Re-examination of the π-Bond Energies in Doubly-Bonded Species: A Theoretical Study

Jun-Xian Chen, Chang Kon Kim, and Chan Kyung Kim

Department of Chemistry, Inha University, Incheon 402-751, Korea. *E-mail: kckyung@inha.ac.kr

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In the extensive studies of silicon chemistry, Walsh has observed that the first bond dissociation energy in SiX₄ species is always lower than the second bond dissociation energy in SiX₃ species. The difference between the first and the second bond dissociation energies has been defined as the divalent state stabilization energy (DSSE). In the early 1990’s, Grev and coworkers have reported that the DSSE can be utilized to rationalize the relationships between a double-bond dissociation energy and a π-bond (and a σ-bond) energy for a double-bonded species consisting of the Group 14 elements. However, by assuming the π-bond dissociation energies have been summarized in eq. 1. The original $D_\sigma$ term, $D_\sigma$(orig), suggested by Grev was shown in eq. 2. However, by assuming that $D(H_2M'H_3) = D(H_2M'H_3)'$ and $D(H_2M'H_3)' = D(H_1M'H_3)'$, the $D_\sigma$(orig) term was simplified to eq. B2. In eq. B2, DSSE terms have been estimated from the first and second bond dissociation energies of the corresponding hydrides, DSSE(H₂M'). The difference between the first and the second bond dissociation energies has been defined as the divalent state stabilization energy (DSSE) term for double-bonded species consisting of the Group 14 elements such as germasilene (H₂Ge=SiH₂) and disilene (H₂Si=SiH₂). These relationships have been developed to be reasonably estimated for a double bond system, if the reliable $D_X$, $D_\sigma$, and DSSE values are available.

$$\begin{align*}
H_2M & \rightarrow H_2M' + H_2
\end{align*}$$

$$\begin{align*}
H_2M & \rightarrow H_2M' + H_2
\end{align*}$$

$$\begin{align*}
D_\sigma = D_\sigma - DSSE(MH_2) - DSSE(M'H_2)
\end{align*}$$

$$\begin{align*}
D_\sigma(\text{orig}) = D(H_2M'H_3) - DSSE(H_2M') - DSSE(H_2M'H_3) + D(H_2M'H_3)
\end{align*}$$

However, the $D_\sigma$ value estimated by using eq. 1 for CH₂=CH₂ was deviated from the generally accepted ones, although the carbon also belongs to the Group 14 element: Experimental estimates of $D_\sigma$ and $D_{\alpha}$ are 171 and 88 kcal mol⁻¹ for CH₂=CH₂ and CH₂=CH₂, respectively, and the DSSE(CH₂) derived by Grev from using the Pople’s previous theoretical results was −6.6 kcal mol⁻¹. So that the $D_\alpha$ value estimated by use of eq. 1 was 69.8 kcal mol⁻¹ for CH₂=CH₂, but the generally accepted $D_\alpha$ values were in the range of 65 ~ 67 kcal mol⁻¹. The differences of 2 ~ 5 kcal mol⁻¹ could be roughly acceptable, but somewhat large for a more accurate prediction.

Anyway, the procedure of eq. 1 seems to be conceptually reasonable and applicable for all kinds of doubly-bonded species. If so, the deviation of the $D_\sigma$ value estimated by using eq. 1 for CH₂=CH₂ could be caused from the approximations mentioned above. Therefore, in this work, the $D_\sigma$ values obtained by using the $D_\sigma$(orig) term have been compared to the $D_\sigma$ term for double-bonded species consisting of the Group 14 elements.

Calculations

It has been known that the QCISD(T) method well reproduces the results obtained by using the full configuration interaction (FCI) method, particularly for near equilibrium geometries. Therefore, in this work, geometry optimizations and frequency calculations have been carried out at the QCISD(T) level of theory with 6-311++G(3df, 2p) in order to acquire accurate results comparable to an accuracy of the G2 theory. However, even if the theoretical level employed is a highly sophisticated, there are still residual inaccuracies. To correct these inaccuracies, the concept of “isogyric comparison” using the dissociation of H₂ has been utilized: The calculated electronic energy

$$\begin{align*}
E(H) = -0.49982 \text{ hartree},
\end{align*}$$

was corrected to give the exact value of −0.5 hartree. So that the correction of −0.18 millihartree was added to each bound unpaired valence electron of H atom. Moreover the dissociation energy of H₂ was 1.17086 hartree at the QCISD(T)/6-311++G(3df, 2p) level, but the exact value was known to be 1.17446 hartree. Therefore, in this work, total isogyric correction, $E_\text{ic}$ (in millihartree), could be calculated using eq. 3, where $n_\alpha$ and $n_\beta$ are the
number of α and β valence electrons, respectively. For example, in a homolytic bond dissociation reaction, the number of unpaired electrons is not conserved, and thus the differences in the number of α and β valence electrons between the reactants and dissociated products are 1 and -1, respectively. As a result, \( \Delta E_c \) = 2.03 kcal mol\(^{-1}\) has been used for the processes including the homolytic bond dissociations. All the calculations have been performed by using the Gaussian 03 program.\(^{11}\)

\[
E_{\text{ec}} = -0.18n_\alpha - 3.42n_\beta
\] (3)

Results and Discussion

To confirm the validity of the approximation, \( D(H_3M-H) = D(H-H_2MM'H_3) \), dissociation energies for the group 14 elements were calculated at the QCISD(T)/6-311++(3df, 2p) level, and the results are collected in Table 1. Table 1 showed that the differences between \( D(H_3M-H) \) and \( D(H-H_2MM'H_3) \), \( \delta D = (D(H_3M-H) - D(H-H_2MM'H_3)) \), were smaller than 10 kcal mol\(^{-1}\) as suggested by Grev.\(^{2b}\) This indicates that the approximation of \( D(H_3M-H) \approx D(H-H_2MM'H_3) \) could be useful in general purposes such as to predict a tendency of bond strength. However, in determining the \( D_e \) value by use of eq. 1 the relatively large errors could be introduced from these approximations, because the errors were the sum of the two approximations. For example, difference between \( D(H_3Ge-H) \) and \( D(H-H_2GeGeH_3) \) was only 2.2 kcal mol\(^{-1}\) and this could be generally acceptable for the approximation of \( D(H_3Ge-H) \approx D(H-H_2GeGeH_3) \). However this error was doubled in estimating the \( D_e \) value by use of eq. 1. As a result, the error of 4.4 kcal mol\(^{-1}\) seems to be larger for an accurate work.

The \( D_e'(\text{orig}) \) term could be simplified as eq. 4, since the \( D(H_3M-H) \) and \( D(H-H_2MM'H_3) \) were also included in the definition of DSSE(H3M) and DSSE(H3M') respectively, as noted above. In eq. 4, the two terms in square brackets corresponded to the energy differences between the first bond dissociation of a hydride in \( H_2MM'H_3 \) and the second bond dissociation in the corresponding hydride, \( H_2M \) or \( M'H_2 \). These were somewhat different from the DSSE defined by Walsh in determining the first bond dissociation energy, i.e., the DSSE in eq. 1 has been estimated both from the first and the second bond dissociation energies of the corresponding hydrides, DSSE(H3M) = \( D(H_3M-H) - D(MH_2-H) \) or DSSE(H3M') = \( D(H_3M'-H) - D(M'H_2-H) \). Therefore, in this work, the two terms in square brackets were denoted as DSSE' as shown in eqs. 5 and 6, and thus eq. 4 could be rewritten as eq. B2.

\[
D_e'(\text{orig}) = D(H_3M-M'H_3) - \left[ D(H-H_2MM'H_3) - D(H-MH_2) \right] - (D(H_2MM'H_2-H)) \]
(4)

DSSE'(Mh2) = \( D(H-H_2MM'H_3) - D(MH_2-H) \)  
(5)

DSSE'(M'H2) = \( D(H_2MM'H_2-H) - D(M'H_2-H) \)  
(6)

\[
D_e'(\text{orig}) = D_e - \text{DSSE'}(Mh2) - \text{DSSE'}(M'H2)
\]  
(7)

Table 1. The bond dissociation energies (kcal mol\(^{-1}\)), \( D(H_3M-H) \) and \( D(H-H_2MM'H_3) \), calculated at QCISD(T)/6-311++(3df,2p) level of theory. Values were obtained from zero-point corrected energies and isogyric corrections.

<table>
<thead>
<tr>
<th>MH2</th>
<th>D(H3M-H)</th>
<th>H2MM'H3</th>
<th>D(H-H2MM'H3)</th>
<th>( \delta D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>103.0</td>
<td>H2CCH3</td>
<td>99.4</td>
<td>3.6</td>
</tr>
<tr>
<td>SiH4</td>
<td>89.9</td>
<td>H2SiH3</td>
<td>99.8</td>
<td>3.2</td>
</tr>
<tr>
<td>GeH4</td>
<td>83.4</td>
<td>H2GeH3</td>
<td>100.8</td>
<td>2.2</td>
</tr>
</tbody>
</table>

\( \delta D = D(H_3M-H) - D(H-H_2MM'H_3) \)

Table 2. The DSSE, DSSE' and \( D_e \) values (kcal mol\(^{-1}\)) calculated at QCISD(T)/6-311++(3df,2p) level of theory. Values were obtained from zero-point corrected energies and isogyric corrections.

<table>
<thead>
<tr>
<th>MH2MH2</th>
<th>DSSE</th>
<th>DSSE'</th>
<th>( D_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeH2 = GeH2</td>
<td>26.2</td>
<td>26.2</td>
<td>26.8</td>
</tr>
<tr>
<td>GeH2 = SiH2</td>
<td>26.2</td>
<td>26.2</td>
<td>24.0</td>
</tr>
<tr>
<td>SiH2 = SiH2</td>
<td>26.2</td>
<td>23.7</td>
<td>23.7</td>
</tr>
<tr>
<td>SiH2 = CH2</td>
<td>23.7</td>
<td>23.7</td>
<td>21.0</td>
</tr>
<tr>
<td>CH2 = CH2</td>
<td>23.7</td>
<td>23.7</td>
<td>21.0</td>
</tr>
</tbody>
</table>

In order to compare the differences in \( D_e \) values estimated by using the DSSE and the DSSE' corrections, the \( D_e \) values for the doubly-bonded species consisting of group 14 elements were estimated theoretically at the QCISD(T)/6-311++(3df,2p) level, since most of experimental \( D_{MH2-M'H2} \) and \( D_e \) values were unavailable in literature. Nevertheless, the calculated results could expect to be quite reliable, because the calculated \( D_c = c \) (171.7 kcal mol\(^{-1}\)) for CH2 = CH2 and CH3 (87.7 kcal mol\(^{-1}\)) for CH2 and CH3 were agreed well with the experimental ones (\( D_{c = c} \approx 171 \) and \( D_e \approx 88 \) kcal mol\(^{-1}\)).\(^{3,4}\) The estimated \( D_e \) values are summarized in Table 2. Examination of Table 2 showed that the \( D_e \) values obtained by using the DSSE' corrections were very close to the corresponding literature values, but those estimated by using the DSSE corrections showed relatively large errors. For example, the \( D_e \) values for GeH2 = GeH2 estimated to be 28.8 and 24.4 kcal mol\(^{-1}\) by the DSSE and DSSE' corrections, respectively, but the convincing literature value was 25.0 kcal mol\(^{-1}\). Especially, the difference in the \( D_e \) value for CH2 = CH2 by the DSSE corrections was in the range of 6 ~ 7 kcal mol\(^{-1}\) but was reduced considerably by the DSSE' corrections. This clearly indicates that the DSSE' corrections could be more accurate.
for estimating the $D_\pi$ values, even though the DSSE corrections were also reasonable in some cases. Since the DSSE’ corrections for various doubly-bonded species have not been reported, systematic studies are in progress in our lab.

Conclusions

The aim of this study was to examine a reliable methodology to estimate the $D_\pi$ values for doubly-bonded species. Although the approximate procedure suggested by Grev and coworkers seems to be conceptually reasonable and applicable to all kinds of doubly-bonded species, the $D_\pi$ value estimated by using eq. 1 were largely deviated from the convincing literature values in some cases. In this work, the $D_\pi$ values estimated from the DSSE and DSSE’ corrections have been examined and compared with literature values. To achieve a higher accuracy, the $D_\pi$ values were estimated at QCISD(T)/6-311++G(3df, 2p) level of theory combined with isogyric correction. Our results showed that the DSSE’ corrections in eq. 7 are more reliable and adequate in estimating the $D_\pi$ values in doubly-bonded species.

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References