

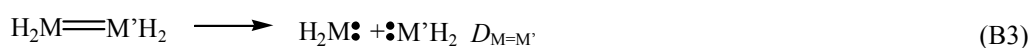
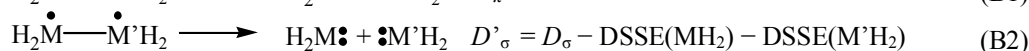
## Re-examination of the $\pi$ -Bond Energies in Doubly-Bonded Species: A Theoretical Study

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In the extensive studies of silicon chemistry, Walsh<sup>1</sup> has observed that the first bond dissociation energy in  $\text{SiX}_4$  species is always lower than the second bond dissociation energy in  $\bullet\text{SiX}_3$  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<sup>2</sup> have reported that the DSSE can be utilized to rationalize the relationships between a double-bond dissociation energy and a  $\pi$ -bond (and a  $\sigma$ -bond) energy for a double-bonded species consisting of the Group 14 elements such as germsilene ( $\text{H}_2\text{Ge}=\text{SiH}_2$ ) and disilene ( $\text{H}_2\text{Si}=\text{SiH}_2$ ). These relationships have been summarized in eq. 1. The original  $D'_\sigma$  term,  $D'_\sigma(\text{orig})$ , suggested by Grev was shown in eq. 2.<sup>2b</sup> However, by assuming that  $D(\text{H}_3\text{M}-\text{H}) \approx D(\text{H}-\text{H}_2\text{MM}'\text{H}_3)$  and  $D(\text{H}_3\text{M}'-\text{H}) \approx D(\text{H}_3\text{MM}'\text{H}_2-\text{H})$ , the  $D'_\sigma(\text{orig})$  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,  $\text{DSSE}(\text{H}_2\text{M}) = D(\text{H}_3\text{M}-\text{H}) - D(\text{H}_2\text{M}-\text{H})$  and  $\text{DSSE}(\text{H}_2\text{M}') = D(\text{H}_3\text{M}'-\text{H}) - D(\text{H}_2\text{M}'-\text{H})$ , which certainly introduced errors of less than 10 kcal mol<sup>-1</sup>.<sup>2b</sup> For  $\text{H}_2\text{Ge}=\text{SiH}_2$  and  $\text{H}_2\text{Ge}=\text{GeH}_2$ , however, the  $D_{\text{M}=\text{M}'}$  values estimated by use of eq. 1 are well agreed with those reported earlier. This indicates that the  $\pi$ -bond energy,  $D_\pi$ , could be reasonably estimated for a double bond system, if the reliable  $D_{\text{X}=\text{Y}}$ ,  $D_\sigma$  and DSSE values are available.



$$D_{\text{M}=\text{M}'} = D_\pi + D_\sigma - \text{DSSE}(\text{MH}_2) - \text{DSSE}(\text{M}'\text{H}_2) \quad (1)$$

$$D'_\sigma(\text{orig}) = D(\text{H}_3\text{M}-\text{M}'\text{H}_3) - \text{DSSE}(\text{H}_2\text{M}) - \text{DSSE}(\text{H}_2\text{M}') + D(\text{H}_3\text{M}-\text{H}) - D(\text{H}-\text{H}_2\text{MM}'\text{H}_3) + D(\text{H}_3\text{M}'-\text{H}) - D(\text{H}_3\text{MM}'\text{H}_2-\text{H}) \quad (2)$$

However, the  $D_\pi$  value estimated by using eq. 1 for  $\text{CH}_2=\text{CH}_2$  was deviated from the generally accepted ones, although the carbon also belongs to the Group 14 element: Experimental estimates of  $D_{\text{X}=\text{Y}}$  and  $D_\sigma$  are 171 and 88 kcal mol<sup>-1</sup> for  $\text{CH}_2=\text{CH}_2$  and  $\text{CH}_3-\text{CH}_3$ , respectively,<sup>3,4</sup> and the  $\text{DSSE}(\text{CH}_2)$  derived by Grev from using the Pople's previous theoretical results<sup>5</sup> was -6.6 kcal mol<sup>-1</sup>. So that the  $D_\pi$  value estimated by use of eq. 1 was 69.8 kcal mol<sup>-1</sup> for  $\text{CH}_2=\text{CH}_2$ , but the generally accepted  $D_\pi$

values were in the range of 65 ~ 67 kcal mol<sup>-1</sup>.<sup>6</sup> The differences of 2 ~ 5 kcal mol<sup>-1</sup> 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  $D_\pi$  value estimated by using eq. 1 for  $\text{CH}_2=\text{CH}_2$  could be caused from the approximations mentioned above. Therefore, in this work, the  $D_\pi$  values obtained by using the  $D'_\sigma(\text{orig})$  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<sup>7</sup> well reproduces the results obtained by using the full configuration interaction (FCI) method, particularly for near equilibrium geometries.<sup>8</sup> 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.<sup>9</sup> 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'<sup>10</sup> using the dissociation of  $\text{H}_2$  has been utilized: The calculated electronic energy

of H atom at this level of theory,  $E(\text{H}) = -0.49982$  hartree, 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  $\text{H}_2$  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  $\alpha$  and  $\beta$  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  $\alpha$  and  $\beta$  valence electrons between the reactants and dissociated products are 1 and -1, respectively. As a result,  $\Delta E_{ic} = 2.03 \text{ kcal mol}^{-1}$  has been used for the processes including the homolytic bond dissociations. All the calculations have been performed by using the Gaussian 03 program.<sup>11</sup>

$$E_{ic} = -0.18n_{\alpha} - 3.42n_{\beta} \quad (3)$$

### Results and Discussion

To confirm the validity of the approximation,  $D(\text{H}_3\text{M}-\text{H}) \approx D(\text{H}-\text{H}_2\text{MM}'\text{H}_3)$ , 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  $D(\text{H}_3\text{M}-\text{H})$  and  $D(\text{H}-\text{H}_2\text{MM}'\text{H}_3)$ ,  $\delta D = D(\text{H}_3\text{M}-\text{H}) - D(\text{H}-\text{H}_2\text{MM}'\text{H}_3)$ , were smaller than  $10 \text{ kcal mol}^{-1}$  as suggested by Grev.<sup>2b</sup> This indicates that the approximation of  $D(\text{H}_3\text{M}-\text{H}) \approx D(\text{H}-\text{H}_2\text{MM}'\text{H}_3)$  could be useful in general purposes such as to predict a tendency of bond strength. However, in determining the  $D_{\pi}$  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  $D(\text{H}_3\text{Ge}-\text{H})$  and  $D(\text{H}-\text{H}_2\text{GeGeH}_3)$  was only  $2.2 \text{ kcal mol}^{-1}$  and this could be generally acceptable for the approximation of  $D(\text{H}_3\text{Ge}-\text{H}) \approx D(\text{H}-\text{H}_2\text{GeGeH}_3)$ . However this error was doubled in estimating the  $D_{\pi}$  value by use of eq. 1. As a result, the error of  $4.4 \text{ kcal mol}^{-1}$  seems to be larger for an accurate work.

The  $D'_{\sigma}$  (*orig*) term could be simplified as eq. 4, since the  $D(\text{H}_3\text{M}-\text{H})$  and  $D(\text{H}_3\text{M}'-\text{H})$  were also included in the definition of  $\text{DSSE}(\text{H}_2\text{M})$  and  $\text{DSSE}'(\text{H}_2\text{M}')$ , 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 hydrogen in  $\text{H}_3\text{MM}'\text{H}_3$  and the second bond dissociation in the corresponding hydride,  $\text{H}_3\text{M}\cdot$  or  $\cdot\text{M}'\text{H}_3$ . 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,  $\text{DSSE}(\text{H}_2\text{M}) = D(\text{H}_3\text{M}-\text{H}) - D(\cdot\text{MH}_2-\text{H})$  or  $\text{DSSE}'(\text{H}_2\text{M}') = D(\text{H}_3\text{M}'-\text{H}) - D(\cdot\text{M}'\text{H}_2-\text{H})$ . Therefore, in this work, the two terms in square brackets were denoted as  $\text{DSSE}'$  as shown in eqs. 5 and 6, and thus eq. 4 could be rewritten as eq. 7, which is similar to eq. B2.

$$D'_{\sigma}(\text{orig}) = D(\text{H}_3\text{M}-\text{M}'\text{H}_3) - [D(\text{H}-\text{H}_2\text{MM}'\text{H}_3) - D(\text{H}-\text{MH}_2)] - [D(\text{H}_3\text{MM}'\text{H}_2-\text{H}) - D(\text{H}_2\text{M}'-\text{H})] \quad (4)$$

$$\text{DSSE}'(\text{MH}_2) = D(\text{H}-\text{H}_2\text{MM}'\text{H}_3) - D(\cdot\text{MH}_2-\text{H}) \quad (5)$$

$$\text{DSSE}'(\text{M}'\text{H}_2) = D(\text{H}_3\text{MM}'\text{H}_2-\text{H}) - D(\cdot\text{M}'\text{H}_2-\text{H}) \quad (6)$$

$$D'_{\sigma}(\text{orig}) = D_{\sigma} - \text{DSSE}'(\text{MH}_2) - \text{DSSE}'(\text{M}'\text{H}_2) \quad (7)$$

**Table 1.** The bond dissociation energies ( $\text{kcal mol}^{-1}$ ),  $D(\text{H}_3\text{M}-\text{H})$  and  $D(\text{H}-\text{H}_2\text{MM}'\text{H}_3)$ , calculated at QCISD(T)/6-311++G(3df,2p) level of theory. Values were obtained from zero-point corrected energies and isogyric corrections.

MH <sub>4</sub>	$D(\text{H}_3\text{M}-\text{H})$	H <sub>3</sub> MM'H <sub>3</sub>	$D(\text{H}-\text{H}_2\text{MM}'\text{H}_3)$	$\delta D^a$
CH <sub>4</sub>	103.0	H <sub>3</sub> CCH <sub>3</sub>	99.4	3.6
		H <sub>3</sub> CSiH <sub>3</sub>	99.8	3.2
		H <sub>3</sub> CGeH <sub>3</sub>	100.8	2.2
SiH <sub>4</sub>	89.9	H <sub>3</sub> SiCH <sub>3</sub>	90.9	-1.0
		H <sub>3</sub> SiSiH <sub>3</sub>	87.2	2.7
		H <sub>3</sub> SiGeH <sub>3</sub>	87.5	2.4
GeH <sub>4</sub>	83.4	H <sub>3</sub> GeCH <sub>3</sub>	84.0	-0.6
		H <sub>3</sub> GeSiH <sub>3</sub>	80.9	2.5
		H <sub>3</sub> GeGeH <sub>3</sub>	81.2	2.2

$$^a\delta D = D(\text{H}_3\text{M}-\text{H}) - D(\text{H}-\text{H}_2\text{MM}'\text{H}_3)$$

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

MH <sub>2</sub> =M'H <sub>2</sub>	DSSE		DSSE'		$D_{\pi}$		
	MH <sub>2</sub>	M'H <sub>2</sub>	MH <sub>2</sub>	M'H <sub>2</sub>	DSSE corr.	DSSE' corr.	literatures
GeH <sub>2</sub> =CH <sub>2</sub>	26.2	-5.6	26.8	-7.8	35.8	34.2	31 <sup>a</sup>
GeH <sub>2</sub> =GeH <sub>2</sub>	26.2	26.2	24.0	24.0	28.8	24.4	25 <sup>a</sup>
GeH <sub>2</sub> =SiH <sub>2</sub>	26.2	23.7	23.7	21.3	29.8	24.9	25 <sup>a</sup>
SiH <sub>2</sub> =SiH <sub>2</sub>	23.7	23.7	21.0	21.0	31.1	25.8	25, <sup>a</sup> 25.6 <sup>b</sup>
SiH <sub>2</sub> =CH <sub>2</sub>	23.7	-5.6	24.7	-8.8	40.7	38.5	35.6, <sup>c</sup> 39.5 <sup>b</sup>
CH <sub>2</sub> =CH <sub>2</sub>	-5.6	-5.6	-9.2	-9.2	72.8	65.6	65.4, <sup>c</sup> 66.8 <sup>b</sup>

<sup>a</sup>Avakyan, V. G.; Guse'nikov, S. L.; Guse'nikov, L. E. *J. Organometallic Chem.* **2003**, 686, 257. <sup>b</sup>Ref. (6a). <sup>c</sup>Ref. (6b).

In order to compare the differences in  $D_{\pi}$  values estimated by using the DSSE and the DSSE' corrections, the  $D_{\pi}$  values for the doubly-bonded species consisting of group 14 elements were estimated theoretically at the QCISD(T)/6-311++G(3df,2p) level, since most of experimental  $D_{\text{M}=\text{M}'}$  and  $D_{\sigma}$  values were unavailable in literature. Nevertheless, the calculated results could expect to be quite reliable, because the calculated  $D_{\text{C}=\text{C}}$  ( $171.7 \text{ kcal mol}^{-1}$ ) for  $\text{CH}_2=\text{CH}_2$  and  $D_{\sigma}$  ( $87.7 \text{ kcal mol}^{-1}$ ) for  $\text{CH}_3-\text{CH}_3$  were agreed well with the experimental ones ( $D_{\text{C}=\text{C}} = 171$  and  $D_{\sigma} = 88 \text{ kcal mol}^{-1}$ ).<sup>3,4</sup> The estimated  $D_{\pi}$  values are summarized in Table 2. Examination of Table 2 showed that the  $D_{\pi}$  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  $D_{\pi}$  values for  $\text{GeH}_2=\text{GeH}_2$  were estimated to be  $28.8$  and  $24.4 \text{ kcal mol}^{-1}$  by the DSSE and DSSE' corrections, respectively, but the convincing literature value was  $25.0 \text{ kcal mol}^{-1}$ . Especially, the difference in the  $D_{\pi}$  value for  $\text{CH}_2=\text{CH}_2$  by the DSSE corrections was in the range of  $6 \sim 7 \text{ kcal mol}^{-1}$  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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