions vary according to different reactions. The vectors d(1) and d(2) are used to connect the pivots with their associated reactants center of mass (COM). The variable reaction coordinate is defined as distance of the vector connecting the two pivot points of the reactants. The distances will be fixed with a specified stepsize through the assigned distance range. All three vectors s, d(1), and d(2) will be sampled over the entire phase space simultaneously at fixed distances.
2.0 References:

(1) Jensen F. *Introduction to computational Chemistry*, Wiley: New York, **1999**.

(2) Levine, I. N. *Quantum Chemistry, Fifth Ed.*, Prentice-Hall, Inc.; New Jersey, **2000**.

(3) Baer, M. *Beyond Born-Oppenheimer: Electronic non-Adiabatic Coupling Terms and Conical Intersections*, John Wiley & Sons, Inc.; Hoboken, N. J., Chapter 2, **2006**.


Chapter 2

Computational Study of the Initial Stage of Diborane Pyrolysis

2.1 Introduction

The gas-phase pyrolysis of diborane is considered one of the most complicated processes in the entire field of chemistry. Historically, pyrolysis of diborane has been used to prepare various polyboranes under different conditions. Many experimental studies have been reported on the diborane pyrolysis and decomposition pathways, using such techniques as mass spectrometry, chemical vapor deposition, isotope exchange, and gas chromatography. Unfortunately, controversy surrounding the mechanism has not been resolved, even with the initial stage. Generally, the first steps (eq 1 and eq 2a-c) are as follows:

\[
\begin{align*}
B_2H_6 & \rightleftharpoons 2BH_3 \quad (1) \\
B_2H_6 + BH_3 & \rightarrow B_3H_7 + H_2 \quad (2a) \\
\text{or} \\
B_2H_6 + BH_3 & \rightleftharpoons B_3H_9 \quad (2b) \\
B_3H_9 & \rightleftharpoons B_3H_7 + H_2 \quad (2c) \\
2B_2H_6 & \rightleftharpoons B_3H_9 + BH_3 \quad (3)
\end{align*}
\]

It is widely accepted that the symmetric dissociation of diborane initiates the pyrolysis. However, several groups consider that the rate-determining step might be the
concerted formation and decomposition of B₂H₉ (eq 2a) or decomposition of B₂H₉ after its formation (eq 2b-c). The most recent experiments carried out by Greatrex et al. demonstrated that reaction 2a might be the rate-limiting step. An alternative mechanism initiated by reaction 3 was also proposed by Long et al. after an extensive systematic study of boron hydride reactions. This mechanism was also supported by Söderlund et al. It should be pointed out that reaction 3 has been largely ignored in the last decades. We suggest a reappraisal of the contribution of this step.

The 3/2 order dependence of the rate on the diborane concentration in the initial stage has been well established over the temperature range 373 to 550 K with an activation energy in the range of 22.0 - 29.0 kcal/mol (Table 1). This strongly implies that a tribor on species is involved in the rate-limiting step. Other important experimental observations include the inhibition by added H₂, which can also alter the product distribution. Relative rates of pyrolysis of B₂H₆ and B₂D₆ were studied by mass spectrometry, from which a primary isotope effect k_H/k_D of 5.0 was determined, while a recent experimental reinvestigation yielded a smaller ratio of 2.57. While previous kinetic studies have revealed additional details of this unusually complex reaction, in general, they support the above conclusions.

The calculated activation energy can be matched with the observed barrier. For example, if reaction 1 is the initial step and reaction 2a is the rate-limiting step, the overall reaction activation energy can be expressed as eq 4 where the 1.5 RT term relates activation enthalpy to activation energy for a 3/2 order rate law (rate = K₁¹/²k₂a[B₂H₆]³/₂).
Table 1. Reaction activation energy (kcal/mol) of the pyrolysis of diborane

<table>
<thead>
<tr>
<th>$\Delta E_a$ (kcal/mol)</th>
<th>Temperature (K)</th>
<th>Year</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exptl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.0±1.43</td>
<td>398-451</td>
<td>2000</td>
<td>23$_b$</td>
</tr>
<tr>
<td>25.6</td>
<td>350-530</td>
<td>1993</td>
<td>26</td>
</tr>
<tr>
<td>24.5±0.8</td>
<td>393-453</td>
<td>1989</td>
<td>17</td>
</tr>
<tr>
<td>22.1±1.6</td>
<td>323-473</td>
<td>1987</td>
<td>14</td>
</tr>
<tr>
<td>10.1±0.3$_a$</td>
<td>385-421</td>
<td>1973</td>
<td>25</td>
</tr>
<tr>
<td>29.0</td>
<td>343-473</td>
<td>1960</td>
<td>13</td>
</tr>
<tr>
<td>27.1±1.0</td>
<td>443-553</td>
<td>1960</td>
<td>23$_a$</td>
</tr>
<tr>
<td>27.4</td>
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<td>25.5±0.5</td>
<td>373</td>
<td>1951</td>
<td>22</td>
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<tr>
<td>Calculation</td>
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<tr>
<td>28.65(G4)</td>
<td>420</td>
<td>2013</td>
<td>this work</td>
</tr>
<tr>
<td>28.00(W1BD)</td>
<td>420</td>
<td>2013</td>
<td>this work</td>
</tr>
<tr>
<td>27.35$_b$</td>
<td>420</td>
<td>2013</td>
<td>this work</td>
</tr>
</tbody>
</table>

a) The activation barrier was determined with a gas re-circulation device. It is not clear why the value is much lower than other results.

b) The enthalpy at 0 K of the B$_2$H$_6$ $\rightarrow$ 2 BH$_3$ reaction was taken from quantum Monte Carlo calculations in ref 62 and combined with G4 theory.

$$E_a = \Delta H_{\text{overall}}^f + 1.5RT = 0.5\Delta H_{rx1} + \Delta H_{2a}^f + 1.5RT$$ (4)

Two major difficulties are encountered in the experimental studies. First, the intermediates are difficult to identify due to their reactivity.$^{5,6}$ Second, because the experiments are generally carried out in a flask, the initial rates are difficult to isolate from competing secondary reactions.$^3$ A noteworthy exception was the study by Fernández et al.$^{25}$ where a gas recirculating technique was used to probe the initial rate.
Unfortunately, the exceptionally low activation barrier that was obtained for diborane pyrolysis (10.1 kcal/mol) suggests that there was some experimental difficulty.

On the theoretical side, uncertainty exists as to the structure of the intermediates. For example, two isomers of B$_3$H$_6$ have been proposed, a cyclic C$_{3v}$ structure and a penta-coordinate C$_2$ butterfly structure. In addition, at least two isomers of B$_3$H$_7$ have been proposed, a double-bridged form and a single-bridged form. Due to the experimental difficulties of investigating the intermediate steps, high-level theoretical calculations may be the best tool to unravel the reaction mechanism. Over the last sixty years, quantum chemistry calculations have contributed to understanding the structures and reactivity of the boron hydrides. In this work, we have investigated the possible mechanisms of the initial stage of diborane pyrolysis with high-level theory with the hope to shed light on the mechanism.

### 2.2 Computational methods

Frequencies and geometry optimizations for all boron hydrides involved in the reactions (Figure 1) were calculated using the G4 composite method. The accuracy of the B3LYP/6-31G(2df,p) geometries (part of the G4 composite method) was checked by comparing with geometries on the minimum-energy pathway using the CCSD(T) method with the 6-311G(d,p) basis set. Stationary points in the low-lying pathways were also calculated by using the W1BD composite method. Intrinsic reaction coordinate (IRC) calculations were used to connect the reactant and product through a specific transition structure.
The minimum energy path (MEP) for the barrierless association of two boranes to form diborane has been determined by constrained optimization fixing the B-B distance to separations of 3.4 to 1.8 Å with a step size of 0.1 Å and optimizing all other variables. Single-point energy calculations at each geometry were made at the G4 level of theory. Vibrational frequencies along the reaction path were calculated after projecting out the reaction coordinate.
Figure 1. Optimized structures of the reactants, intermediates, and transition structures for the dissociation of B$_2$H$_6$ and the reaction of BH$_3$ + B$_2$H$_6$ at the G4 level. All the structures are also confirmed at the CCSD(T)/6-311G(d,p) level. All bond distances are in angstroms.

Equilibrium constants have been calculated from computed free energies ($K_p=\exp(-\Delta G^0/RT)$, where zero-point corrections, heat capacity corrections, and entropies have been included using standard techniques. All electronic structure calculations have been performed using the Gaussian 09 program suite. The direct VRC$^{47,48}$-VTST$^{49,50}$ method has been applied to calculate the rate constants of the barrierless association of BH$_3$ to diborane using the M06/MG3S and M06L/MG3S methods.$^{51,52}$ For the reaction B$_3$H$_9 \rightarrow$B$_3$H$_7$+H$_2$, which has a tight barrier, variational transition state theory with interpolated single-point energies (VTST$^{49,50}$-ISPE$^{53}$, dual-level direct dynamics method) has been used to calculate the rate constants. Geometries and frequencies were generated
at the B3LYP/6-31G(2df,p) level of theory, while the reactants, transition structure, and products were re-determined with W1BD theory to improve the reaction energies. Rate constants were further corrected by zero-curvature tunneling (ZCT)\textsuperscript{54} and small-curvature tunneling (SCT)\textsuperscript{54} for tunneling effects.

Variable reaction coordinate - variational transition state theory (VRC-VTST) was used to investigate the kinetics of association of BH\textsubscript{3}, which is very similar to the association of CH\textsubscript{3} radicals. Pivot points were fixed at 0.25 Å along the C\textsubscript{3} axis. A VRC reaction path was constructed by varying the distance between the pivot points in the range of 1.7 Å to 3.4 Å with a 0.1 Å step size. The VRC method avoids the difficulty of computing the inter-fragment modes where the transition from rotations in the reactants to vibrations in the product is very difficult to treat accurately. The M06/MG3S and M06L/MG3S methods were used because Truhlar and co-workers\textsuperscript{55} found these methods to be accurate in the CH\textsubscript{3} association reaction. The rate constants have been calculated using Polyrate.\textsuperscript{57} Gaussrate has been used as the interface between Gaussian 09 and Polyrate.\textsuperscript{55} The natural bond orbital (NBO)\textsuperscript{58} analysis was performed using the default NBO package in Gaussian 09.

2.3 Results and Discussion

The potential energy surface (including zero-point energy corrections) involving B\textsubscript{2}H\textsubscript{6} + BH\textsubscript{3} was thoroughly explored at the G4 level (Figure 2). Good agreement is found with the transition structure (TS(c)) to form B\textsubscript{3}H\textsubscript{6}(c) and the transition structure (TS(cf)) to form B\textsubscript{3}H\textsubscript{7}(f)+ H\textsubscript{2} located at the G4 level and those reported by Lipscomb and co-workers\textsuperscript{15} at the approximate MP2/6-31G(d) level. In particular, TS(c) features the
unusual triple-bridged hydrogen with B-H distances of 1.315, 1.420, and 1.590 Å. The calculated reaction enthalpies at 0 K from $\text{B}_3\text{H}_6 + \text{BH}_3$ to $\text{B}_3\text{H}_9(c)$ and to $\text{B}_3\text{H}_7(f) + \text{H}_2$ agree to within about 3 kcal/mol of those reported by Lipscomb and co-workers\textsuperscript{15} at the approximate CCSD(T)/6-31G(d)//MP2/6-31G(d) level. The significant difference between the two studies is the discovery of a new pathway through a pentacordinate $\text{B}_3\text{H}_9$ intermediate with $C_2$ symmetry ($\text{B}_3\text{H}_9(a)$), which is less stable than $\text{B}_3\text{H}_9(c)$ but is formed from $\text{B}_3\text{H}_6 + \text{BH}_3$ without an activation barrier. The activation enthalpy (0 K) for elimination of $\text{H}_2$ from $\text{B}_3\text{H}_9(a)$ is 14.1 kcal/mol, larger than the barrier for loss of $\text{H}_2$ from $\text{B}_3\text{H}_9(c)$ (11.7 kcal/mol). Through the $\text{B}_3\text{H}_9(a)$ intermediate, elimination of $\text{H}_2$ has the larger barrier (14.1 kcal/mol), while through the $\text{B}_3\text{H}_9(c)$ intermediate, formation from $\text{B}_3\text{H}_6 + \text{BH}_3$ has the larger barrier (13.5 kcal/mol). Duke \textit{et al.}\textsuperscript{27} have described the structure of $\text{B}_3\text{H}_9(a)$, also known as the butterfly structure, and even predicted that the species could be important in the pyrolysis mechanism of diborane but they did not report any transition structures.

Both $\text{B}_3\text{H}_9(a)$ and $\text{B}_3\text{H}_9(c)$ lose $\text{H}_2$ to form a higher-energy isomer of $\text{B}_3\text{H}_7$ ($\text{B}_3\text{H}_7(d)$ and $\text{B}_3\text{H}_7(f)$, respectively). However, very small barriers exist for the rearrangement of both to the global minimum $\text{B}_3\text{H}_7(e)$. From these steps, a mechanism can be postulated for the initial stage of diborane pyrolysis. The elementary step of this mechanism is the dissociation of diborane. Since the reverse reaction is the archetype for all fast boron hydride association reactions and since it has such elegant beauty, it deserves special treatment.
2.3. Association of BH$_3$

Although the reaction $2$ BH$_3 \rightarrow B_2H_6$ is the inorganic version of the association of two methyl radicals to form ethane, it has not received nearly as much attention. The estimate of the rate constant at the high pressure limit for BH$_3$ association at 545 K is $6.6 \times 10^{-11}$ cm$^3$·molecule⁻¹·s⁻¹ which is about double the rate constant for CH$_3$ association at the same temperature ($3.8 \times 10^{-11}$ cm$^3$·molecule⁻¹·s⁻¹). This is unusual because the CH$_3$ association is more than twice as exothermic as the BH$_3$ association (90.8 kcal/mol versus 36±3 kcal/mol). It is possible that the motion of the fragments at the bottleneck may
be more restricted in the CH$_3$ association reaction than in the BH$_3$ association which results in a smaller rate constant. However, the difference in rate constants may be within experimental uncertainty since the experimental rate constant for BH$_3$ association itself has a large uncertainty.$^{59}$

To confirm the reliability of the level of theory, the symmetric dissociation energies of diborane using various methods have been collected in Table 2. They agree well with the experimental range of 36±3 kcal/mol as well as with the most accurate quantum Monte Carlo calculation (36.59 kcal/mol).$^{6,62}$ The equilibrium isotope effect for B$_2$H$_6$/B$_2$D$_6$ computed at the W1BD level at 400 K is $K_H/K_D = 2.0$, which is the same value as that reported by Lipscomb and co-workers.$^{16}$

Since the association of BH$_3$ is barrierless, the reaction path was computed by reducing the B-B distance from 3.1 to 1.9 Å in steps of 0.1 Å (Figure 3). At each point along the reaction path, vibrational frequencies were computed by projecting out the transition vector. Free energies at 420 K were computed along the reaction path at the G4 level for B-B separations of 1.9 to 3.1 Å, in this range all of the projected vibrational frequencies are positive. The maximum on the free-energy curve occurs at R(B-B) = 2.9 Å where the free energy is 6.7 kcal/mol higher

<table>
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<tr>
<th>Level of theory</th>
<th>$\Delta E$</th>
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<th>$\Delta G(420K)$</th>
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</thead>
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<tr>
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<td>37.2</td>
<td>39.5</td>
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<td>42.1</td>
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<td>34.1</td>
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<td>35.8</td>
<td>38.1</td>
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<td>CCSD(T)/aug-cc-pVTZ</td>
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<td>36.1</td>
<td>38.5</td>
<td>23.5</td>
</tr>
<tr>
<td>MP2/aug-cc-pVTZ</td>
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<td>37.6</td>
<td>39.9</td>
<td>24.9</td>
</tr>
<tr>
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<td>39.8</td>
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<td>------</td>
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<tr>
<td>MP2/cc-PVTZ(^h)</td>
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<tr>
<td>Diffuse Monte Carlo(^c)</td>
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<td>Exptl(^d)</td>
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<td></td>
<td></td>
<td>36±3</td>
</tr>
</tbody>
</table>

a) Scale factor for vibrational frequencies: 0.978.
b) Scale factor for vibrational frequencies: 0.95.
c) Ref 62.
d) Ref 6.

than that of the separated BH\(_3\) fragments. At the B-B distance of 2.9 Å, the enthalpy is
2.6 kcal/mol lower than that for two BH\(_3\) units, consistent with a barrierless reaction. The
potential energy surface calculated by DeFrees et al.\(^63\) at the MP2/6-31G(d) level of
theory is in good agreement with our results.

NBO analysis, an effective tool to study donor-acceptor interactions, has been
performed on points along the reaction surface at the MP2/aug-cc-pVTZ level of theory.
Comparing second-order perturbative interaction values (\(\Delta E^{(2)}\)) within NBO theory
allows the estimation of stabilization energies which represent the strength of the donor-
acceptor interactions.\(^64\) The \(\Delta E^{(2)}\) of \(\sigma_{B-H}\) from one BH\(_3\) fragment to the \(n^*\) orbital of the
other BH\(_3\) fragment at the free energy maximum (B-B = 2.9 Å) is 25.3 kcal/mol, while all
other interactions are under 1 kcal/mol, indicating that the donor-acceptor interaction of
\(\sigma_{B-H}\) with \(n^*\) is an important interaction in this association. Since the enthalpy at the free
energy maximum is not much reduced from that of two boranes, other changes (such as
the B-H bond distance) are destabilizing.
Figure 3. Reaction paths for dissociation of diborane. Quantities calculated at G4 level of theory are enthalpies, free energies, and entropy contributions to free energies. The sum of quantities of BH$_3$ and BH$_3$ at infinity distance have been taken as zero. The distance of extending B-B bond in diborane has been taken as the calibration for the reaction paths. The reaction coordinate has been projected out.

The symmetry of the reaction path for dissociation of diborane has been discussed previously.$^{59,63,65}$ Angle and bond length changes of diborane along the reaction path have been monitored in Figure 4. From 2.0 Å to 2.6 Å, the B3LYP/6-31G(2df,p), reaction path maintains C$_{2v}$ symmetry. After 2.6 Å, the C$_{2v}$ symmetry
Figure 4. Comparison of two B-H(bridge)-B angle changes along the reaction coordinate.

All the geometries are optimized at the B3LYP/6-31G(2df,p) level of theory. is reduced to \( C_s \) where the B-H(1)-B and B-H(2)-B angles are unequal. To investigate the origin of symmetry-breaking, NBO analysis was performed along the reaction path at the MP2/aug-cc-pVTZ level of theory (Figure 5). The sum of two unequal donor-acceptor interactions in the \( C_s \)-symmetry path are larger than the sum of two equal donor-acceptor interactions in the \( C_{2h} \)-symmetry path.
Figure 5. NBO 2nd order donor-acceptor stabilization energies for the reaction of BH$_3$ + BH$_3$ along the reaction path. C$_s$ (B1-H2-B2) and C$_s$ (B1-H1-B2) represent the $\sigma_{B-H} \rightarrow n^*$ interaction between H1 and B2, H2 and B1 respectively along the C$_s$ reaction path. C$_{2h}$ represents the $\sigma_{B-H} \rightarrow n^*$ interaction either H1-B2 or H2-B1 since they kept the same along the C$_{2h}$ reaction path.

The high-pressure limit rate constants of association of BH$_3$ have been calculated at the M06/MG3S and M06L/MG3S levels of theory (Figure 6) rather than the dissociation rate constants of diborane because there were no direct experimental rate constants for the dissociation process. The dissociation rate constant of B$_2$H$_6$ (needed for the pyrolysis mechanism) can be easily obtained from the forward rate constant and the
equilibrium constant. The best experimental determination of the BH₃ association rate constant resulted from a study on the thermal decomposition of BH₃CO. ⁵⁹ The experimental value corrected to the high pressure limit yielded a rate constant at 545 K of 10^{10.6±0.4} liter·mol⁻¹·s⁻¹ or 6.6x10⁻¹¹ cm³·molecule⁻¹·s⁻¹ in units used here. The calculated values evaluated at 550 K are 1.0x10⁻¹⁰, 8.2x10⁻¹¹, and 1.6x10⁻¹⁰ cm³·molecule⁻¹·s⁻¹ at M06L/MG3S with VRC-VTST, M06/MG3S with VRC-VTST, and G4 with VTST, respectively.

2.3.B Pyrolysis of B₂H₆

2.3.B.1. Unimolecular Step as Initial Step (U path)

The present calculations of B₃H₉ and B₃H₇ isomers are in good agreement with previous studies.¹⁵,¹⁶,²⁸,³⁶ In the search for the lowest-energy pathway, there has been discussion about whether the reaction proceeds as a two-step process with a B₃H₉ intermediate or as a single-step process, bypassing the B₃H₉ intermediate. The origin of the debate is that the calculated energy of the B₃H₉ C₃ᵥ-symmetry structure, when combined with one half of the B₂H₆ dissociation energy, leads to an activation barrier too large to be consistent with experiment.
The first step of the U path is the dissociation of diborane which was discussed in the previous section. The schematic enthalpy (0 K) diagram of the B$_2$H$_6$ + BH$_3$ reactions (Figure 2) is initiated with the barrierless reaction to form B$_3$H$_9$(a). The B$_3$H$_9$(c) species with C$_{3v}$ symmetry is the most stable isomer of B$_3$H$_9$ but it is separated from B$_2$H$_6$ + BH$_3$ by a 13.5 kcal/mol barrier. While the penta-coordinate B$_3$H$_9$(a) with four bridging hydrogens and one terminal hydrogen is unknown, the butterfly structure of Al$_3$H$_9$ is known in the solid state.$^{66,67}$ In addition, a related butterfly structure of B$_4$H$_{10}$ has been found to play a key role in its reactivity.$^{68}$
From $\text{B}_3\text{H}_9(a)$, there are two reaction paths; either the butterfly $\text{B}_3\text{H}_9$ can isomerize to $\text{B}_3\text{H}_9(c)$ via a six-membered ring transition structure TS(ac) with an activation barrier of 28.6 kcal/mol followed by hydrogen release via TS(cf) to generate $\text{B}_3\text{H}_7(f) + \text{H}_2$, or pass over a 14.1 kcal/mol energy barrier via TS(ab). In the transition structure TS(ab), one terminal H atom and one bridging H atom from $\text{B}_3\text{H}_9(a)$ form an $\text{H}_2$-$\text{B}_3\text{H}_7$ complex ($\text{B}_3\text{H}_9(b)$) which has a very small barrier for $\text{H}_2$ loss to form $\text{B}_3\text{H}_7(f) + \text{H}_2$. From the above PES (including zero-point corrections) of $\text{B}_2\text{H}_6 + \text{BH}_3$, it is apparent that TS(ab) is involved in the rate-limiting step. Since the addition of BH$_3$ to B$_2$H$_6$ forming B$_3$H$_9(a)$ is a barrierless reaction, a reaction path was constructed where the B-B distance is decreased in 0.1 Å steps from 3.9 to 2.1 Å (Figure 7). To further explore the rate-limiting step, free energies at 420 K and other thermal properties of the reaction path are shown in Figure 7.

The butterfly $\text{B}_3\text{H}_9(a)$ is a minimum on the PES (including zero-point corrections). While it is lower in enthalpy ($\Delta H_{420K}$), it is higher in free energy ($\Delta G_{420K}$) relative to $\text{B}_2\text{H}_6 + \text{BH}_3$. This suggests that $\text{B}_3\text{H}_9(a)$ is only a minimum at low temperatures while at 420 K, $\text{B}_3\text{H}_9(a)$ is a point on the reaction path toward $\text{B}_3\text{H}_7(d) + \text{H}_2$. Thus, the postulated concerted reaction between $\text{B}_2\text{H}_6 + \text{BH}_3 \rightarrow \text{B}_3\text{H}_7 + \text{H}_2$ appears to be supported as shown by the free energy surface (420 K) in Figure 8. Except for a small bump when $\text{H}_2$ is lost from $\text{B}_3\text{H}_7(d)$, the free energy surface at 420 K has the general shape of a concerted process. The free energy barrier is 20.8 kcal/mol and the overall reaction is spontaneous by 1.6 kcal/mol.
Figure 7. Reaction paths for BH$_3$ + B$_2$H$_6$. Quantities calculated at G4 level of theory are enthalpies, free energies, electronic energies plus zero-point vibrational energies ($E_e + ZPE$) and entropy contributions to free energies ($T\Delta S$). The sum of quantities of BH$_3$ and BH$_3$ at infinite distance have been taken as zero. The distance of the centered B and the terminal B atoms in diborane has been taken as the calibration for the reaction paths. Reaction coordinate has been projected out.
Figure 8. Free energy diagram in kcal/mol of BH$_3$ reaction with B$_2$H$_6$ at G4 level of theory (420 K).

2.3.B.2 Bimolecular Step as Initial Step (B path)

The pyrolysis can also start via a bimolecular reaction between two B$_2$H$_6$ molecules. At a first glance, entropy considerations would suggest that a bimolecular process could not compete with a unimolecular process except at very high B$_2$H$_6$ pressures. However, the products of the bimolecular reaction are B$_3$H$_9$ + BH$_3$ which already form a larger boron hydride. Thus, the first two steps of the "Unimolecular process" are unimolecular + bimolecular while the "Bimolecular process" are bimolecular + unimolecular. In the derivation of the two mechanistic variations, if the first two steps are considered as fast equilibria, the two variations generate the same rate law (see derivations 2.4 Rate law derivation).
Figure 9. Enthalpy surface for the reaction of $\text{B}_2\text{H}_6 + \text{B}_2\text{H}_6 \rightarrow \text{B}_3\text{H}_9(\text{a},\text{C}_2) + \text{BH}_3$.

Enthalpies (kcal/mol) of $\text{B}_2\text{H}_6 + \text{B}_2\text{H}_6$ at 420 K are taken as zero. The values in parenthesis are free energies. Distances units are Angstroms.

Two bimolecular pathways have been calculated (Figures 9, 10). In the first (Figure 9), the products are $\text{B}_3\text{H}_9(\text{a}) + \text{BH}_3$ (path #1), while in the second (Figure 10), the products are $\text{B}_3\text{H}_9(\text{c}) + \text{BH}_3$ (path #2). The first step along the reaction path (path #1) involves the breaking of one hydrogen bridge and forming a new hydrogen bridge in the $\text{B}_3\text{H}_9(\text{a})$-$\text{BH}_3$ complex ($\text{B}_4\text{H}_{12}(\text{h})$) via transition structure $\text{TS}(\text{g})$. The product $\text{B}_3\text{H}_9(\text{a})$-$\text{BH}_3$ complex decomposes to $\text{B}_3\text{H}_9(\text{a})$ and $\text{BH}_3$ via transition structure $\text{TS}(\text{i})$. The complex $\text{B}_4\text{H}_{12}(\text{h})$, transition structure $\text{TS}(\text{g})$ and $\text{TS}(\text{i})$ all have very similar enthalpies. One BH$_4$ structural unit in all three
Figure 10. Enthalpy surface for the reaction of $\text{B}_2\text{H}_6 + \text{B}_2\text{H}_6 \rightarrow \text{B}_3\text{H}_9(\text{c},\text{C}_3v) + \text{BH}_3$.

Enthalpies (kcal/mol) of $\text{B}_2\text{H}_6 + \text{B}_2\text{H}_6$ at 420 K are taken as zero. The values in parenthesis are free energies. Distances units are Angstroms.

structures (intermediate and transition structures) is nearly static during the reaction. In the reaction path forming $\text{B}_3\text{H}_9(\text{c})$ (path #2), the two $\text{B}_2\text{H}_6$ molecules unite to form a three-membered ring transition structure (TS(j)). The complex $\text{B}_4\text{H}_{12}(\text{k})$ loses $\text{BH}_3$ spontaneously by 7.9 kcal/mol at 420 K.

The two pathways (#1 and #2) have free energy barriers (420 K) of 40.9 and 47.2 kcal/mol, respectively and are endothermic by 33.3 and 33.8 kcal/mol, respectively. Thus, pathway #1 forming $\text{B}_3\text{H}_9(\text{a})$ is preferred. If the mechanistic derivation assumes fast equilibria for the initial two steps, then the equilibrium constant (not the rate
constant) enters the rate law. The following steps of the mechanism involve the reaction of the products (BH₃ and B₃H₉(a)). The BH₃ reacts with B₂H₆ as described above (eq 2b) while B₃H₉(a) decomposes to B₃H₇(d) + H₂ as described above (eq 2c).

2.3.B.3. General Discussion and Comparison with Experiment

From the above discussion, we propose two possible mechanistic variations. We name them as the Unimolecular (U path) and Bimolecular (B path) paths according to the initial step.

\[
\text{B}_2\text{H}_6 \leftrightarrow 2 \text{BH}_3 \quad k_{U1}, k_{-U1}, K_{U1} \quad (U1)
\]

\[
\text{B}_2\text{H}_6 + \text{BH}_3 \leftrightarrow \text{B}_3\text{H}_7 + \text{H}_2 \quad k_{U2}, k_{-U2}, K_{U2} \quad (U2)
\]

\[
\text{B}_2\text{H}_6 + \text{B}_3\text{H}_7 \rightarrow \text{B}_4\text{H}_{10} + \text{BH}_3 \quad k_{U3} \quad (U3)
\]

Rate expression = \[ \frac{d([\text{B}_2\text{H}_6])}{dt} = 2k_{U3} [\text{B}_2\text{H}_6] \frac{K_{U1}^{1/2} k_{U2} [\text{B}_2\text{H}_6]^{3/2} k_{U2} [\text{H}_2] + k_{U3} [\text{B}_2\text{H}_6]}{k_{U2} [\text{H}_2] + k_{U3} [\text{B}_2\text{H}_6]} \quad (U4) \]

\[ \Delta E_a = \Delta H^\ddagger_{\text{overall}} + 1.5RT = 0.5\Delta H_{U1} + \Delta H^\ddagger_{U2} + 1.5RT \text{ when } k_{U3} [\text{B}_2\text{H}_6] \gg k_{U2} [\text{H}_2] \]

In the initial stage, \( k_{U3} [\text{B}_2\text{H}_6] \gg k_{U2} [\text{H}_2] \), the right-hand side simplifies to \( 2K_{U1}^{1/2} k_{U2} [\text{B}_2\text{H}_6]^{3/2} \). The calculated activation energies (420 K) at the G4 and W1BD levels of theory are 28.65 and 28.00 kcal/mol, respectively. When the partial pressure of H₂ becomes significant, the rate of the pyrolysis is predicted to decrease which is consistent with experimental observations. The overall pyrolysis rate constants.
\( k_{\text{overall}} = 2K_{U1}^{1/2}k_{U2} \) calculated by various methods (Table 3) are smaller than experiment by three orders of magnitude. Deuterium isotope effects of \( k_H/k_D \) have also been explored in Table 4. Our results are in the range of a recent experiment at 420 K, but disagree with Enrione et al.\textsuperscript{18b} at 361 K. Our calculated ratios are in satisfactory agreement with recent experimental results if experimental uncertainties are considered.\textsuperscript{17}

Table 3. Rate constants (cm\(^{3/2}\)molecule\(^{-1/2}\)s\(^{-1}\)) of pyrolysis of \( \text{B}_2\text{H}_6 \) at 420 K\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>( K_{U1}^c )</th>
<th>( k_{U2}^d )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CVT</td>
</tr>
<tr>
<td>W1BD</td>
<td>2.99E-14</td>
</tr>
<tr>
<td>G4</td>
<td>4.41E-14</td>
</tr>
<tr>
<td>M06L/MG3S</td>
<td>8.73E-15</td>
</tr>
<tr>
<td>MP2/cc-pVTZ</td>
<td>1.95E-14</td>
</tr>
<tr>
<td>Expt\textsuperscript{e}</td>
<td></td>
</tr>
</tbody>
</table>

a) \( k_{\text{overall}} = 2K_{U1}^{1/2}k_{U2} \).

b) The rate constant, \( k_{U2} \), is computed with the VTST-ISPE method. The geometries at the reaction path were calculated at B3LYP/6-31G(2df,p) level. The higher-level electronic structure calculations at the W1BD level were used to correct the energies along the reaction path.

c) W1BD, G4, M06L/MG3S, and MP2/cc-pVTZ are the levels of theory used to calculate \( K_{U1} \).

d) CVT, TST/ZCT, CVT/ZCT, TST/SCT, and CVT/SCT are the methods used to correct the rate constants in eq U2 for tunneling effects (see Polyrate manual).

e) Ref 16.
Table 4. Ratio of rate constants ($k_H/k_D$) for the pyrolysis of $\text{B}_2\text{H}_6/\text{B}_2\text{D}_6$ at 420 K\textsuperscript{a,d}

<table>
<thead>
<tr>
<th></th>
<th>CVT</th>
<th>TST/ZCT</th>
<th>CVT/ZCT</th>
<th>TST/SCT</th>
<th>CVT/SCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1BD</td>
<td>2.25</td>
<td>1.54</td>
<td>1.83</td>
<td>1.60</td>
<td>3.75</td>
</tr>
<tr>
<td>G4</td>
<td>2.22</td>
<td>1.53</td>
<td>1.82</td>
<td>1.59</td>
<td>3.70</td>
</tr>
<tr>
<td>M06L/MG3S</td>
<td>2.34</td>
<td>1.61</td>
<td>1.93</td>
<td>1.68</td>
<td>3.90</td>
</tr>
<tr>
<td>MP2/cc-pVTZ</td>
<td>1.94</td>
<td>1.34</td>
<td>1.60</td>
<td>1.39</td>
<td>3.26</td>
</tr>
<tr>
<td>Exp</td>
<td></td>
<td></td>
<td></td>
<td>1.92-3.22e</td>
<td>(\approx 5)</td>
</tr>
</tbody>
</table>

\textsuperscript{a)} $k_{(\text{overall})} = 2K_{U1}^{1/2}k_{U2}$.

\textsuperscript{b)} The rate constant, $k_{U2}$, is computed with the VTST-ISPE method. The geometries at the reaction path were calculated at B3LYP/6-31G(2df,p) level. The higher-level electronic structure calculations at W1BD level were used to correct the energies along the reaction path.

\textsuperscript{c)} W1BD, G4, M06L/MG3S and MP2/cc-pVTZ are the levels of theory used to calculate $K_{U1}$.

\textsuperscript{d)} CVT, TST/ZCT, CVT/ZCT, TST/SCT, and CVT/SCT are the methods used to correct the rate constants in eq U2 for tunneling effects (see Polyrate manual).

\textsuperscript{e)} Ref 17.

\textsuperscript{f)} Ref 18b.

In the B path the steady-state approximation was employed along with the sum of reaction B1 and -B2 (gives $\text{B}_2\text{H}_6 \rightarrow 2 \text{BH}_3$) to derive a mechanistic rate law. The B path was proposed originally by Long \textit{et al.}\textsuperscript{20a} who made a careful analysis of previous experiment work.
\[2 \text{B}_2\text{H}_6 \rightleftharpoons \text{BH}_3 + \text{B}_3\text{H}_9(a) \quad k_{B1}, k_{-B1}, K_{B1} \quad \text{(B1)}\]

\[\text{BH}_3 + \text{B}_2\text{H}_6 \rightleftharpoons \text{B}_3\text{H}_9(a) \quad k_{B2}, k_{-B2}, K_{B2} \quad \text{(B2)}\]

\[\text{B}_3\text{H}_9(a) \rightarrow \text{B}_3\text{H}_7 + \text{H}_2 \quad k_{B3} \quad \text{(B3)}\]

\[\text{B}_2\text{H}_6 + \text{B}_3\text{H}_7 \rightarrow \text{B}_4\text{H}_{10} + \text{BH}_3 \quad k_{U3} \quad \text{(U3)}\]

Rate expression \[= \frac{d(\text{B}_2\text{H}_6)}{dt} = 2K_{B1}^{1/2}K_{B2}^{1/2}k_{B3}[\text{B}_2\text{H}_6]^{3/2} \quad \text{(B4)}\]

\[\Delta E_a = \Delta H^\ddagger_{\text{overall}} + 1.5RT = \Delta H_{B1} + \Delta H_{B2} + \Delta H^\ddagger_{B3} + 1.5RT\]

The calculated reaction activation energy is 28.65 kcal/mol, the same as the U path at 420 K at the same level of theory.

The rate of consumption of diborane can be accelerated through diborane scavenging reactions such as reaction U3. As the reaction proceeds, many additional reactive intermediates are formed which can also react with \text{B}_2\text{H}_6. Thus, additional reactions will deplete \text{B}_2\text{H}_6 in competition with the initial reactions and may have the overall effect of reducing the effective activation barrier and increasing the consumption rate of diborane.

2.4 Rate law deviation

2.4.A. U Path

\[\text{B}_2\text{H}_6 \rightleftharpoons 2 \text{BH}_3 \quad k_{U1}, k_{-U1}, K_{U1} \quad \text{(U1)}\]

\[\text{B}_2\text{H}_6 + \text{BH}_3 \rightleftharpoons \text{B}_3\text{H}_7 + \text{H}_2 \quad k_{U2}, k_{-U2}, K_{U2} \quad \text{(U2)}\]

- 44 -
\[ \text{B}_2\text{H}_6 + \text{B}_3\text{H}_7 \rightarrow \text{B}_4\text{H}_{10} + \text{BH}_3 \quad k_{U3} \]  

**Steady state approximation:**

\[ \frac{d(\text{B}_2\text{H}_6)}{dt} = -k_{U1}[\text{B}_2\text{H}_6] - k_{U2}[\text{B}_2\text{H}_6][\text{BH}_3] + k_{U2}[\text{B}_3\text{H}_7][\text{H}_2] - k_{U3}[\text{B}_2\text{H}_6][\text{B}_3\text{H}_7] + k_{U1}[\text{BH}_3] \]  

(a)

\[ \frac{d(\text{BH}_3)}{dt} = 2k_{U1}[\text{B}_2\text{H}_6] - k_{U2}[\text{B}_2\text{H}_6][\text{BH}_3] + k_{U2}[\text{B}_3\text{H}_7][\text{H}_2] + k_{U3}[\text{B}_2\text{H}_6][\text{B}_3\text{H}_7] - 2k_{U1}[\text{BH}_3]^2 = 0 \]  

(b)

\[ \frac{d(\text{B}_3\text{H}_7)}{dt} = k_{U2}[\text{B}_2\text{H}_6][\text{BH}_3] - k_{U2}[\text{B}_3\text{H}_7][\text{H}_2] - k_{U3}[\text{B}_2\text{H}_6][\text{B}_3\text{H}_7] = 0 \]  

(c)

Equation (b) + (c),

\[ k_{U1}[\text{B}_2\text{H}_6] = k_{U1}[\text{BH}_3]^2, \quad [\text{BH}_3] = (K_{U1}[\text{B}_2\text{H}_6])^{1/2} \]  

(e)

Equation (a) + (c),

\[ \frac{d(\text{B}_2\text{H}_6)}{dt} = -2k_{U3}[\text{B}_2\text{H}_6][\text{B}_3\text{H}_7] \]  

(f)

from equation (c),

\[ [\text{B}_3\text{H}_7] = \frac{k_{U2}[\text{B}_2\text{H}_6][\text{BH}_3]}{k_{U2}[\text{H}_2] + k_{U3}[\text{B}_2\text{H}_6]} \]  

(g)

Therefore, rate expression = \[ -\frac{d(\text{B}_2\text{H}_6)}{dt} = 2k_{U1}[\text{B}_2\text{H}_6] \frac{K_{U1}^{1/2}k_{U2}[\text{B}_2\text{H}_6]^{1/2}}{k_{U2}[\text{H}_2] + k_{U3}[\text{B}_2\text{H}_6]} \]  

(h)

**2.4.B B Path**

\[ 2 \text{B}_2\text{H}_6 \underset{k_{B1}}{\overset{k_{B1}}{\rightleftharpoons}} \text{B}_3\text{H}_6(\text{a}) + \text{BH}_3 \quad k_{B1}, k_{B1}, K_{B1} \]  

(B1)

\[ \text{B}_2\text{H}_6 + \text{BH}_3 \underset{k_{B2}}{\overset{k_{B2}}{\rightleftharpoons}} \text{B}_3\text{H}_6(\text{a}) \quad k_{B2}, k_{B2}, K_{B2} \]  

(B2)

\[ \text{B}_3\text{H}_6(\text{a}) \rightarrow \text{B}_3\text{H}_7 + \text{H}_2 \quad k_{B3} \]  

(B3)
\[ \text{B}_2\text{H}_6 + \text{B}_3\text{H}_7 \rightarrow \text{B}_4\text{H}_{10} + \text{BH}_3 \]  \( k_{U3} \)  \( \text{(U3)} \)

**Steady state approximation:**

\[
\frac{d(\text{B}_2\text{H}_6)}{dt} = -2k_{B1}[\text{B}_2\text{H}_6]^2 + 2k_{B1}[\text{B}_3\text{H}_9(\text{a})][\text{BH}_3] - k_{B2}[\text{B}_2\text{H}_6][\text{BH}_3] + k_{B2}[\text{B}_3\text{H}_9(\text{a})] - k_{U3}[\text{B}_2\text{H}_6][\text{B}_3\text{H}_7]  \quad \text{(i)}
\]

\[
\frac{d(\text{BH}_3)}{dt} = k_{B1}[\text{B}_2\text{H}_6]^2 - k_{B1}[\text{B}_3\text{H}_9(\text{a})][\text{BH}_3] - k_{B2}[\text{B}_2\text{H}_6][\text{BH}_3] + k_{B2}[\text{B}_3\text{H}_9(\text{a})] + k_{U3}[\text{B}_2\text{H}_6][\text{B}_3\text{H}_7] = 0  \quad \text{(j)}
\]

\[
\frac{d(\text{B}_3\text{H}_7)}{dt} = k_{B3}[\text{B}_3\text{H}_9(\text{a})] - k_{U3}[\text{B}_3\text{H}_7][\text{B}_2\text{H}_6] = 0  \quad \text{(k)}
\]

Equation (h) ~ (i),

\[
\frac{d(\text{B}_2\text{H}_6)}{dt} = -3k_{B1}[\text{B}_2\text{H}_6]^2 + 3k_{B1}[\text{B}_3\text{H}_9(\text{a})][\text{BH}_3] - 2k_{U3}[\text{B}_2\text{H}_6][\text{B}_3\text{H}_7]  \quad \text{(l)}
\]

Since reaction (B1) and (B2) have been assumed to be in fast equilibrium,

\[ k_{B3} \ll k_{B2}, \; k_{U3} \ll k_{B2} \]

\[ k_{B1}[\text{B}_2\text{H}_6]^2 - k_{B1}[\text{B}_3\text{H}_9(\text{a})][\text{BH}_3] \approx 0  \quad \text{(m)}
\]

\[ [\text{B}_3\text{H}_9(\text{a})] - K_{B2}[\text{B}_2\text{H}_6][\text{BH}_3] \approx 0  \quad \text{(n)}
\]

From equation (m) and (n)

\[ [\text{BH}_3]^2 - K_{B1}K_{B2}^{-1}[\text{B}_2\text{H}_6] \approx 0  \quad \text{(o)}
\]

Therefore,

\[ -\frac{d(\text{B}_2\text{H}_6)}{dt} = 2k_{U3}[\text{B}_2\text{H}_6][\text{B}_3\text{H}_7] = 2k_{B3}[\text{B}_3\text{H}_9(\text{a})]  \quad \text{(r)}
\]

Put (n) and (m) into (r),

rate expression \[ = -\frac{d(\text{B}_2\text{H}_6)}{dt} = 2K_{B1}^{1/2}K_{B2}^{1/2}\text{B}_2\text{H}_6^{3/2} \quad \text{(s)}\]

**2.5 Conclusion**
The gas-phase kinetics of the initial stage of diborane pyrolysis has been probed at different levels of theory with variational transition state theory (VTST). The \( \text{B}_3\text{H}_9 \) isomer with \( C_{3v} \) symmetry does not play a role in the pyrolysis mechanism. Instead, a novel \( \text{B}_3\text{H}_9 \) butterfly structure with \( C_2 \) symmetry is on the free energy surface between \( \text{B}_2\text{H}_6 + \text{BH}_3 \) and \( \text{B}_3\text{H}_7 + \text{H}_2 \). The overall activation barrier is 28.65 kcal/mol at the G4 level. Two reaction variations have been proposed to elucidate the pyrolysis of diborane (U and B paths) which differ by the initial reaction step (unimolecular or bimolecular). Both variations reduce to the same rate law if the initial steps are assumed to be in fast equilibrium. Our long-term goal is to unravel the entire process to the formation of \( \text{B}_{10}\text{H}_{14} \).
2.6 References:


(58) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO Version 3.1*.


Chapter 3
Evaluating the Role of Triborane(7) as Catalyst in the Pyrolysis of Tetraborane(10)

3.1 Introduction

Pyrolyses of various boron hydrides have drawn much experimental attention.\textsuperscript{1-9} The complexity of the reactions makes unraveling aspects of their kinetics daunting. In a previous study of the initial stage of diborane pyrolysis, we showed that even the simplest boron hydride, B\textsubscript{2}H\textsubscript{6}, presented considerable challenges.\textsuperscript{10} As the second smallest stable boron hydride, B\textsubscript{4}H\textsubscript{10} [tetraborane(10)] also plays an important role in thermal reactions of boron hydrides thermal reactions.\textsuperscript{11} There is still doubt concerning the mechanism and even the initial order of the reaction.\textsuperscript{12-15}

Two reactions (1a) and (1b), both first order in B\textsubscript{4}H\textsubscript{10}, have been claimed to be the rate-limiting step in the initial stages of pyrolysis.\textsuperscript{16-23} Reaction 1a was

\begin{align*}
\text{B}_4\text{H}_{10} & \rightarrow \text{B}_4\text{H}_8 + \text{H}_2 & (1a) \\
\text{B}_4\text{H}_{10} & \rightarrow \text{B}_3\text{H}_7 + \text{BH}_3 & (1b)
\end{align*}

proposed as the rate-determining step from several experimental observations. First, the reaction between B\textsubscript{4}H\textsubscript{10} and ethylene yielded B\textsubscript{4}H\textsubscript{8}(C\textsubscript{2}H\textsubscript{4}) while the reaction between deuterated ethylene and B\textsubscript{4}H\textsubscript{10} yielded B\textsubscript{4}H\textsubscript{8}(C\textsubscript{2}D\textsubscript{4}).\textsuperscript{24-25} Next, B\textsubscript{4}H\textsubscript{8}D\textsubscript{2} was captured as the product of the reaction between B\textsubscript{4}H\textsubscript{8}CO and D\textsubscript{2}.\textsuperscript{16} Also, mass-spectrometric analysis supported B\textsubscript{4}H\textsubscript{8} but not BH\textsubscript{3} or B\textsubscript{3}H\textsubscript{7} as a reactive intermediate.\textsuperscript{19,20,22} Later publications
by Greenwood and co-workers\textsuperscript{4,5} were consistent with the proposal of reaction 1a as the rate-limiting step. However, Koski\textsuperscript{23} excluded reaction 1a based on their observation that D\textsubscript{2} did not exchange with B\textsubscript{4}H\textsubscript{10}, leading Greatrex \textit{et al.}\textsuperscript{4a,6} to suggest that the observation was a "worrying inconsistency in urgent need of reinvestigation". Nevertheless, Long\textsuperscript{14} partially followed the mechanism of B\textsubscript{4}H\textsubscript{10} pyrolysis suggested by Koski.

It is well established that the initial stage of B\textsubscript{4}H\textsubscript{10} pyrolysis is first order in the B\textsubscript{4}H\textsubscript{10} concentration in the temperature range 293 to 333 K\textsuperscript{4,5} with an observed activation energy of 23.7 kcal/mol. It is worth noting that Koski reported a 3/2 order dependence on the B\textsubscript{4}H\textsubscript{10} concentration with a very low activation energy of 16.2 kcal/mol (Table 1).\textsuperscript{23} Greenwood and co-workers\textsuperscript{6} found that added hydrogen inhibited B\textsubscript{4}H\textsubscript{10} pyrolysis while the reaction order and activation energy remained unchanged. The elimination of H\textsubscript{2} and BH\textsubscript{3} from B\textsubscript{4}H\textsubscript{10} was studied computationally by McKee\textsuperscript{26a}. At the estimated MP4/6-311G(d,p)//MP2/6-31G(d) level of theory with corrections to 400 K, the enthalpy of activation for loss of H\textsubscript{2} was 26.8 kcal/mol and for loss of BH\textsubscript{3} was estimated to be 39.0 kcal/mol. The former value was fortuitously close to the experimental value of 23.7 kcal/mol reported by Greenwood and co-workers for pyrolysis of B\textsubscript{4}H\textsubscript{10}\textsuperscript{4,5}.

Several theoretical studies have focused on different isomers of B\textsubscript{4}H\textsubscript{10} and B\textsubscript{4}H\textsubscript{8}\textsuperscript{26,27} For example, Ramakrishna and Duke\textsuperscript{27b} considered six isomers of B\textsubscript{4}H\textsubscript{10} and computed their interconversion pathways. Relative energies for various boron hydrides and several borane pyrolytic reactions associated with B\textsubscript{4}H\textsubscript{10} were also calculated.\textsuperscript{28} In this work, the pyrolysis mechanism of B\textsubscript{4}H\textsubscript{10} has been explored at the G4 level of theory.

Table 1. Reaction activation energy (kcal/mol) of pyrolysis of B\textsubscript{4}H\textsubscript{10}
<table>
<thead>
<tr>
<th>ΔEᵦ</th>
<th>Order</th>
<th>Temperature (K)</th>
<th>Year</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.2</td>
<td>1.5</td>
<td>313-333</td>
<td>1969</td>
<td>23</td>
</tr>
<tr>
<td>23.71±0.19</td>
<td>1.0</td>
<td>313-351</td>
<td>1984</td>
<td>4a</td>
</tr>
<tr>
<td>23.76±0.81</td>
<td>1.0</td>
<td>313-351</td>
<td>1986</td>
<td>4b</td>
</tr>
<tr>
<td>23.52±0.33ᵃ</td>
<td>1.0</td>
<td>313-351</td>
<td>1989</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Calculation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.8</td>
<td>1.0</td>
<td>400</td>
<td>1990</td>
<td></td>
</tr>
<tr>
<td>35.0(eq 1a)</td>
<td>1.0</td>
<td>333</td>
<td>2013</td>
<td>this work</td>
</tr>
<tr>
<td>21.2(eq 3)</td>
<td>1.0ᵇ</td>
<td>333</td>
<td>2013</td>
<td>this work</td>
</tr>
</tbody>
</table>

a) The activation energy was measured in the presence of added H₂.

b) The ratio of [B₃H₇]/[H₂] was assumed to be constant at 1.2 x 10⁻⁴.

### 3.2 Computational methods

All the standard calculations were carried out with the Gaussian 09 package. All boron hydrides were optimized and harmonic frequencies were calculated using B3LYP/6-31G(2df,p) which is part of the G4 composite method. The connection between the reactant and product through a specific transition structure was obtained through the intrinsic reaction coordinate (IRC) method.

The minimum energy path (MEP) for the barrierless dissociation of B₄H₁₀(b) to B₃H₇ and BH₃ was constructed by constrained optimization. The B-B distance was varied from 3.1 to 1.9 Å with a step size of 0.1 Å and all other variables were optimized via B3LYP/6-31G(2df,p). Single-point energy calculations along the reaction path were made at the G4 level of theory. The transition vector was projected out of the Hessian for points along the reaction path.

The zero-point corrections, heat capacity corrections, and entropies were computed to evaluate equilibrium constants using $K_p=\exp(-\Delta G^0/RT)$. Dual-level direct
dynamics method (VTST\textsuperscript{32,33}-ISPE\textsuperscript{34}) was employed to calculate the rate constant of $\text{B}_4\text{H}_{10} \rightarrow \text{B}_4\text{H}_8 + \text{H}_2$ where the lower level of theory was B3LYP/6-31G(2df,p) and the higher level of theory (used for reactant, transition structure, and products) was G4 theory.

3.3 Results and Discussion

3.3.A. Unimolecular $\text{B}_4\text{H}_{10}$ Reactions

The elimination of $\text{H}_2$ from $\text{B}_4\text{H}_{10}$ was thoroughly studied at the G4 level (Figure 1) where good agreement was found with a previous study\textsuperscript{26} of the same reaction ($\text{B}_4\text{H}_{10}(a) \rightarrow \text{TS(ad)} \rightarrow \text{B}_4\text{H}_8 + \text{H}_2$) at the approximate MP2/6-31G(d) level. The transition structure is very late as judged by the short H-H distance in TS(ad) (0.7574 Å). The activation barrier for loss of $\text{H}_2$ using G4 theory at 0 K (33.8 kcal/mol) is 7.0 higher than the value reported previously (400 K) and 10 kcal/mol larger than the experiment value reported by Greenwood and co-workers\textsuperscript{4,5} at 333 K. The large difference between theory and experiment may indicate that eq 1a is not the rate-determining step in $\text{B}_4\text{H}_{10}$ pyrolysis as has been previously assumed.

To further verify the accuracy of the G4 level, other levels of theory were used to determine the activation barrier including the highest level used in this study, W1BD. As can be seen in Table 2, the G4 and W1BD levels agree to within 1 kcal/mol.

In $\text{B}_4\text{H}_{10}$, loss of BH$_3$ is preceded by the isomerization to a higher-energy isomer $\text{B}_4\text{H}_{10}(b)$ which is less stable than $\text{B}_4\text{H}_{10}(a)$ by 10.5 kcal/mol and separated by a 27.9 kcal/mol transition structure (TS(ab)). The values from a previous study at the estimated MP4/6-311+G(d,p)+ZPC level were 10.4 and 26.9 kcal/mol, respectively.\textsuperscript{26a} Duke et
calculated 13.0 and 22.5 kcal/mol at the MP2/6-31G(d,p), respectively. The loss of BH$_3$ from B$_4$H$_{10}$(b) is endothermic by 28.2 kcal/mol at 0 K with no reverse activation barrier.

Table 2 Comparison of calculated energy barriers (kcal/mol) at 333 K

<table>
<thead>
<tr>
<th>Level of theory</th>
<th>B$<em>4$H$</em>{10}$ → B$_4$H$_8$+H$_2$</th>
<th>B$<em>4$H$</em>{10}$ → B$_3$H$_7$+BH$_3$ $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔH$^\ddagger$</td>
<td>ΔG$^\ddagger$</td>
</tr>
<tr>
<td>TST/VTST</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W1BD</td>
<td>34.3</td>
<td>33.0</td>
</tr>
<tr>
<td>G4</td>
<td>34.3</td>
<td>33.1</td>
</tr>
<tr>
<td>MP2/aug-cc-pVTZ</td>
<td>35.7</td>
<td>34.2</td>
</tr>
<tr>
<td>B3LYP/6-31G(2df,p)</td>
<td>32.3</td>
<td>31.0</td>
</tr>
<tr>
<td>MP4/6-311G(d,p)$^a$</td>
<td>26.8</td>
<td></td>
</tr>
<tr>
<td>VTST-ISPE$^c$</td>
<td>32.4</td>
<td>31.4</td>
</tr>
</tbody>
</table>

a) Estimated at 400 K, also see Ref 26a.

b) The reaction path at G4 level of theory is shown in Figure 5. For W1BD reaction path, the G4 geometry at each point was re-optimized at the W1BD level of theory. Vibrational frequencies along the reaction path were calculated after projecting out the reaction coordinate.

c) Dual-level direct dynamics (VTST-ISPE) is used where B3LYP/6-31G(2df,p) is the low-level and G4 is the high-level. The ΔH$^\ddagger$ and ΔG$^\ddagger$ values were obtained from the activation energy and rate constant at 333 K from the VTST-ISPE results.
Figure 1. Enthalpy (kcal/mol) path at 0 K for the reaction of $\text{B}_4\text{H}_{10}$ → $\text{B}_3\text{H}_7 + \text{BH}_3$ and $\text{B}_4\text{H}_{10} \rightarrow \text{B}_4\text{H}_8 + \text{H}_2$. Enthalpy of $\text{B}_4\text{H}_{10}(a)$ is taken as zero.

$\text{B}_4\text{H}_{10} + \text{BH}_3$: The schematic enthalpy (0 K) diagram of the $\text{B}_4\text{H}_{10} + \text{BH}_3$ reaction (Figure 2) is initiated with the barrierless association to form a $\text{B}_4\text{H}_{10}$-$\text{BH}_3$ complex ($\text{B}_5\text{H}_{13}(e)$). The complex can then either surmount an 8.0 kcal/mol barrier to form $\text{B}_3\text{H}_7(c)$ plus diborane through transition structure TS(ef) ($\Delta H^\ddagger=8.0$ kcal/mol) or eliminate $\text{H}_2$ to form $\text{B}_4\text{H}_{11}(g)$ through transition structure TS(eg) ($\Delta H^\ddagger=12.7 (9.7+3.0)$ kcal/mol). Structure $\text{B}_3\text{H}_{11}(g)$ is a newly reported isomer of $\text{B}_3\text{H}_{11}$ with a BH$_2$ group replacing a terminal hydrogen of $\text{B}_4\text{H}_{10}$. The barrier from $\text{B}_3\text{H}_{11}(g)$ to
Figure 2. Enthalpy (kcal/mol) path at 0 K for the reaction of B₄H₁₀(a) + BH₃ → B₃H₇(c) + B₂H₆ and B₄H₁₀(a) + BH₃ → B₃H₁₁(i) + H₂. Enthalpies of B₄H₁₀(a) + BH₃ are taken as zero. The hydrogen in circle represents that the formed hydrogen does not involve in the following reactions.

B₃H₁₁(h) and finally to the experimentally observed B₃H₁₁(i) is low due to the empty orbital on the terminal BH₂ group. The path to B₂H₆ + B₃H₇(c) should dominate over the path to B₃H₁₁(g) since the barrier is 4.7 kcal/mol smaller at 0 K which rules out BH₃ as a catalyst in the reaction B₄H₁₀ + BH₃ → H₂ + B₃H₁₁ → B₄H₈ + BH₃.

B₄H₁₀ + B₃H₇: B₄H₁₀(a) + B₃H₇(c) will barrierlessly associate to B₄H₁₀-B₃H₇ (B₇H₁₇(j))
which can further form B\textsubscript{7}H\textsubscript{17}(k) through transition structure TS(jk) (\(\Delta H^\ddagger=8.9 \text{ kcal/mol}\), Figure 3). B\textsubscript{7}H\textsubscript{17}(k) can be viewed as a coupled-cage of B\textsubscript{3}H\textsubscript{9} and B\textsubscript{4}H\textsubscript{10}(a) with a B-B single bond which can release B\textsubscript{2}H\textsubscript{6} through a 19.8 kcal/mol barrier via TS(kg) or release H\textsubscript{2} to form B\textsubscript{7}H\textsubscript{15}(l) via transition structure TS(kl) with an activation barrier of 9.6 kcal/mol. B\textsubscript{7}H\textsubscript{15}(l) can rearrange through three intermediates, B\textsubscript{7}H\textsubscript{15}(m), B\textsubscript{7}H\textsubscript{15}(n), B\textsubscript{7}H\textsubscript{15}(o) to form B\textsubscript{4}H\textsubscript{8}(d) plus B\textsubscript{3}H\textsubscript{7}(c). The overall reaction is B\textsubscript{4}H\textsubscript{10}(a) + B\textsubscript{3}H\textsubscript{7}(c) \rightarrow B\textsubscript{4}H\textsubscript{8}(d) + H\textsubscript{2} + B\textsubscript{3}H\textsubscript{7}(c) which shows that B\textsubscript{3}H\textsubscript{7} can catalyze the elimination of H\textsubscript{2} from B\textsubscript{4}H\textsubscript{10}.

\textbf{B\textsubscript{4}H\textsubscript{10} + B\textsubscript{4}H\textsubscript{8}}: The PES diagram with zero-point energy corrections of B\textsubscript{4}H\textsubscript{10}(a) + B\textsubscript{4}H\textsubscript{8}(d) is shown in Figure 4. The first intermediate formed is a C\textsubscript{2}-symmetry B\textsubscript{8}H\textsubscript{18}(p) species which is a coupled-cage of two B\textsubscript{4}H\textsubscript{10} boron hydrides (with two terminal hydrogen atoms removed). The transition structure TS(pq) which connects B\textsubscript{8}H\textsubscript{18}(p) and B\textsubscript{8}H\textsubscript{18}(q) is analogous to the B\textsubscript{4}H\textsubscript{10}(a) \rightarrow TS(ab) \rightarrow B\textsubscript{4}H\textsubscript{10}(b) step in Figure 1 with corresponding activation barriers of 26.9 and 27.9 kcal/mol, respectively; intermediate B\textsubscript{8}H\textsubscript{18}(q) has a pentacoordinated boron center. B\textsubscript{8}H\textsubscript{18}(q) can form B\textsubscript{5}H\textsubscript{11}(g) + B\textsubscript{3}H\textsubscript{7}(c) without a reverse activation barrier. The conversion of B\textsubscript{5}H\textsubscript{11}(g) to B\textsubscript{3}H\textsubscript{11}(i) was discussed above.

B\textsubscript{8}H\textsubscript{18}(p) can also release hydrogen to form B\textsubscript{8}H\textsubscript{16}(r) through transition structure TS(pr) which is analogous to B\textsubscript{4}H\textsubscript{10}(a) \rightarrow TS(ad) \rightarrow B\textsubscript{4}H\textsubscript{8}(d) + H\textsubscript{2} in Figure 1 with corresponding activation barriers of 32.8 and 33.8 kcal/mol, respectively. From B\textsubscript{8}H\textsubscript{16}(r), the reaction proceeds through B\textsubscript{8}H\textsubscript{16}(s) and then to two B\textsubscript{4}H\textsubscript{8}(d). The overall reactions
form either $B_3H_7(c)$ plus $B_3H_{11}(i)$ or two $B_4H_8(d)$ plus $H_2$. As noted below, the two paths have very similar activation barriers with a slight edge in free energy to the reaction forming $B_3H_7(c)/B_3H_{11}(i)$.

3.3.B. TST versus VTST
It has been assumed that the pyrolysis of B$_4$H$_{10}$ is initialized by the elimination of hydrogen since the reaction is known to be first order in B$_4$H$_{10}$ concentration. A counterexample is from a study by Bond and Pinsky who found that the reaction was 3/2 order in B$_4$H$_{10}$.\textsuperscript{15} However, the reliability of their experiment observations has been questioned by Greenwood.\textsuperscript{4} The free energy paths of B$_4$H$_{10}$(a) → B$_4$H$_8$(d) + H$_2$ and B$_4$H$_{10}$(a) → B$_4$H$_{10}$(b) are straightforward since they both have tight transition structures. However the dissociation of B$_4$H$_{10}$(b) to B$_3$H$_7$(c) + BH$_3$ is a barrierless reaction, which requires application of variational transition state theory (VTST). In this method, a series of structures along the reaction path were calculated and the free energies determined at each point. The maximum free energy along the path at temperature T determines the transition state, \textit{i.e.} the bottleneck. In the B$_4$H$_{10}$ → BH$_3$ + B$_3$H$_7$ reaction, the reaction path was constructed where the B-B distance was decreased in 0.1 Å steps from 3.1 to 1.9 Å, a range where all of the vibrational modes were positive after projecting out the transition vector (Figure 5). The free energy maximum is 6.6 kcal/mol higher than separated BH$_3$ and B$_3$H$_7$(c) (Figure 6). This result is also consistent with our previous study of the dissociation path of diborane, another barrierless reaction. At the G4 level, the free energy maximum on the dissociation path of diborane was 6.7 kcal/mol at 420 K larger than two separated BH$_3$ units.\textsuperscript{10}
Figure 4. Enthalpy (kcal/mol) path at 0 K for the reaction of B\(_4\)H\(_{10}\)(a) + B\(_4\)H\(_8\)(d) → B\(_5\)H\(_{11}\)(g) + B\(_3\)H\(_7\)(c) and B\(_4\)H\(_{10}\)(a) + B\(_4\)H\(_8\)(d) → B\(_4\)H\(_8\)(d) + H\(_2\) + B\(_4\)H\(_8\)(c).

Enthalpies of B\(_4\)H\(_{10}\)(a) + B\(_3\)H\(_7\)(c) are taken as zero. The hydrogen in circle represents that the formed hydrogen does not involve in the following reactions.

When 6.6 kcal/mol is added to the free energy of B\(_3\)H\(_7\)(c) + BH\(_3\), the activation free energy B\(_4\)H\(_{10}\)(a) → B\(_4\)H\(_8\)(d) + H\(_2\) is more favorable by 1.0 kcal/mol than B\(_4\)H\(_{10}\)(a) → B\(_3\)H\(_7\)(c) + BH\(_3\) at 333 K. The preference does not change at different temperatures as seen in Table 3.
From our above discussion, BH$_3$, B$_3$H$_7$(c) and B$_4$H$_8$(d) can all serve as scavenging species to accelerate the consumption of B$_4$H$_{10}$ (Table 4). The free
Figure 6. Comparison of free energy (kcal/mol) path at 333 K for the reaction of \( \text{B}_4\text{H}_{10}(a) \)

\[ \rightarrow \text{B}_3\text{H}_7(c) + \text{BH}_3 \]

Free energy of \( \text{B}_4\text{H}_{10}(a) \) is taken as zero.

energy barriers for the reaction of \( \text{B}_4\text{H}_{10} + \text{BH}_3 \) and \( \text{B}_4\text{H}_{10} + \text{B}_3\text{H}_7 \) are significantly smaller than that of \( \text{B}_4\text{H}_{10} + \text{B}_4\text{H}_8 \) (\( \Delta G^\ddagger = 14.8 \) and 19.7 compared to 33.2 kcal/mol at 333 K). Of the two unimolecular reactions of \( \text{B}_4\text{H}_{10} \), the elimination of \( \text{H}_2 \) is slightly favored over the elimination of \( \text{BH}_3 \). Another piece of evidence suggesting that generation of \( \text{BH}_3 \) is not important as the initial step is the fact that \( \text{B}_2\text{H}_6 \) is not formed in early stages of \( \text{B}_4\text{H}_{10} \) pyrolysis which would be expected from the dimerization of \( \text{BH}_3 \). Also, the
formation of BH$_3$ should slow the consumption of B$_4$H$_{10}$ because B$_2$H$_6$ (formed from 2BH$_3$ without activation barrier) can react further with B$_3$H$_7$(c) to form BH$_3$ plus B$_4$H$_{10}$. Greenwood et al.$^4$ also suggested elimination of H$_2$ as the initial step from a similar analysis of the experimental data.

Table 3. Comparison of calculated free energy barriers (kcal/mol) at different temperatures at the G4 level of theory

<table>
<thead>
<tr>
<th>Reaction</th>
<th>373K</th>
<th>333K</th>
<th>313K</th>
<th>293K</th>
</tr>
</thead>
<tbody>
<tr>
<td>B$<em>4$H$</em>{10}$→B$_4$H$_8$+H$_2$</td>
<td>32.95</td>
<td>33.10</td>
<td>33.17</td>
<td>33.24</td>
</tr>
<tr>
<td>B$<em>4$H$</em>{10}$→B$_3$H$_7$+BH$_3$</td>
<td>34.02</td>
<td>34.12</td>
<td>34.36</td>
<td>35.02</td>
</tr>
</tbody>
</table>

Table 4. Calculated reaction activation enthalpies, reaction activation free energies, reaction heats and reaction free energies (kcal/mol) at 333 K with G4 level of theory

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH$^a$</th>
<th>ΔG$^a$</th>
<th>ΔH</th>
<th>ΔG</th>
</tr>
</thead>
<tbody>
<tr>
<td>B$<em>4$H$</em>{10}$→B$_3$H$_7$+BH$_3$</td>
<td>38.2</td>
<td>34.1</td>
<td>40.7</td>
<td>27.5</td>
</tr>
<tr>
<td>B$<em>4$H$</em>{10}$→B$_4$H$_8$+H$_2$</td>
<td>34.3</td>
<td>33.1</td>
<td>17.7</td>
<td>7.7</td>
</tr>
<tr>
<td>B$<em>4$H$</em>{10}$+BH$_3$→B$_2$H$_6$+B$_3$H$_7$</td>
<td>4.0</td>
<td>14.8</td>
<td>1.4</td>
<td>-0.2</td>
</tr>
<tr>
<td>B$<em>4$H$</em>{10}$+BH$_3$→B$<em>3$H$</em>{11}$+H$_2$</td>
<td>8.5</td>
<td>19.9</td>
<td>-15.6</td>
<td>-12.9</td>
</tr>
<tr>
<td>B$<em>4$H$</em>{10}$+B$_3$H$_7$→B$_4$H$_8$+H$_2$+B$_3$H$_7$</td>
<td>17.7</td>
<td>19.2</td>
<td>17.7</td>
<td>7.7</td>
</tr>
<tr>
<td>B$<em>4$H$</em>{10}$+B$_4$H$_8$→B$_3$H$_7$+B$<em>3$H$</em>{11}$</td>
<td>28.8</td>
<td>33.2</td>
<td>28.8</td>
<td>26.6</td>
</tr>
<tr>
<td>B$<em>4$H$</em>{10}$+B$_4$H$_8$→B$_4$H$_8$+B$_4$H$_8$+H$_2$</td>
<td>22.7</td>
<td>34.7</td>
<td>17.7</td>
<td>7.7</td>
</tr>
</tbody>
</table>

a) Values for the overall reaction. For example, B$_4$H$_{10}$→BH$_3$+B$_3$H$_7$ represents B$_4$H$_{10}$(a) forming the final products BH$_3$ and B$_3$H$_7$(c).

b) The free energy maximum of B$_4$H$_{10}$→BH$_3$+B$_3$H$_7$ is 6.6 kcal/mol higher than the separated BH$_3$ and B$_3$H$_7$. Thus, 6.6 kcal/mol was added to the ΔG of B$_3$H$_7$ + B$_3$H$_{11}$ to estimate the free energy maximum of B$_4$H$_{10}$+B$_4$H$_8$→B$_3$H$_7$+B$_3$H$_{11}$. Also see details in text.
3.3.C. Role of B$_3$H$_7$ and B$_4$H$_8$ as catalyst

To explore B$_3$H$_7$ as a catalyst in more detail, enthalpies (0 K and 333 K) and free energies (333 K) are given in Figure 7 for reactants, intermediates, transition structures, and products in the B$_4$H$_{10}$(a) + B$_3$H$_7$(c) → B$_4$H$_8$(d) + H$_2$ + B$_3$H$_7$(c) reaction as well as for the direct reaction B$_4$H$_{10}$(a) → B$_4$H$_8$(d) + H$_2$. The activation barrier decreases significantly for the catalyzed reaction compared to the uncatalyzed one (ΔH$^\ddagger$=17.7 to 34.3 kcal/mol at 333 K). The reaction path for the catalyzed reaction has six intermediates and can be divided into three stages (Figure 7): formation of B$_7$H$_{17}$, elimination of H$_2$, and decomposition of B$_7$H$_{15}$ into B$_3$H$_7$ + B$_4$H$_8$. A coupled-cage is formed between B$_3$H$_7$ and B$_4$H$_{10}$ in the first step to (B$_7$H$_{17}$(k)). In the second stage, H$_2$ is lost from the B$_3$H$_7$ portion of the coupled-cage. The activation barrier for loss of H$_2$ (B$_7$H$_{17}$(kl)) is very similar to the barrier for loss of H$_2$ from B$_3$H$_9$-C$_3$v (ΔH$^\ddagger$=10.2 to 11.7 kcal/mol at 333 K). In the third stage, the coupled-cage B$_7$H$_{15}$(m) undergoes a hydrogen atom transfer to generate B$_3$H$_{15}$(o) which decomposes to B$_3$H$_7$(c) plus B$_4$H$_8$(d).

The B$_4$H$_8$ intermediate can also act as a catalyst as shown in Figure 8 by the reactions B$_4$H$_{10}$(a) + B$_4$H$_8$(d) → B$_4$H$_8$(d) + B$_4$H$_8$(d) + H$_2$ and B$_4$H$_{10}$(a) → B$_4$H$_8$(d) + H$_2$ (enthalpies at 0 K and 333 K and free energies at 333 K). Similar to B$_3$H$_7$, B$_4$H$_8$ lowers the activation barrier for loss of H$_2$ from B$_4$H$_{10}$ relative to the uncatalyzed reaction (ΔH$^\ddagger$=22.7 vs 34.3 kcal/mol at 333 K). However, the effect of entropy cancels the advantage and the catalyzed reaction actually has a larger free energy of
Figure 7. Comparison of activation enthalpy (kcal/mol) path at 0 K for the reaction of \( \text{B}_4\text{H}_{10}(a) \rightarrow \text{B}_4\text{H}_8(d) + \text{H}_2 \) and \( \text{B}_4\text{H}_{10}(a) + \text{B}_3\text{H}_7(c) \rightarrow \text{B}_3\text{H}_7(c) + \text{B}_4\text{H}_8(d) + \text{H}_2 \). Enthalpies and free energy of \( \text{B}_4\text{H}_{10}(a) \) are taken as zero. Enthalpies and free energy of \( \text{B}_4\text{H}_{10}(a) + \text{B}_3\text{H}_7(c) \) are taken as zero. All the numbers on the path are calibrated to the relative zero point and their format is as following:

Enthalpy (0 K)/Enthalpy (333 K) and the number in the square bracket is free energy at 333 K. The entire reaction can be divided into three stages: formation of \( \text{B}_3\text{H}_{17} \), elimination of \( \text{H}_2 \), and decomposition of \( \text{B}_3\text{H}_{15} \) into \( \text{B}_3\text{H}_7 + \text{B}_4\text{H}_8 \). All the geometries of transition structures and stationary points in the curves can be found in Figure 3.
Figure 8. Comparison of activation enthalpy (kcal/mol) path at 0 K Enthalpies and free energy of $\text{B}_4\text{H}_{10}(a)$ are taken as zero. Enthalpies and free energy of $\text{B}_4\text{H}_{10}(a) + \text{B}_4\text{H}_8(d)$ are taken as zero. All the numbers on the path are calibrated to the relative zero point and their format is as following: Enthalpy (0 K)/Enthalpy (333 k) and the number in the square bracket is free energy at 333 K. The entire reaction can be divided into three stages: formation of $\text{B}_8\text{H}_{18}$, elimination of $\text{H}_2$, and decomposition of $\text{B}_8\text{H}_{16}$ into $\text{B}_4\text{H}_8 + \text{B}_4\text{H}_8$. In the range of $\text{B}_8\text{H}_{16} \rightarrow \text{B}_4\text{H}_8(d) + \text{B}_4\text{H}_8(d)$, the energy properties of $\text{H}_2$ are also added to the path. All the geometries of transition structures and stationary points in the curves can be found in Figure 4. Activation at 333 K compared to the uncatalyzed reaction ($\Delta G^{\ddagger} = 34.7$ to 33.1 kcal/mol at 333 K). The mechanism is similar to the $\text{B}_3\text{H}_7 + \text{B}_4\text{H}_{10}$ reaction. A $C_2$-symmetry
coupled-cage between two \( \text{B}_4\text{H}_6 \) fragments is formed (\( \text{B}_8\text{H}_{18}(p) \)) which loses \( \text{H}_2 \) from one side. The resulting coupled-cage between \( \text{B}_4\text{H}_7 \) and \( \text{B}_4\text{H}_9 \) (\( \text{B}_8\text{H}_{16}(r) \)) migrates a hydrogen atom (from the \( \text{B}_4\text{H}_9 \) side to the \( \text{B}_4\text{H}_7 \) side) and fragments to two \( \text{B}_4\text{H}_8(d) \) species.

3.3. D. Pyrolysis Mechanism

Several mechanisms of the initial stage of \( \text{B}_4\text{H}_{10} \) pyrolysis have been proposed.\(^3,^4\)

One typical example\(^4\) is eq 1a,c:

\[
\begin{align*}
\text{B}_4\text{H}_{10} & \rightarrow \text{B}_4\text{H}_8 + \text{H}_2 & (1a) \\
\text{B}_4\text{H}_{10} + \text{B}_4\text{H}_8 & \rightarrow \text{B}_3\text{H}_7 + \text{B}_5\text{H}_{11} & (1c)
\end{align*}
\]

where eq 1a is the rate-limiting step. The reactions that may be involved in the pyrolysis are presented as following:

\[
\begin{align*}
\text{B}_4\text{H}_{10} & \rightarrow \text{B}_4\text{H}_8 + \text{H}_2 & (1a) \\
\text{B}_4\text{H}_{10}(a) & \rightarrow \text{B}_4\text{H}_{10}(b) & (2b) \\
\text{B}_4\text{H}_{10}(b) & \rightarrow \text{B}_3\text{H}_7 + \text{BH}_3 & (2c) \\
\text{B}_4\text{H}_{10} + \text{BH}_3 & \rightarrow \text{B}_2\text{H}_6 + \text{B}_3\text{H}_7 & (2d) \\
\text{B}_4\text{H}_{10} + \text{B}_3\text{H}_7 & \rightarrow \text{B}_3\text{H}_7 + \text{B}_4\text{H}_8 & (2e) \\
\text{B}_3\text{H}_7 & \rightarrow \text{B}_3\text{H}_7 + \text{B}_3\text{H}_7 & (2f) \\
\text{B}_3\text{H}_7 & \rightarrow \text{B}_3\text{H}_7 + \text{B}_4\text{H}_8 & (2g) \\
\text{B}_4\text{H}_{10} + \text{B}_4\text{H}_8 & \rightarrow \text{B}_3\text{H}_7 + \text{B}_3\text{H}_{11} & (1c) \\
\text{B}_4\text{H}_{10} + \text{B}_4\text{H}_8 & \rightarrow \text{B}_4\text{H}_8 + \text{B}_4\text{H}_8 + \text{H}_2 & (2h) \\
\text{B}_3\text{H}_7 + \text{B}_3\text{H}_7 & \rightarrow \text{Solid} + m\text{H}_2 & (2i)
\end{align*}
\]

From our previous discussion, eq 2b-2d are not important.
The reaction mechanism can be summarized in Figure 9. Briefly, \( \text{B}_4\text{H}_{10} \) eliminates hydrogen, then \( \text{B}_4\text{H}_8 \) reacts with \( \text{B}_4\text{H}_{10} \) to produce \( \text{B}_3\text{H}_{11} \) and \( \text{B}_3\text{H}_7 \). \( \text{B}_3\text{H}_7 \) can then catalyze elimination of \( \text{H}_2 \) from \( \text{B}_4\text{H}_{10} \) which forms more \( \text{B}_4\text{H}_8 \) and generates more \( \text{B}_3\text{H}_7 \) which will accumulate and polymerize to a solid.

We propose the following mechanism:

**Initiation:** \[ \text{B}_4\text{H}_{10} \rightarrow \text{B}_4\text{H}_8 + \text{H}_2 \quad k_0 \quad (1a) \]

**Propagation:**
\[
\begin{align*}
\text{B}_4\text{H}_{10} + \text{B}_3\text{H}_7 & \rightarrow \text{B}_7\text{H}_{17} \quad k_1, k_1, K_1 \\
\text{B}_7\text{H}_{17} & \rightarrow \text{B}_7\text{H}_{15} + \text{H}_2 \quad k_2, k_2, K_2 \\
\text{B}_7\text{H}_{15} & \rightarrow \text{B}_4\text{H}_8 + \text{B}_3\text{H}_7 \quad k_3 \\
\text{B}_4\text{H}_{10} + \text{B}_4\text{H}_8 & \rightarrow \text{B}_3\text{H}_7 + \text{B}_5\text{H}_{11} \quad k_4 \quad (1c) \\
\end{align*}
\]

**Termination:** \[ \text{B}_3\text{H}_7 + \text{B}_3\text{H}_7 \rightarrow \text{Solid} + m\text{H}_2 \quad (2i) \]

where the overall reaction is \( 2\text{B}_4\text{H}_{10} \rightarrow \text{B}_5\text{H}_{11} + \text{H}_2 + \text{B}_3\text{H}_7 \) in propagation stage and

\[ 2\text{B}_4\text{H}_{10} \rightarrow \text{B}_5\text{H}_{11} + (1+m)\text{H}_2 \]

in propagation plus termination stages.

It is worthwhile to discuss how the experimental data were collected. The species (\( \text{B}_4\text{H}_{10}, \text{B}_3\text{H}_{11}, \text{H}_2 \)) in the gas mixture were collected after a particular time interval of at least 60s after the reaction started. Even at the very first experimental point, both \( \text{H}_2 \) and \( \text{B}_3\text{H}_{11} \) were already produced. Thus, the experimental rate measurements may take place after the incubation period where the catalytic boron hydride \( \text{B}_3\text{H}_7 \) is formed. In our mechanism, the experimentally collected data should be associated with the second stage (Propagation) in the Figure 9. The
steady-state approximation is used to deduce the rate law (see section 3.4.A).

\[
\frac{d[B_4H_{10}]}{dt} = -2k_3K_1K_2[B_4H_{10}][B_3H_7]/[H_2] \quad (3)
\]

The mechanism in which reaction (1a) serves as the rate limiting step is inappropriate because the calculated activation barrier is about 10 kcal/mol higher than the experimental value (Table 1). For our mechanism to be consistent with the observed first order dependence on \(B_4H_{10}\) concentration, the ratio of \([B_3H_7]/[H_2]\) should be approximately constant. This ratio also can be estimated comparing the calculated rate constants to the experimentally observed ones. The experiment and calculated rates
agree if the ratio is $1.2 \times 10^4$ at 333 K (also see 3.4 B and 3.4.C) which is reasonable since $\text{B}_3\text{H}_7$ is a reactive intermediate. From the rate law in eq 3, the theoretically calculated activation energy of the $\text{B}_4\text{H}_{10}$ pyrolysis is 21.2 kcal/mol (3.4 S-4). One issue with our mechanism is that one hydrogen is produced for each $\text{B}_5\text{H}_{11}$ while the experimental ratio is approximately two. It is likely that the surplus hydrogen comes from the polymerization of $\text{B}_3\text{H}_7$ and $\text{B}_4\text{H}_8$ to a solid as well as from the reaction of $\text{B}_4\text{H}_{10}(a) + \text{B}_4\text{H}_8(d) \rightarrow \text{B}_4\text{H}_6(d) + \text{B}_4\text{H}_8(d) + \text{H}_2$. As the reaction proceeds, the reactive intermediates $\text{BH}_3$, $\text{B}_3\text{H}_7$ and $\text{B}_4\text{H}_8$ will react to form higher boron hydrides up to $\text{B}_{10}\text{H}_{14}$ (and release additional $\text{H}_2$).

### 3.4 Rate law deviation

#### 3.4.A

\[
\begin{align*}
\text{B}_4\text{H}_{10} + \text{B}_3\text{H}_7 & \rightleftharpoons \text{B}_7\text{H}_{17} & k_1, k_1, K_1 \quad (2e) \\
\text{B}_7\text{H}_{17} & \rightarrow \text{B}_7\text{H}_{15} + \text{H}_2 & k_2, k_2, K_2 \quad (2f) \\
\text{B}_7\text{H}_{15} & \rightarrow \text{B}_4\text{H}_8 + \text{B}_3\text{H}_7 & k_3 \quad (2g) \\
\text{B}_4\text{H}_{10} + \text{B}_4\text{H}_8 & \rightarrow \text{B}_3\text{H}_7 + \text{B}_5\text{H}_{11} & k_4 \quad (1c)
\end{align*}
\]

\[
\begin{align*}
\frac{d(\text{B}_4\text{H}_{10})}{dt} &= -k_1[\text{B}_4\text{H}_{10}][\text{B}_3\text{H}_7]+k_1[\text{B}_7\text{H}_{17}]-k_4[\text{B}_4\text{H}_{10}][\text{B}_4\text{H}_8] \quad (\text{SA-1}) \\
\frac{d(\text{B}_4\text{H}_8)}{dt} &= k_3[\text{B}_7\text{H}_{15}]-k_4[\text{B}_4\text{H}_{10}][\text{B}_4\text{H}_8] = 0 \quad (\text{SA-2}) \\
\frac{d(\text{B}_7\text{H}_{17})}{dt} &= k_1[\text{B}_4\text{H}_{10}][\text{B}_3\text{H}_7]-k_1[\text{B}_7\text{H}_{17}]-k_2[\text{B}_7\text{H}_{17}]+k_2[\text{B}_7\text{H}_{15}][\text{H}_2] = 0 \quad (\text{SA-3}) \\
\frac{d(\text{B}_7\text{H}_{15})}{dt} &= k_2[\text{B}_7\text{H}_{17}]-k_2[\text{B}_7\text{H}_{15}][\text{H}_2]-k_5[\text{B}_7\text{H}_{15}] = 0 \quad (\text{SA-4})
\end{align*}
\]

Insert (SA-2), (SA-3), and (SA-4) into (SA-1):
\[
\frac{d(B_4H_{10})}{dt} = -2k_3[B_7H_{15}] \quad (SA-5)
\]

From (SA-1), (SA-2) and (SA-3),

\[
[B_7H_{15}] = k_1k_2[B_4H_{10}][B_3H_7]/\{k_2[H_2] + k_3 + k_2k_3/k_1\} \quad (SA-6)
\]

\[k_2[H_2] >> k_3 + k_2k_3/k_1\]

Therefore, \[k_3[B_7H_{15}] - k_3K_1K_2[B_4H_{10}][B_3H_7]/[H_2]\] \quad (SA-7)

\[
\frac{d(B_4H_{10})}{dt} = -2k_3K_1K_2[B_4H_{10}][B_3H_7]/[H_2] \quad (SA-8)
\]

We assume that the ratio \([B_3H_7]/[H_2] \approx \text{constant}\)

**3.4.B. Plot for the pyrolysis of \(B_4H_{10}\).**

The experiment data from reference (4b) has been re-plotted according to the following equation:

\[
k = K(k_B T/h) \cdot \exp(\Delta S^\ddagger/R) \cdot \exp(-\Delta H^\ddagger/RT) \quad (SB-1)
\]

Thus, the experimentally observed activation free energy is 25.3 kcal/mol.

**3.4.C. Estimated ratio of \(B_3H_7\) to \(H_2\).** Transition state theory was applied (Equation S3-1).

\[
k = (k_B T/h) \exp(-\Delta G^\ddagger/RT) \quad (SC-1)
\]

\[
k_{\text{expt}} = k = -2k_3K_1K_2[B_4H_{10}][B_3H_7]/[H_2] \quad (SC-2)
\]

Therefore:

\[
\exp(-\Delta G^\ddagger_{\text{expt}}/RT) = 2 \exp(-\Delta G^\ddagger_3/RT) \cdot \exp(-\Delta G_1/RT) \cdot \exp(-\Delta G_2/RT)[B_3H_7]/[H_2] \quad (SC-3)
\]

\(\Delta G^\ddagger_{\text{expt}}\) is the experimentally observed activation free energy which is 25.3 kcal/mol.

\(\Delta G^\ddagger_3, \ \Delta G_1, \ \text{and } \Delta G_2\) are activation free energy of reaction (2g) and the reaction free energies of (2e) and (2f) the in S-1, respectively.
Insert $\Delta G_3^+ + \Delta G_1 + \Delta G_2$ at 333 K (19.2 kcal/mol) into equation (SC-3) to estimated the ratio of $B_3H_7$ to $H_2$ as $1.2 \times 10^4$.

3.4.D. To calculate the activation energy the Arrhenius equation and the estimated ratio of $B_3H_7$ to $H_2$ are used.

$$k_{\text{expt}} = -2k_3K_1K_2[B_3H_7]/[H_2] \quad (\text{SD-1})$$

According to the Arrhenius equation:

$$k = A \cdot \exp(-E_a/RT) \quad (\text{SD-2})$$

$$A_{\text{calc}} \cdot \exp(-E_{\text{calc}}/RT)$$

$$= 2A_3 \cdot \exp(-('\Delta H_{13}^r+\text{RT})/\text{RT}) \cdot A_1 \cdot \exp(\Delta H_1/\text{RT}) \cdot A_2 \cdot \exp(\Delta H_2/\text{RT}) [B_3H_7]/[H_2] \quad (\text{SD-3})$$

$$= 2A_3A_1A_2\exp(-('\Delta H_{13}^r + \text{RT} + \Delta H_1 + \Delta H_2)[B_3H_7]/[H_2]) \quad (\text{SD-4})$$

Insert $\Delta H_{13}^r + \text{RT} + \Delta H_1 + \Delta H_2$ at 333 K (14.6 kcal/mol),

$$[B_3H_7]/[H_2] = \exp(-6.6(\text{kcal/mol})/\text{RT})$$

Thus, $E_{\text{calc}} = 14.6 + 6.6 = 21.2$ kcal/mol

$\Delta H_{13}^r$, $\Delta H_1$, and $\Delta H_2$ is the activation enthalpy of reaction (2g) and the reaction enthalpies of (2e) and (2f) in S-1, respectively.

3.5 Conclusion: The gas-phase kinetics of the initial stages of $B_4H_{10}$ pyrolysis have been studied by accurate computational methods. Conventional transition state theory (TST) and variational transition state theory (VTST) have been employed to elucidate the reaction mechanism. The reaction $B_4H_{10} \rightarrow B_4H_8 + H_2$ can proceed with or without the
B₃H₇ catalysis with very different activation energies. The uncatalyzed reaction is considered as the initiation reaction. Thereafter, the hydrogen-releasing path will take place with B₃H₇ acting as a catalyst. As the reaction proceeds, hydrogen may be produced through the polymerization of intermediates. The overall activation energy is 21.2 kcal/mol which is about 2 kcal/mol smaller than the experimental values.
3.6 Reference:


