Theoretical Study on Dissociation Mechanisms of Di-ethyl Berylliums and Di-t-butyl Berylliums

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The potential energy surfaces (PES) of unimolecular dissociation reactions for di-ethyl beryllium and di-t-butyl beryllium are investigated by B3LYP, CCSD(T), and G3B3 approaches. Possible reaction pathways through either the radical or transition state (TS) of the molecules are considered. The geometries, vibrational frequencies and relative energies for various stationary points are determined. From the study of energetics, the TS pathways arising from concerted molecular eliminations are indicated to be the main dissociation pathways for both molecules. The PES differences of the dissociation reactions are investigated. The activation energies and rate constants will be helpful for investigating the predictive ability of the reaction in further theoretical and experimental research.

Key words: Di-t-butyl beryllium, Dissociation reaction, Transition state, Rate constant, G3B3 theory

I. INTRODUCTION

Metal hydrides are of great scientific and technological interest in view of their potential applications such as in hydrogen storage, fuel cells, and internal combustion engines [1, 2], as well as in inertial confinement fusion, e.g., beryllium hydride (BeH2) [3]. However, the syntheses and characterizations of the candidate systems for these metal hydrides are tedious, and thus hinder the ways to investigate these fascinating compounds. An alternative and complementary approach is to utilize quantum chemistry (QC) methods, it may help to orientate the synthesis process toward meaningful systems. The QC methods can provide reliable numerical estimation of properties of the candidate systems, improve the understanding of the phenomena happening in the synthesis, help the establishment of the relationships between the geometry structures and relevant properties of the species found in synthesis, and explore the microscopic interaction mechanism of the reactions during the synthesis process, etc. All of these can help to ameliorate the material synthesis process.

Di-t-butyl beryllium (BeC2(CH3)6) has attracted a lot of research interests in the past years since it was indicated to be an important type of materials for the synthesis of the BeH2. For example, the preparation of BeH2 may be done via the pyrolysis of the etherate or ether-free complex of this compound in the vapour phase, as well as the pyrolysis of the di-t-butyl beryllium-etherate complex dissolved in a high-boiling inert solvent [4–6]. Due to the importance of di-t-butyl beryllium, the investigations on molecular geometrical structures and vibrational properties of this compound have been conducted in experiments [7, 8]. However, the effort to probe relevant pyrolysis mechanism for this compound to form BeH2 at the atomistic and electronic levels seems to be not yet referred to date, and therefore, how to elucidate this issue comes to be important.

In this work, we report a detailed analysis on the unimolecule dissociation reactions of the di-t-butyl beryllium in vapor phases by means of QC first principles calculations. The attraction of the vapour phase unimolecular study lies in the opportunity not only to study the intrinsic nature of this molecule, but also to probe relevant properties in relatively complicated environment as a meaningful model. Although it has never been used in the preparation of BeH2 experimentally to the best of our knowledge, the di-ethyl beryllium (BeC2H4(CH3)2) compound is also studied in this work since it can be considered as an appropriate model system for comparison. It is interesting to analyze the differences in dissociation reactions between two compounds as a function of the alkyl groups. Due to the tractable number of electrons in the molecule, di-ethyl and di-t-butyl berylliums are indeed amenable to high level QC calculations, and therefore, may also serve as a testing arena for the QC

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II. METHODS

The full molecular geometries and harmonic vibrational frequencies of different species involved in the dissociation reactions of di-ethyl beryllium and di-t-butyl beryllium molecules, i.e., the reactants, products, intermediates, and transition states, were obtained using the non-local hybrid three-parameter B3LYP density functional approach [9–11]. This approach has been demonstrated to be a cost-effective method in the structural determinations for such molecular systems in previous studies [12–15]. Considering the efficiency and accuracy, the standard Wachters-Hay all-electron basis set 6-311++G(d,p) [16–18] was adopted. Harmonic vibrational frequency analyses were performed for the characterization of the stationary points, i.e., the number of imaginary frequencies (0 or 1) was used to verify the species whether a minimum or a transition state. Connections between the reactants, intermediates, transition states, and products were confirmed by the intrinsic reaction coordinate (IRC) [19–21] calculations. Thermodynamic corrections were obtained by assuming the species as an ideal gas, considering harmonic vibrational frequencies, and using the rigid rotor approximation by standard statistical methods [22] with associated scale factor [23].

To pinpoint the energies of different species, especially for the energies related with the barrier heights and reaction heats, which are the most sensitive parameters in all reaction calculations, the high level corrected CCSD(T) [24] single-point calculations were performed at the B3LYP optimized geometries with the 6-311++G(d,p) basis set. Moreover, the G3B3 theory [25] was also employed in this work since it was indicated that the reaction barriers obtained by the G3B3 theory can be in good agreement with the experiments without any further adjustments of the energies [26]. All the calculations described above were implemented with Gaussian 09 suite of programs [27].

III. RESULTS

A. Reactant conformations

Table 1 summarizes the main geometric structure parameters for the di-ethyl and di-t-butyl beryllium. As presented in Table I, the calculated results are in good agreement with the available experimental observations [7], which confirms that the present methodology of computations in structural determinations is reliable and accurate.

![Diagram](image_url)

**FIG. 1 Conformations of di-ethyl beryllium and di-t-butyl beryllium.**

TABLE I Bond lengths and bond angles of molecular di-t-butyl beryllium.

<table>
<thead>
<tr>
<th>Bond length/Å</th>
<th>Bond angle/(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>Exp. [17]</td>
</tr>
<tr>
<td>Be–C</td>
<td>1.703</td>
</tr>
<tr>
<td>C–C</td>
<td>1.547</td>
</tr>
<tr>
<td>H–C</td>
<td>1.097</td>
</tr>
</tbody>
</table>

Figure 1 shows the structures of the reactant BeC₂H₄(CH₃)₂ and BeC₂(CH₃)₆ molecules optimized at the B3LYP/6-311++G(d,p) level of theory. For the BeC₂H₄(CH₃)₂, our calculations identify two unique stable conformations, differ in the dihedral angles of C–C–C–C (53.7° and −141.9°), and are noted as the cis-BeC₂H₄(CH₃)₂ and trans-BeC₂H₄(CH₃)₂, respectively. Relative electronic energies of these two conformations are calculated to be within 0.04 kcal/mol in all the three methods, where the cis-BeC₂H₄(CH₃)₂ is slightly favorable in energy in the CCSD(T) and G3B3 approaches. The zero-point vibrational energies as well as the thermal corrections are found to be essentially the same for the cis- and trans-conformations. Thus, our calculations focus on the cis-BeC₂H₄(CH₃)₂, and the results of the trans-configuration are very analogous to those of the cis-species, which are just listed together without further discussion.

For the BeC₂(CH₃)₆, there is only one stable conformation located due to its high D₃h symmetry, in which the two side -C(CH₃)₃ groups are stagger about 54.3° or −65.7° in the dihedral angles of C–C. Table I summarizes the main geometric structure parameters for the di-t-butyl beryllium. As presented in Table I, the calculated results are in good agreement with the available experimental observations [7], which confirms that the present methodology of computations in structural determinations is reliable and accurate.
B. Dissociation pathways

As illustrated in Fig.1, for the cis-BeC₂H₄(CH₃)₂, within all the fourteen covalent bonds, only four of them are inequipotential when considering the symmetry of the molecule, i.e., C₂−C₃ (represents C₂−C₃ and C₉−C₁₀), C₂−Be (represents C₂−Be and C₁₀−Be), C₃−H₆ (represents C₃−H₆,7,8 and C₉−H₁₁,12,13), and C₂−H₇ (represents C₂−H₇,8 and C₁₀−H₁₄,15). Consequently, six distinct potential pathways have been considered for the dissociation reaction of the cis-BeC₂H₄(CH₃)₂ based on the four unique bonds. In which, four pathways proceed through direct bond ruptures to product radicals, and two through concerted eliminations to form transition states. They are organized into the two following procedures.

In procedure I, the following five reaction pathways are considered (here one CH₂CH₃ group is noted as a pseudo H⁺ atom for the convenience): the rupture of C₂−C₃ bond (path A, Eq.(1)), the rupture of C₂−Be bond (path B, Eq.(2)), the rupture of C₃−H₆ bond (path C, Eq.(3)), the rupture of C₂−H₇ bond (path D, Eq.(4)), H₆ approaches Be-concerted 2,3-elimination reaction (path E, Eq.(5)) as follows:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{Be}^-\text{H}^+ & \rightarrow \cdot\text{CH}_3 + \cdot\text{CH}_2\text{Be}^-\text{H}^+ \quad (1) \\
\text{CH}_3\text{CH}_2\text{Be}^-\text{H}^+ & \rightarrow \cdot\text{CH}_2\text{CH}_3 + \cdot\text{Be}^-\text{H}^+ \quad (2) \\
\text{CH}_3\text{CH}_2\text{Be}^-\text{H}^+ & \rightarrow \cdot\text{CH}_2\text{CH}_2 - \text{Be}^-\text{H}^+ + \cdot\text{H} \quad (3) \\
\text{CH}_3\text{CH}_2\text{Be}^-\text{H}^+ & \rightarrow \cdot\text{CH}_3\text{CH} - \text{Be}^-\text{H}^+ + \cdot\text{H} \quad (4) \\
\text{CH}_3\text{CH}_2\text{Be}^-\text{H}^+ & \rightarrow \text{TS}_1 \rightarrow \cdot\text{C}_2\text{H}_4 + \text{HBe}^-\text{H}^+ \quad (5)
\end{align*}
\]

Theoretically, there may be also a few other dissociation pathways in the following possible procedure depending on the products of procedure I. However, the A−D

FIG. 2 Structures of the transition states, intermediates, and products in paths of E and F.
pathways are highly energetically unfavorable compared to the E pathway (as indicated in the following text). Therefore, we do not consider the cases of pathways in procedure II, only the one reaction path F based on E is included in procedure II, that is path F as follows,

$$\text{CH}_3\text{−CH}_2\text{−Be}^\dagger \rightarrow \text{TS}2 \rightarrow \text{C}_2\text{H}_4 + \text{BeH}_2$$ (6)

Thus, only E and F have been counted into for the case of di-t-butyl beryllium BeC$_2$(CH$_3$)$_6$ due to the similar bonding nature of the two molecules.

Figure 2 shows the geometric structures for the transition states, intermediates, and products involved in the paths of E and F as optimized at the B3LYP/6-311++G(d,p) level. The stationary nature of the structures was confirmed by the harmonic vibrational frequency analyses, i.e., the reactants, products, and intermediate possess all real frequencies, whereas the transition states possess only one imaginary frequency. The G3B3 energy profiles of the potential energy surface for all considered dissociation reaction pathways are illustrated in Fig.3 and Fig.4 for the di-ethyl beryllium and di-t-butyl beryllium, respectively. Each of the reaction pathways is discussed, unless noted otherwise, the G3B3 energies are defaulted. More details for the results of the calculated energies at the B3LYP/6-311++G(d,p), CCSD(T)/6-311++G(d,p), and G3B3 levels, and the calculated enthalpies at the G3B3 level for all the involved species are summarized in Table II.

### C. Rate constants

According to the transition state theory (TST) in its kinetic thermodynamic accustomed version [28], the rate constant, $k(T)$, is determined by the following expression:

$$k(T) = \frac{k_B T}{h} \exp\left(\frac{S_a}{R}\right) \exp\left(-\frac{E_a}{RT}\right)$$ (7)

where $T$ is the reaction temperature, and $k_B$, $h$, and $R$ are the Boltzmann constant, Planck constant, and gas constant, respectively. The activation energy $E_a$ and activation entropy $S_a$ are derived from the enthalpy and entropy differences between the transition states and reactants, respectively. Figure 5 shows the calculated rate constants of path E and F for the cis-BeC$_2$H$_4$(CH$_3$)$_2$ and BeC$_2$(CH$_3$)$_6$ at different reference temperatures. The calculated rate constants exhibit a typical non-Arrhenius behavior with the entropy term dependent upon the temperature. They are fitted to the following

\[\text{TABLE II Relative energies $E_0$ and $H_{298}$ (in kcal/mol) of different species in dissociation reactions.}\]

<table>
<thead>
<tr>
<th>Species</th>
<th>$E_0$/kcal/mol</th>
<th>$H_{298}$/kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-BeC$_2$H$_4$(CH$_3$)$_2$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>trans-BeC$_2$H$_4$(CH$_3$)$_2$</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>TS1</td>
<td>32.15</td>
<td>34.72</td>
</tr>
<tr>
<td>IM1</td>
<td>26.98</td>
<td>26.20</td>
</tr>
<tr>
<td>TS3</td>
<td>32.06</td>
<td>34.53</td>
</tr>
<tr>
<td>IM3</td>
<td>27.38</td>
<td>25.55</td>
</tr>
<tr>
<td>P1+P2</td>
<td>55.00</td>
<td>59.41</td>
</tr>
<tr>
<td>TS2(+P2)</td>
<td>49.35</td>
<td>52.08</td>
</tr>
<tr>
<td>IM2(+P2)</td>
<td>52.50</td>
<td>56.13</td>
</tr>
<tr>
<td>P2+P3(+P2)</td>
<td>52.50</td>
<td>56.15</td>
</tr>
<tr>
<td>Path A</td>
<td>72.32</td>
<td>77.64</td>
</tr>
<tr>
<td>Path B</td>
<td>80.68</td>
<td>85.02</td>
</tr>
<tr>
<td>Path C</td>
<td>86.84</td>
<td>90.04</td>
</tr>
<tr>
<td>Path D</td>
<td>87.99</td>
<td>92.60</td>
</tr>
<tr>
<td>BeC$_2$(CH$_3$)$_6$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>TS4</td>
<td>28.72</td>
<td>29.65</td>
</tr>
<tr>
<td>P4+P5</td>
<td>15.61</td>
<td>22.17</td>
</tr>
<tr>
<td>TS5(+P5)</td>
<td>29.23</td>
<td>37.78</td>
</tr>
<tr>
<td>IM4(+P5)</td>
<td>27.43</td>
<td>35.89</td>
</tr>
<tr>
<td>P5+P3(+P5)</td>
<td>31.31</td>
<td>42.24</td>
</tr>
</tbody>
</table>

\[\text{FIG. 3 Potential energy surface of cis-BeC$_2$H$_4$(CH$_3$)$_2$ dissociation based on G3B3 relative energies (0 K) with the energy of cis-BeC$_2$H$_4$(CH$_3$)$_2$ and HBeCH$_2$CH$_3$ (HBeH$^\dagger$) set as zero (solid line: path E, dashed line: path F).}\]

\[\text{FIG. 4 Potential energy surface of BeC$_2$(CH$_3$)$_6$ dissociation based on G3B3 relative energies (0 K) with the energy of BeC$_2$(CH$_3$)$_6$ and HBeC(CH$_3$)$_3$ (HBeH$^\dagger$) set as zero (solid line: path E, dashed line: path F).}\]
frequency of 548 i cm
via the transition state TS1 (see Fig.2 and Fig.3). The
reactant cisated bond angles and bond lengths, in going from the
and Fig.2, there are significant changes in the associ-
level of theory. Moreover, as may be seen from Fig.1
and Fig.2, have been explored by the B3LYP,
fig.3. From the presented PES, the most energy fa-
that of path E by 44 kcal/mol (T=0 K), a relatively huge quanti-
energy barriers of these direct dissociations are from
77.6 kcal/mol to 91.1 kcal/mol, i.e., higher than that
energy barriers in kinetics and thermodynamics calcula-
Even with the inclusion of the temperature effect, these
four pathways can be basically neglected at T<900 K.
This is why we do not consider them in procedure II.
As the path E to yield TS species essentially occurs
within intra-molecule reactions, leads to the minimal
pathway integral among the five pathways, the favor
of path E is in principle understandable. Similarly,
in the procedure II, the possible dissociation pathway
for the semi-finished product obtained in the first pro-
cure, CH3CH2BeH, is predicted to yield the final
products of C2H4 and BeH2 via the intermediate IM2
(C2H4 ··· HBeH) and transition state TS2 of path F.
It is meaningful to notice that the geometrical
shapes are very similar between the di-ethyl beryl-
lum and ethane (CH3(CH3)), with the BeCH2CH3 of
the di-ethyl beryllium substituted by the H† (i.e.,
BeC2H4(CH3)2→CH3CH2BeH†). However, the disso-
ciation pathways of the two counterparts seem to be rather
different. The pyrolysis of the ethane (about 900 K) is
recognized to produce C2H4, H2 and a bit CH4 first
through the direct rupture of C–C bond [29, 30] (i.e.,
path A), and then via the combination or dissociation
reactions among the so-obtained radicals. Indeed, there
is no transition state like TS1 or TS2 found in the
ethane case. However, as described above, the dom-
inant dissociation pathway is indicated to be path E
and F for the BeC2H4(CH3)2, and other pathways aris-
ing from the direct ruptures of covalent bonds are less
consequential. The presence of transition states for the
BeC2H4(CH3)2 may be understood by the conventional
chemical concept, that is, compared with the H atom
with one s electron only, Be atom has additional p elec-
trons so that has more capability to contact other atoms
through the s and p hybridization simultaneously, to
create new chemical bonds in a reaction. It may be
seen by comparing the HOMOs of these two molecules.
The contours of HOMO on H† (Be) and H of oppo-
site Cα atom are adjacent in the CH3CH2H†, while the
counterparts are away in the CH3CH3, and in the TS1
of the di-ethyl beryllium dissociation path E (see Fig.6).
Similar to the di-ethyl beryllium BeC2H4(CH3)2,
the dominant dissociation reaction pathway for the

\[
\begin{align*}
\text{formula with three } A, n, \text{ and } B \text{ parameters:} \quad & k(T) = AT^n \exp \left( \frac{-B}{T} \right) \quad (8) \\
\text{over the temperature range of 298–600 K for path E} \quad & k(T) = 9.73 \times 10^9 T^{0.75} \exp \left( \frac{-16682.1}{T} \right) \quad (9) \\
\text{and F of cis-BeC2H4(CH3)2 (Eq.(9) and Eq.(10))} \quad & k(T) = 3.12 \times 10^{10} T^{0.70} \exp \left( \frac{-15536.3}{T} \right) \quad (10) \\
\text{and BeC2(CH3)6 (Eqs.(11) and Eq.(12)) respectively as follows} \quad & k(T) = 2.12 \times 10^{9} T^{1.47} \exp \left( \frac{-14855.4}{T} \right) \quad (11) \\
\text{IV. DISCUSSION} \quad & k(T) = 4.14 \times 10^{10} T^{0.91} \exp \left( \frac{-7376.8}{T} \right) \quad (12)
\end{align*}
\]
di-t-butyl beryllium $\text{BeC}_2(\text{CH}_3)_6$ is via the path E and F (see Fig.4), to produce $\text{CH}_2\text{C}(\text{CH}_3)_2$ and $\text{BeH}_2$. However, as shown in Fig.3 and Fig.4, for the $\text{BeC}_2(\text{CH}_3)_6$ in procedure I, the dissociation energy barrier is lower than the corresponding value of the $\text{BeC}_2\text{H}_4(\text{CH}_3)_2$ by 3.8 kcal/mol, while the combination energy barrier of reverse reaction is higher than that of the $\text{BeC}_2\text{H}_4(\text{CH}_3)_2$ by 2.4 kcal/mol. Moreover, in the procedure II, the dissociation energy barrier of $\text{BeC}_2(\text{CH}_3)_6$ is about half of the corresponding value of the $\text{BeC}_2\text{H}_4(\text{CH}_3)_2$. These differences imply that it is relatively effortless to form the important TS to perform dissociation reaction for the $\text{BeC}_2(\text{CH}_3)_6$ (see Fig.5), this indicates that the experimentally obtained beryllium hydride may be usually not by other alkyl beryllium compounds but the di-t-butyl beryllium dissociation. It is understandable as follows: as the increasing of the number of the substituting alkyl groups, the increased repulsion between H atoms leads to a H atom much easier to contact with the Be atom to form a transition state. Nevertheless, the calculations indicate that the reaction barriers of the two pathways are still large for the $\text{BeC}_2(\text{CH}_3)_6$, lead to the conclusion that the dissociation reaction is not feasible at the low temperatures. Although the reaction barriers are hardly affected by the temperatures in the whole range of 298–598 K, the rate constant of dissociation reactions increase nine order of magnitude from the room temperature of 298.15 K to the experimental temperatures of 493 K (see Fig.5). It is reasonable to assume that these dissociation pathways are feasible at such temperature levels.

As mentioned above, to highly accurately probe the PES profiles of dissociation reactions, the energies of involved species have been calculated by three methods, i.e., B3LYP, CCSD(T), and G3B3, in this work. As seen in Fig.5, the relative energies of these species depend substantially on the computational methods, but the overall trends are similar for these methods. The CCSD(T) and G3B3 results are well close to each other within the indiscernible 1 kcal/mol for the important path E and F, mutually validating each other. Dissimilarly, the B3LYP yields comparable results in the relative energies of TS-reactant species compared to the G3B3 results, while there presents huge differences in the relative energies of product-reactant species between these two methods, where the under-estimation in B3LYP relative to G3B3 approach may reach 10 kcal/mol (as occurring for the di-t-butyl beryllium). Indeed, the B3LYP method often engenders poor quantities when the energy calculations involved in the species with different scales, may be due to its relatively inferior treatment on electron correlation in theoretical (compared to the superior CCSD(T) and G3B3 here), so that the B3LYP predictions may be less trustworthy. Coincidently, previous study has demonstrated that the B3LYP method trends to considerably underestimate the experimental reaction enthalpy of the unimolecular dissociation (~10 kcal/mol) [26]. It is expected that the further experimental results about di-t-butyl beryllium dissociation are referred to examine the theoretical conclusion in this work.

V. CONCLUSION

Extensive investigations on the potential energy profiles of unimolecular dissociation reactions of the di-ethyl and di-t-butyl berylliums have been performed by ab initio calculations. Possible reaction pathways including four direct bonding ruptures and two concerted eliminations for the molecules have been considered. The geometries, vibrational frequencies, and relative energies for various stationary points, and the reaction enthalpies and energy barriers are determined. Due to high reaction barriers, the dissociation reactions arising from direct bonding ruptures can be negligible. The TS reactions resulting from concerted eliminations (path E and path F) are indicated to be the main dissociation pathways for both two molecules. The PES differences of dissociation reactions for two molecules have been discussed. The relative importance of the elementary pathways with low barriers and the reaction rate constant has been discussed quantitatively. The theoretical results will help in understanding the further experiments and validating the theoretical conjecture of this work by the experiments.

VI. ACKNOWLEDGMENTS

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