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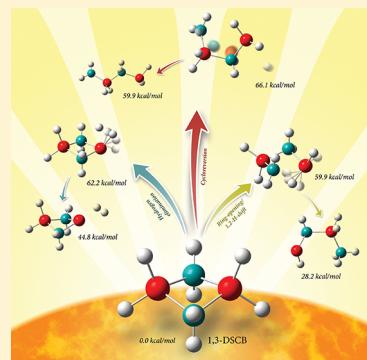
# Theoretical Study on the Ring-Opening of 1,3-Disilacyclobutane and H<sub>2</sub> Elimination

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## Supporting Information

**ABSTRACT:** The kinetics and thermochemistry of the decomposition pathways for 1,3-disilacyclobutane (1,3-DSCB) in the gas phase were studied using the second-order Møller–Plesset (MP2) perturbation theory and coupled cluster methods with single, double, and perturbative triple excitations (CCSD(T)). The reactions examined include 2 + 2 cycloreversion to form two silenes by either a concerted or a stepwise mechanism, 1,1-, 1,2-, and 1,3-H<sub>2</sub> elimination, and the ring-opening initiated by 1,2-H shift to form an open-chain 1,3-disilabut-1-ylidene, which undergoes further decomposition to produce two pairs of silene/silylene species. The structures of the transition states for the concerted and the stepwise 2 + 2 cycloreversion pathways are found to resemble closely those reported for the head-to-tail and head-to-head dimerization, respectively. Comparison of the activation barriers demonstrates unambiguously that the stepwise cycloreversion ( $\Delta H_0^\ddagger = 66.1$  kcal/mol) is favored over the concerted one ( $\Delta H_0^\ddagger = 77.3$  kcal/mol). A new pathway was established from the 1,4-diradical intermediate in the stepwise cycloreversion to form 1-silylmethylsilene via 1,3-H shift. The concerted 1,1-H<sub>2</sub> elimination is shown to have the lowest activation barrier of all H<sub>2</sub> elimination reactions. Overall, the 1,2-H shift in 1,3-DSCB with concerted ring-opening to form 1,3-disilabut-1-ylidene is the most kinetically and thermodynamically favorable decomposition pathway, both at 0 and 298 K.



## INTRODUCTION

The four-membered-ring silacycloalkane molecules have recently attracted a lot of research interest due to their wide range of applications in chemistry<sup>1</sup> and material science.<sup>2</sup> The high ring strain energy and the ability of these molecules to produce reactive silene and silylene species have made them excellent choices as single-source precursors for producing silicon carbide thin films using chemical vapor deposition (CVD) techniques.<sup>3–9</sup> Among all silacyclobutane molecules, 1,3-disilacyclobutane (1,3-DSCB) has a unique structure with a built-in 1:1 Si/C ratio. It has been used in producing silicon carbide<sup>3,10,11</sup> and organosilicon polymers<sup>12,13</sup> via either thermal or laser CVD.

The mechanism and kinetics of the pyrolysis<sup>3,14</sup> and photolysis<sup>11,13,15,16</sup> of 1,3-DSCB have been studied experimentally by several groups. Interestingly, the main decomposition route in the pyrolysis is a ring-opening initiated by a 1,2-H shift to form an open-chain silylene, which undergoes a series of reactions leading to the formation of monomethylsilane (MMS) and dimethylsilane (DMS). Observation of MMS and DMS formation was evident when using 1,3-DSCB as a precursor in the pyrolysis.<sup>3,14</sup> This is in contrast to the well-known results from the thermal decomposition of 1,1-dimethylsilacyclobutane, which was shown to be a clean unimolecular cycloreversion reaction to produce ethene and transient 1,1-dimethylsiline.<sup>1,17,18</sup> Barton et al. found that both cycloreversion and ring-opening initiated by 1,2-H shift occurred in the pyrolysis of 1-silacyclobutane (1-SCB), the monosilacyclobutane analogue of 1,3-DSCB; however, the

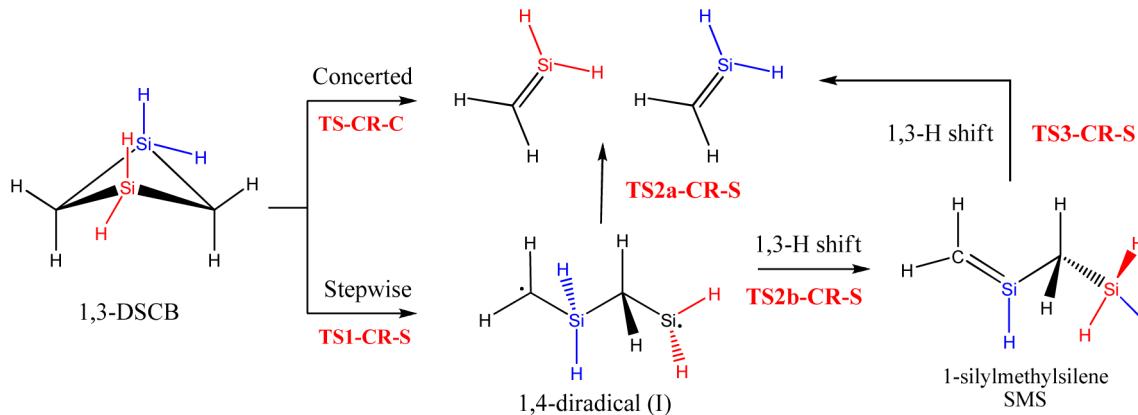
product from the latter is only 16% of the one from cycloreversion.<sup>19</sup> The decomposition in the photolysis of 1,3-DSCB, however, occurs mainly via cycloreversion, forming silenes. Bastl et al. reported the formation of MMS and DMS in the photolysis of DSCB, but they determined that silene formation via ring-opening cycloreversion was the dominating reaction.<sup>11</sup>

At the theoretical level, despite the extensive research on the structure, ring puckering, and vibrational spectra of 1,3-DSCB,<sup>20–24</sup> much less is found on its decomposition mechanism and kinetics. Using ab initio and density functional theory (DFT) methods, Gusel'nikov et al.<sup>25,26</sup> studied the 2 + 2 cycloreversion enthalpies of a series of heterocyclobutanes, including 1,3-DSCB. They determined that the cycloreversion of 1,3-DSCB is endothermic by 78.6 kcal/mol. The debate on whether 2 + 2 cycloreversion of cyclobutane to form two ethylene molecules is concerted or stepwise was long-standing. It is now well established that the cycloreversion of cyclobutane proceeds via a stepwise mechanism involving a 1,4-diradical intermediate. Zewail et al.<sup>27,28</sup> have successfully identified the diradical intermediate using femtosecond spectroscopic techniques. For the cycloreversion of 1,3-DSCB, Gusel'nikov et al.<sup>25</sup> inferred that the stepwise route is preferred over the concerted one; however, the transition states were not located. The reverse reaction, i.e., the dimerization of two silenes to form 1,3-DSCB, has also been a subject of theoretical investiga-

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Scheme 1. Stepwise and Concerted 2 + 2 Cycloreversion of DSCB



tions.<sup>29–31</sup> The dimerization was also shown to proceed through a diradical intermediate.

Hydrogen gas was observed in several studies involving the pyrolysis<sup>3,14</sup> and laser photolysis<sup>11,15</sup> of 1,3-DSCB. It is suggested that the formation of hydrogen in 1,3-DSCB photolysis is a result of the dehydrogenation of silene or silylene to form the final solid deposits. Nonetheless, hydrogen elimination from the parent 1,3-DSCB molecule remains a possibility. H<sub>2</sub> molecular elimination was previously reported during the laser-induced decomposition of 1-silacyclobutane (1-SCB).<sup>32</sup> The formation of molecular H<sub>2</sub> plays a key role in the formation of hydrogenated silicon carbides (SiC:H).<sup>33</sup>

Gordon et al.<sup>34</sup> investigated theoretically the three decomposition pathways of 1-SCB, i.e., the 2 + 2 cycloreversion, ring-opening by 1,2-H shift, and 1,1-H<sub>2</sub> elimination. The ring-opening by 1,2-H shift was shown to be both thermodynamically and kinetically competitive with the 2 + 2 cycloreversion. However, a systematic study on the decomposition mechanism of 1,3-DSCB using theoretical methods has never been reported before. In this work, we report a comprehensive investigation to explore the different decomposition pathways of DSCB using the high-level theoretical methods. The reactions of interest involve 2 + 2 cycloreversion to form two silenes by either a concerted or a stepwise mechanism, the ring-opening initiated by 1,2-H shift to form silylene, and 1,1-, 1,2-, and 1,3-H<sub>2</sub> elimination from 1,3-DSCB. For each reaction, the transition state was located, and the activation barrier was calculated. A detailed thermochemical analysis of the reactions investigated was provided by calculating the reaction enthalpies, Gibbs free energies, and entropies.

## THEORETICAL METHODS

Previous studies have shown that calculations using MP2 provide satisfactory results in predicting the structures of mono- and disilacyclobutanes.<sup>24,35</sup> In this work, the geometry optimization and vibration frequencies of the reactants, products, and intermediates for each reaction were calculated using MP2 with the 6-311++G(d,p) basis set. The frozen core approximation was employed in all geometry optimizations. The transition states (TS) were located by performing a TS search followed by geometry optimization and vibration frequency calculation. The TS was identified as having a single imaginary vibration frequency. Some hard-to-find TSs were located by exploring the potential energy surface (PES) along the reaction coordinate and using the highest point as a starting

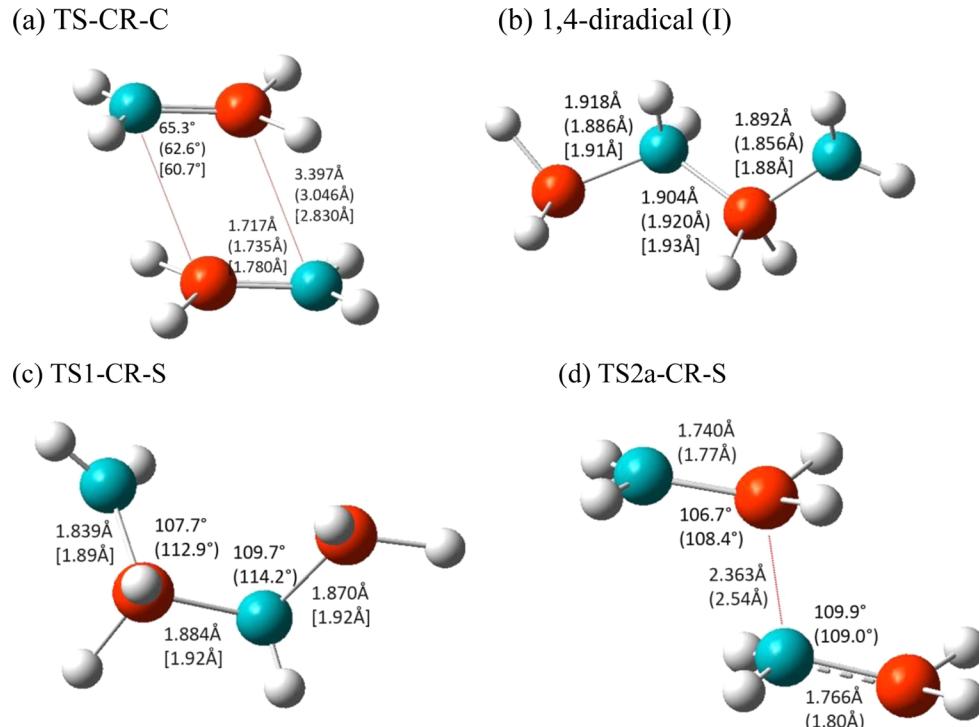
point for TS optimization. Intrinsic reaction coordinate (IRC) was used to confirm that each TS connects the two desired minima. All these were done at the MP2/6-311++G(d,p) level of theory. A high-level PES scan was performed by computing single-point energies at the CCSD(T)/6-311++G(3d,2p) level of theory for different points of the MP2 geometries on the IRC. The highest point in the new PES was considered the correct TS at the CCSD(T) level.

For the reactant and all products, intermediates, and transition states involved in this work, their energies were calculated using the CCSD(T)/6-311++G(3d,2p) on the MP2/6-311++G(d,p) geometries. The full notation for the level of theory for energy calculations is CCSD(T)/6-311++G(3d,2p)//MP2/6-311++G(d,p). Harmonic frequency analysis was carried out at the MP2/6-311++G(d,p) level. Zero-point energies (ZPE) were scaled by a factor of 0.9748 as suggested by Scott and Radom.<sup>36</sup> Enthalpies at 298 K ( $H_{298}$ ) were obtained by adding the quantity ( $H_{298} - H_0$ ) to the enthalpies at 0 K ( $H_0$ ). ( $H_{298} - H_0$ ) was calculated by subtracting the unscaled ZPE from the thermal correction to enthalpy. Gibbs free energies at 298 K ( $G_{298}$ ) were obtained in a similar way using the thermal correction to the Gibbs free energy. Entropies at 298 K ( $S_{298}$ ) were calculated from the values of  $H_{298}$  and  $G_{298}$ . All calculations were performed using the Gaussian09 program.<sup>37</sup>

## RESULTS AND DISCUSSIONS

The ring-opening of 1,3-DSCB via two pathways, i.e., 2 + 2 cycloreversion to form two silenes and simultaneous ring-opening and 1,2-H shift to form silylene, has been studied in this work. In addition, H<sub>2</sub> elimination from 1,3-DSCB, including 1,1-, 1,2-, and 1,3-elimination, has been examined.

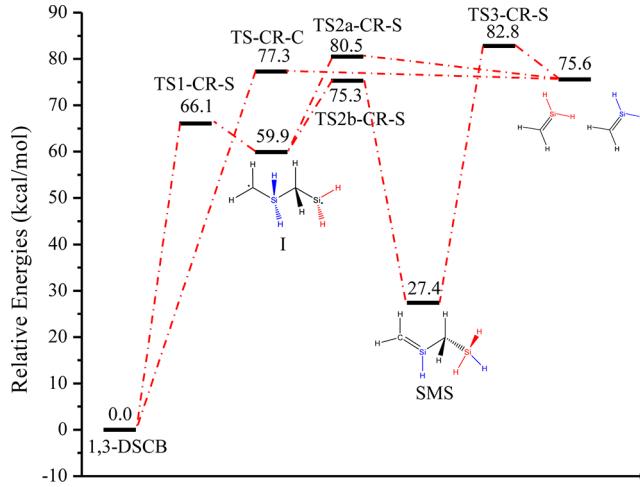
**2 + 2 Cycloreversion.** Both the concerted and stepwise routes for the 2 + 2 cycloreversion of 1,3-DSCB to produce two silenes are illustrated in Scheme 1. Although few studies are found on the 2 + 2 cycloreversion of 1,3-DSCB, the cycloaddition of two silenes has been theoretically investigated.<sup>29–31</sup> Seidl et al.<sup>29</sup> found that the concerted 2s + 2s cycloaddition is allowed due to a relaxation of the Woodward–Hoffmann rules and that it proceeds by a head-to-tail dimerization. The head-to-head dimerization is a stepwise process involving a diradical intermediate to form 1,2-DSCB. Later on, calculations using CAS-SCF<sup>30,31</sup> showed that head-to-head dimerization would produce both 1,3- and 1,2-DSCB through a diradical intermediate.



**Figure 1.** Optimized structure of (a) the transition states involved in the concerted  $2 + 2$  cycloreversion, TS-CR-C; (b) 1,4-diradical (I). The singlet state is found lower in energy than the triplet. For panels a and b, the values in parentheses are obtained from ref 30 at CAS-SCF/3-21G\* level of theory, and in squared brackets from ref 31 at CASPT2/6-311G\* level of theory. (c) TS1-CR-S and (d) TS2a-CR-S. Panels c and d are the transition states involved in the stepwise  $2 + 2$  cycloreversion of 1,3-DSCB. The values in parentheses in these two structures were obtained from ref 31 at CASPT2/6-311G\* level of theory. Si atom, red; C atom, cyan; H atom, gray.

Figure 1a shows the optimized geometry of the transition state for the concerted pathway, labeled as TS-CR-C, found in our work. The structure of this transition state is close to what has been reported for the head-to-tail dimerization of two silenes.<sup>30,31</sup> The structural parameters obtained from the literature are shown in parentheses in Figure 1a for comparison. The 1,4-diradical intermediate (I) (Figure 1b) in the stepwise mechanism is a result of direct homolytic cleavage of the Si–C bond in 1,3-DSCB. It will lead to the formation of two identical silenes by cleaving the central Si–C bond through the transition state labeled as TS2a-CR-S. The two transition states in the stepwise  $2 + 2$  cycloreversion to form silenes, TS1-CR-S and TS2a-CR-S, were located, and their optimized structures are shown in Figure 1c,d, respectively. It is noteworthy to mention that the structures of TS1-CR-S and TS2a-CR-S are close to the ones involved in the head-to-head dimerization of two silenes<sup>31</sup> (values are shown in parentheses for comparison). The fact that both cycloreversion and cycloaddition of 1,3-DSCB proceed through the same transition state can be attributed to the principle of microscopic reversibility.<sup>25</sup>

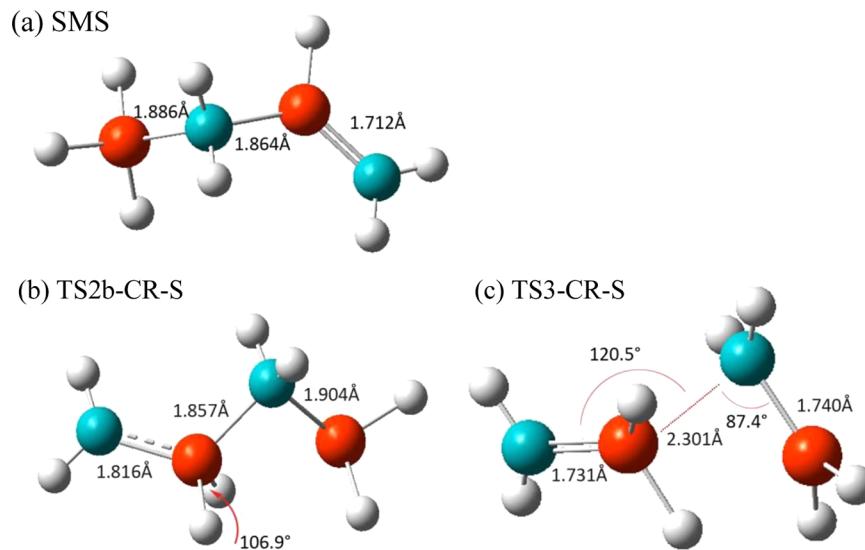
The energy level diagram for concerted and stepwise  $2 + 2$  cycloreversion illustrated in Scheme 1 is shown in Figure 2. All energies were calculated at the CCSD(T)/6-311++G(3d,2p) level on the MP2/6-311++G(d,p) optimized structures, and the scaled ZPE corrections were included. The  $2 + 2$  cycloreversion is found to be endothermic by 75.6 kcal/mol. This is in good agreement with the results from the work of Gusein'nikov et al.<sup>26</sup> who reported a reaction enthalpy of 78.9 kcal/mol at the MP4/6-311G(d)//MP2/6-31G(d) level of theory. The reverse reaction, the cycloaddition of two silenes, was found to be exothermic by 79.1 kcal/mol (by CCSD/DZ+d)<sup>29</sup> and 78.2



**Figure 2.** Energy level diagrams for the concerted and stepwise  $2 + 2$  cycloreversion of 1,3-DSCB (Scheme 1). Energy values represent the relative enthalpies in kcal/mol at 0 K (ZPE corrections included).

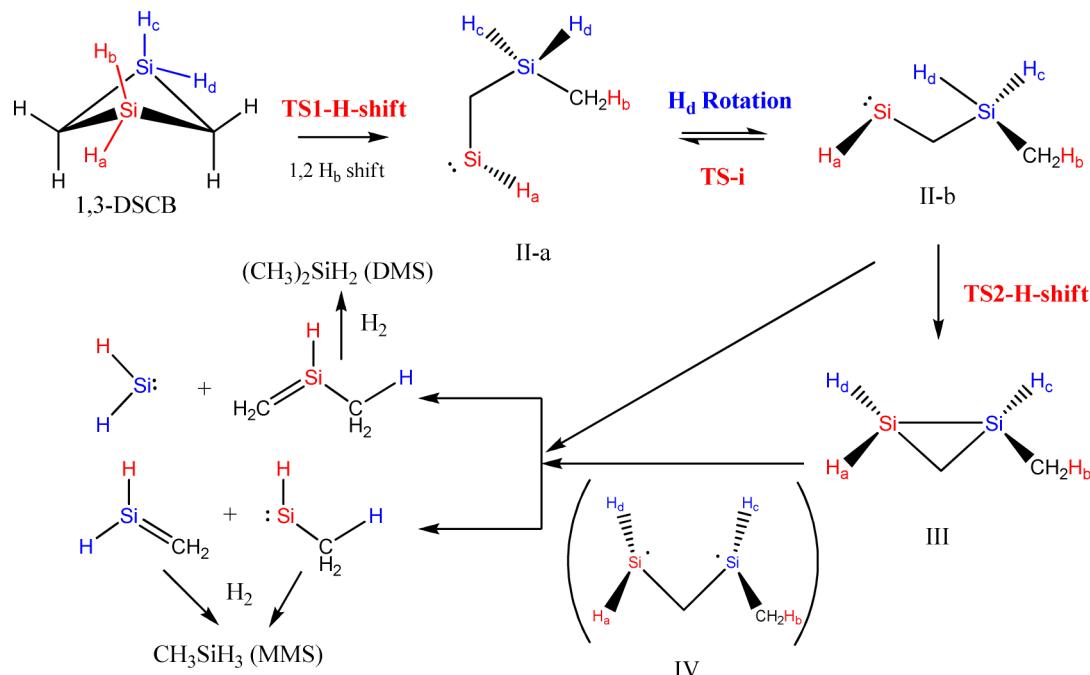
kcal/mol (by CASPT2/6-31G(d)).<sup>31</sup> The diradical intermediate (I) is 59.9 kcal/mol higher in energy than 1,3-DSCB. This is lower than the reported value of 66.7 kcal/mol calculated using MP4/TZ(d)//MP2/6-31G(d).<sup>26</sup> The dissociation of I into two silenes is found to be endothermic by 15.7 kcal/mol, in agreement with previous work<sup>26</sup> (12.2 kcal/mol at MP4/6-311G(d)//MP2/6-31G(d)). This is quite different from the behavior assumed by 1-SCB where the decomposition of the diradical intermediate into ethylene and silene is exothermic.

The transition state corresponding to the concerted  $2 + 2$  cycloreversion, TS-CR-C, is 77.3 kcal/mol higher in energy



**Figure 3.** Optimized structures of (a) 1-silylmethylsilene (SMS); (b) TS2b-CR-S; and (c) TS3-CR-S.

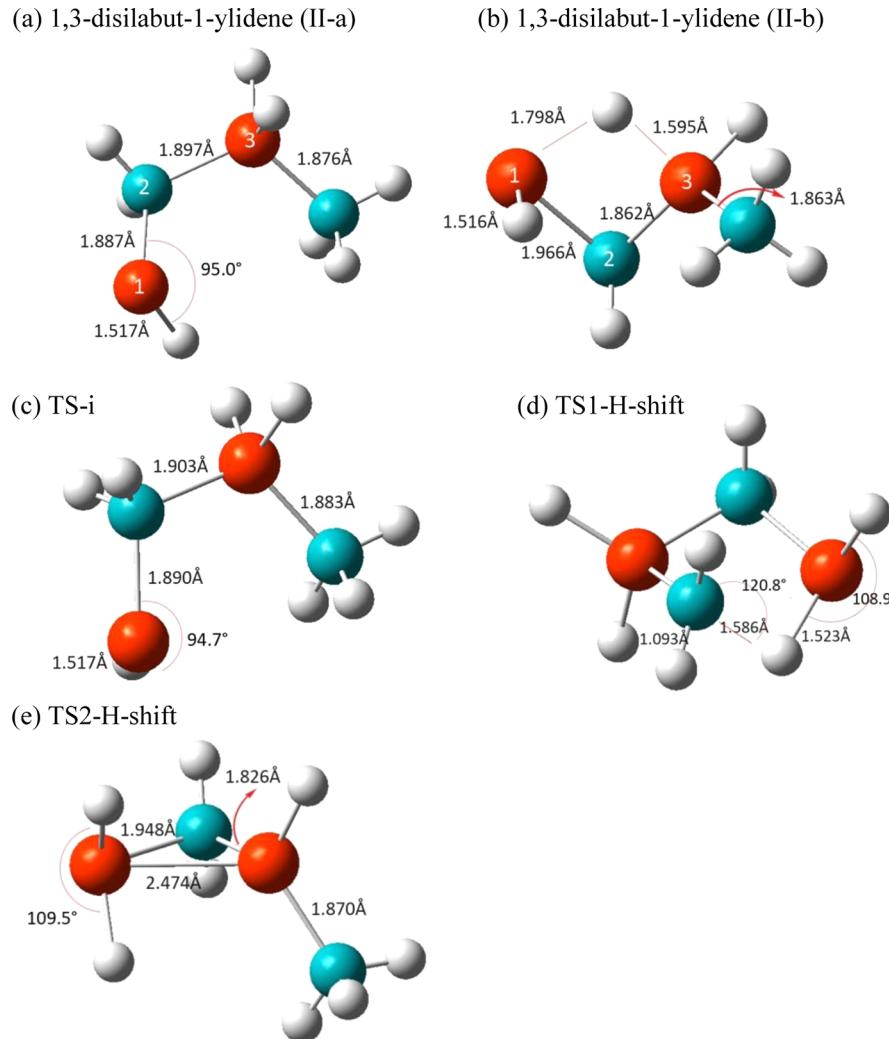
**Scheme 2. Ring-Opening of 1,3-DSCB Initiated by 1,2-H Shift**



than 1,3-DSCB. This is significantly higher than the energy barrier for the ring-opening to form I, which is determined to be 66.1 kcal/mol. Since the scaled ZPE corrections are included in the energy values, the activation barrier value reported here represents more precisely the activation enthalpy at 0 K, denoted as  $\Delta H_0^\ddagger$ . From the diradical intermediate I, an activation enthalpy of 20.6 kcal/mol needs to be provided to form the final product of two silenes. The values of activation enthalpies obtained in this work clearly demonstrates that the stepwise cycloreversion of 1,3-DSCB is favored kinetically over the concerted route, in good agreement with the observations for 1-SCB<sup>34</sup> and cyclobutane.<sup>27,28</sup>

In addition to the formation of silenes from the diradical intermediate I discussed above, we found an alternative pathway from I, which proceeds by a 1,3-H shift from Si to Si, leading to the formation of 1-silylmethylsilene (SMS)

(Figure 3a) via a transition state labeled as TS2b-CR-S (Figure 3b). A 1,3-H shift between the two Si atoms in SMS and the cleavage of the central Si–C bond produces the same two silenes as in the cycloreversion through a transition state labeled as TS3-CR-S (Figure 2c). As shown in Figure 2, the transition state, TS2b-CR-S, is lower by 5.2 kcal/mol in energy than TS2a-CR-S. However, the barrier for the decomposition of SMS into two silenes is quite high at 55.4 kcal/mol. It should be noted that the energy of SMS is significantly lower by 48.2 kcal/mol than those of two silenes. On the basis of our calculations, the formation of SMS should be favored both kinetically and thermodynamically over that of the two silenes from the diradical intermediate I. Unfortunately, no experimental data on this point can be found in the literature. Silicon is known to be reluctant to make  $p_\pi$ – $p_\pi$  bonds.<sup>1</sup> The relative stability of SMS is attributed to the fact that it contains only



**Figure 4.** Optimized structure of (a) 1,3-disilabut-1-ylidene (II-a); (b) 1,3-disilabut-1-ylidene (II-b); (c) TS-i; (d) TS1-H-shift; and (e) TS2-H-shift.

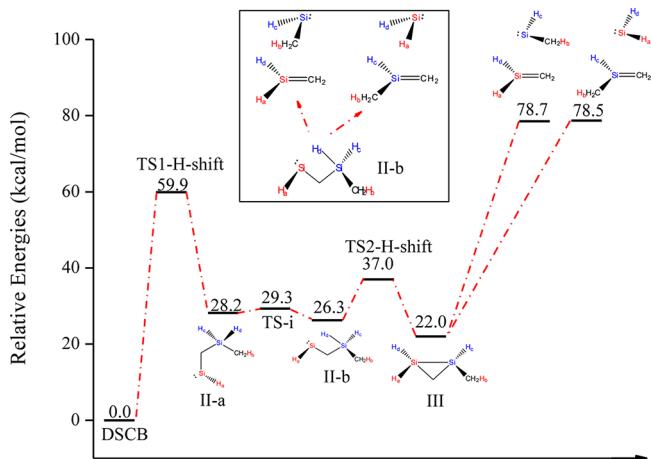
one Si=C double bond, in comparison to the two Si=C bonds in the two silenes.

**Ring-Opening by 1,2-H shift.** The decomposition of 1,3-DSCB initiated by a 1,2-H shift from Si to C accompanied by simultaneous ring-opening was first proposed by Auner et al.<sup>14</sup> As illustrated in Scheme 2, an H shift from one of the two Si atoms to the adjacent C atom leads to the formation of an open-chain silylene, 1,3-disilabut-1-ylidene (II-a, Figure 4a).

Using our calculation method, a slightly more stable isomer of II-a has been found and is labeled II-b (Figure 4b). In II-b, an H atom is almost centered between Si<sub>1</sub> and Si<sub>3</sub> and is involved in  $\sigma$ -interaction with the empty p-orbital at Si<sub>1</sub>. We have located the transition state (TS-i, Figure 4c) for the isomerization between II-a and II-b and found the isomerization barrier to be 1.1 kcal/mol. TS-i has a low imaginary frequency of 95.62 cm<sup>-1</sup>, which accounts for the low barrier between II-a and II-b since the isomerization involves simple H rotation around Si<sub>3</sub>. II-b can cyclize into the disilacyclopropane intermediate (III) via  $\beta$ -insertion reactions. The dissociation of III into two pairs of silene and silylene species is believed to proceed through a 1,3-diradical intermediate (IV) as proposed by Auner et al.<sup>14</sup> Monomethylsilane (MMS) and dimethylsilane (DMS) can be formed from silene/silylene species in the presence of molecular hydrogen as illustrated in Scheme 2. Production of MMS and DMS was observed in both pyrolysis<sup>3,14</sup> and

photolysis<sup>11</sup> of 1,3-DSCB. Although the formation of MMS can also be attributed to the silene produced from the 2 + 2 cycloreversion process, the formation of DMS, however, provides experimental evidence for the occurrence of ring-opening by a 1,2-H shift. We have located the transition state for the simultaneous 1,2-H shift and ring-opening, and it is labeled as TS1-H-shift (Figure 4d). The imaginary frequency of 1224.91 cm<sup>-1</sup> for TS1-H-shift corresponds to H migration from Si to the adjacent C atom as expected. Meanwhile, the transition state connecting II-b and III, labeled as TS2-H-shift (Figure 4e), was also located.

For the decomposition of the intermediate III into the two degenerate pairs of silene and silylene species, we were unable to locate any transition states. It is known that silylene insertion into an olefin proceeds with no energy barrier at the MP2 level of theory.<sup>38,39</sup> We mapped the PES for both the silylene (:SiH<sub>2</sub>) insertion to 1-methylsilene and methylsilylene (:SiH(CH<sub>3</sub>)) to silene. In both cases, the reactants form the cyclic intermediate III with no barrier, in agreement with what has been suggested for the insertion of silylene to propene.<sup>38,39</sup> Interestingly, we found that this type of insertion can produce either disilacyclopropane III or the open-chain silylene II-b, depending on the initial orientation of the two reactants. The two different orientations are illustrated in Figure 5. In the first orientation, the two substituents on Si in the silylene reactants



**Figure 5.** Energy level diagram for the ring-opening of 1,3-DSCB initiated by 1,2-H shift (Scheme 2). Energy values represent the relative enthalpies in kcal/mol at 0 K (ZPE corrections included).

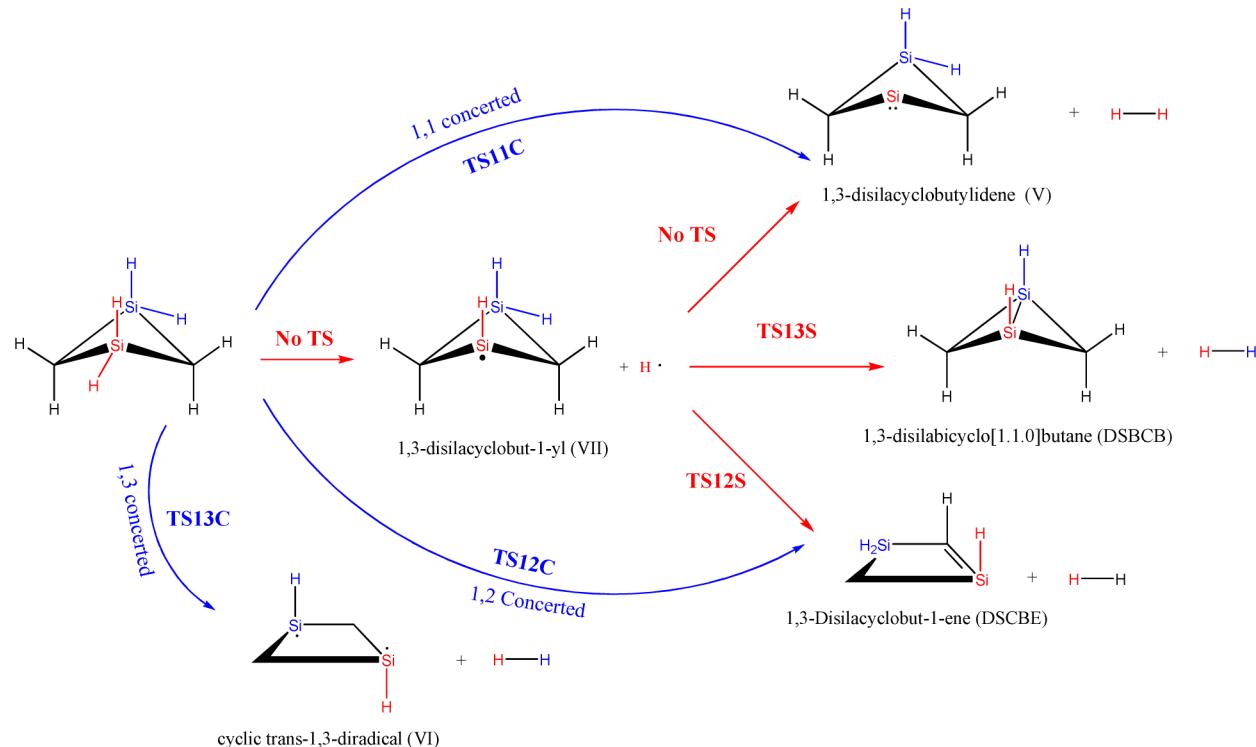
are directed away from the doubly bonded Si in silenes. In this orientation, a Si–Si single-bond forms first due to the proximity of the two Si atoms and results in the formation of the cyclic intermediate III. However, if the two substituents in silylenes are directed toward the doubly bonded silicon (see inset of Figure 5), an H atom fell between the two Si atoms and started interacting with the  $\pi$ -system. This orientation leads to the formation of II-b. To the best of our knowledge, the insertion of small silylene ( $:SiH_2$  or  $:SiH(CH_3)$ ) into silene ( $(CH_3)_2HSi=CH_2$  or  $H_2Si=CH_2$ ) to form an open-chain 1,3-disilabut-1-ylidene (II-b) has never been reported before. As mentioned previously, the decomposition of III into two pairs of the silylene/silene species was proposed to occur through the diradical intermediate IV.<sup>14</sup> We have optimized IV on both

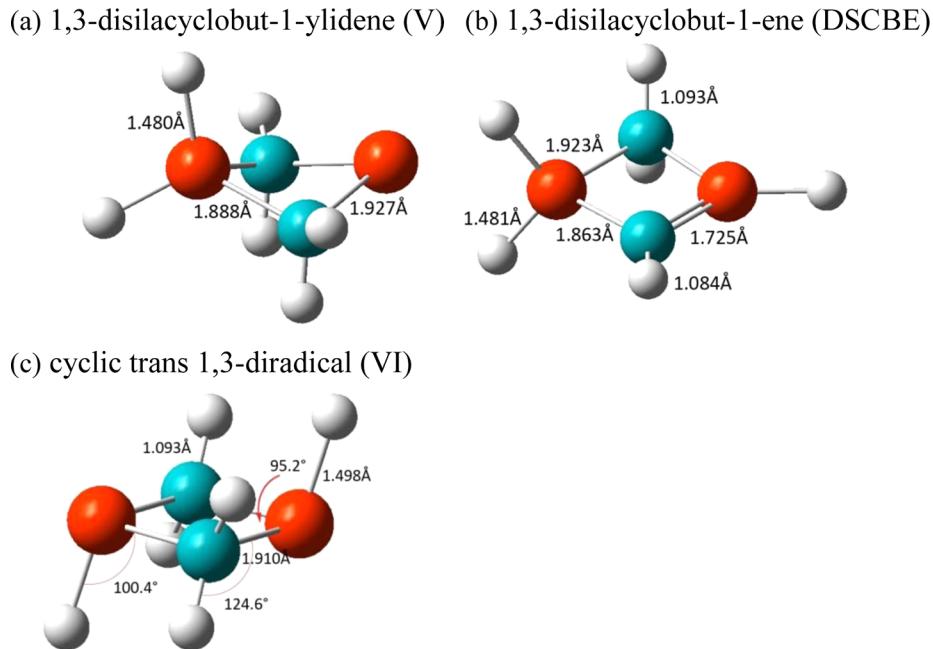
singlet and triplet surfaces and found the Si–Si distance to be 2.752 and 3.209 Å, respectively. Their energies are equal to 41.9 and 54.8 kcal/mol, respectively, above that of DSCB. However, diradical IV has not been located on the PES connecting III with the final products. On the basis of these arguments, we propose that both II-b and III can decompose with no energy barrier to form two degenerate pairs of silylene and silene species. Since III is 4.3 kcal/mol lower than II-b, formation of III is thermodynamically favored.

Figure 5 also shows the energy level diagram for all reactions illustrated in Scheme 2. The overall reaction of 1,3-DSCB decomposition into methylsilylene/silene and silylene/1-methylsilene is endothermic by 78.7 and 78.5 kcal/mol, respectively. This is only slightly higher than the corresponding value of 75.6 kcal/mol for 2 + 2 cycloreversion. The activation enthalpy required to reach the transition state, TS1-H-shift, is determined to be 59.9 kcal/mol. In the study of 1,3-DSCB pyrolysis by Auner and co-workers,<sup>14</sup> the apparent activation energy is measured to be  $230 \pm 4$  kJ/mol (i.e.,  $55 \pm 1$  kcal/mol). Although this activation energy value is not necessarily the same as the one for the formation of the open-chain silylene (II-a) via ring-opening/1,2-H shift. The closeness of our calculated value of 59.9 kcal/mol to the experimental value of 55 kcal/mol suggests that the ring-opening/1,2-H shift is the rate-determining step in the pyrolysis to form DMS and MMS, which were observed as the main products in the experiment.

The activation enthalpy of 59.9 kcal/mol is lower than the value of 66.1 kcal/mol for ring-opening to form 1,4-diradical intermediate (I) in the stepwise cycloreversion. Therefore, the ring-opening of 1,3-DSCB by 1,2-H shift is kinetically favored over the stepwise 2 + 2 cycloreversion. This explains why 1,2-H shift with ring-opening is the main decomposition route in the pyrolysis of 1,3-DSCB as observed in the experiments.<sup>3,14</sup> Similar results were obtained from the theoretical investigation

### Scheme 3. Stepwise and Concerted 1,1-, 1,2-, 1,3-H<sub>2</sub> Elimination Reactions of DSCB





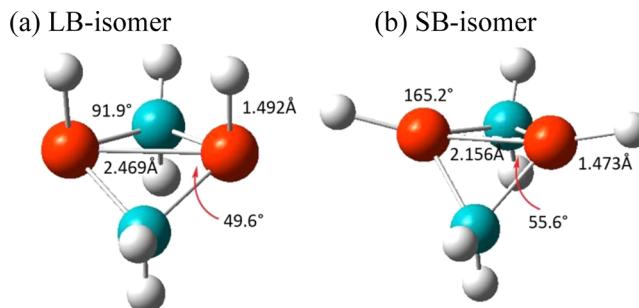
**Figure 6.** Optimized structure of (a) 1,3-disilacyclobut-1-ylidene (V); (b) 1,3-disilacyclobut-1-ene (DSCBE); and (c) cyclic trans 1,3-diradical (VI) resulted, respectively, from the concerted 1,1-, 1,2-, and 1,3-H<sub>2</sub> elimination from 1,3-DSCB.

of decomposition pathways of 1-SCB,<sup>34</sup> where the formation of propylsilylene by 1,2-H shift was determined to be kinetically favorable to the cycloreversion. For 1-SCB, the former is also thermodynamically favored, whereas, for 1,3-DSCB, the two routes are almost equally endothermic.

**1,1-, 1,2-, and 1,3-H<sub>2</sub> Eliminations.** Scheme 3 shows the different pathways to eliminate H<sub>2</sub> from 1,3-DSCB, including 1,1-, 1,2-, and 1,3-H<sub>2</sub> elimination. All three pathways can take place in either a single concerted or a stepwise mechanism. Aside from H<sub>2</sub>, the concerted 1,1-, 1,2-, and 1,3-H<sub>2</sub> eliminations produce 1,3-disilacyclobut-1-ylidene (V), 1,3-disilacyclobut-1-ene (DSCBE), and a cyclic 1,3-diradical (VI), respectively. Their optimized structures are shown in Figure 6. The cyclic silylene species V appeared to be more puckered (puckering dihedral angle = 32.3°) than the parent 1,3-DSCB molecule (25.5°). Meanwhile, both DSCBE and VI are planar. In VI, the two H attached to Si<sub>1</sub> and Si<sub>3</sub> are oriented in a trans-position. The Si=C double bond in the optimized DSCBE is 1.725 Å. This is compared to the experimental value obtained for Si=C of 1.83 ± 0.04 Å<sup>1</sup> in 1,1-dimethylsilene using electron diffraction and microwave spectroscopy.

The stepwise 1,1-, 1,2-, and 1,3-H<sub>2</sub> eliminations all start with the rupture of one of the Si–H bonds to form a 1,3-disilacyclobut-1-yl radical (VII) and an H atom. The H atom then captures a second H bonded to Si<sub>1</sub>, or a neighboring C, or Si<sub>3</sub> to form the final products. It is noted that the stepwise 1,1- and 1,2-H<sub>2</sub> eliminations yield the same products as the concerted mechanisms.

However, the stepwise 1,3-H<sub>2</sub> elimination produces 1,3-disilabicyclo[1.1.0]butane (DSBCB), rather than the cyclic trans-1,3-diradical. Two isomers were found for DSBCB, and Figure 7 shows their optimized structures. The two isomers differ mainly in the Si–Si bridge bond distance and the orientations of the two H atoms on the bridging silicons. At the MP2/6-311++G(d,p) level of theory, the Si–Si bond distance was found to be 2.469 and 2.156 Å for the two isomers, denoted correspondingly as the long-bond (LB) and short-

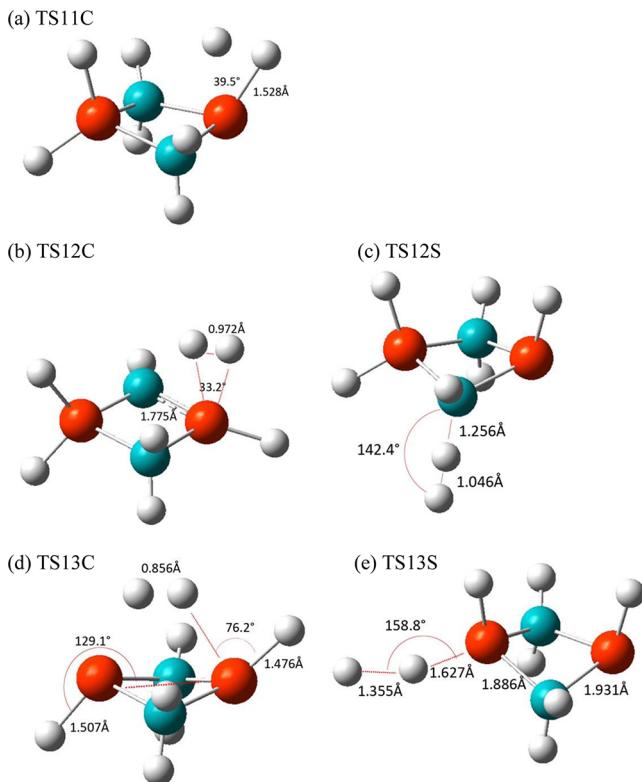


**Figure 7.** Optimized structures of 1,3-disilabicyclo[1.1.0]butane (DSBCB): (a) LB-isomer and (b) SB-isomer.

bond (SB) isomers. The values are close to those of 2.503 and 2.189 Å obtained by Boatz et al.<sup>40</sup> at the GVB/6-31G(d) level of theory. The Si<sub>1</sub>–Si<sub>3</sub> bridge bond distance was calculated to be 2.136 Å in the optimized geometry of DSBCB using SCF/CEP-31G(d) by Kitchen et al.<sup>41</sup> On the basis of our calculation, this is believed to be for the SB isomer. Bond stretch isomerism in DSBCB has been theoretically investigated in several studies.<sup>40–43</sup> These studies agreed on the relative stability of the LB isomer of DSBC to the SB isomer. Our calculations show that the LB isomer is 22.4 kcal/mol lower in energy than the SB isomer. This is in good agreement with the previously reported value of 23.0 kcal/mol obtained at the GVB/6-31G(d)/GVB/3-21G(d) level of theory.<sup>40</sup> The relative stability of the LB-isomer to the SB-isomer became evident when the first synthesized 1,3-disilabicyclo[1.1.0]butane derivative reported in 2001<sup>44</sup> was proven to have characteristics of the LB isomer. The X-ray single crystal analysis showed the distance of the Si–Si bridge bond to be 2.412(1) Å in the derivative.

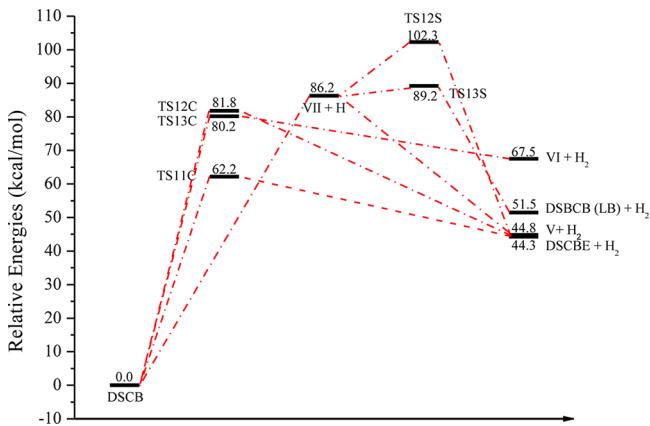
The first step in the stepwise mechanism involves the homolytic cleavage of the Si–H to produce two radicals and was found to proceed with no transition state. The transition states for the second steps in the stepwise 1,2- and 1,3-

eliminations have been located, and they are labeled as TS12S and TS13S, respectively. The hydrogen atom abstracts an H from Si<sub>1</sub> in VII without an activation barrier to form V. The corresponding transition states for the concerted 1,1-, 1,2-, and 1,3-H<sub>2</sub> eliminations are labeled as TS11C, TS12C, and TS13C, respectively. The optimized structures for these five transition states involved in the H<sub>2</sub> eliminations are shown in Figure 8.



**Figure 8.** Optimized structures of the transition states for the H<sub>2</sub> elimination from 1,3-DSCB. (a) TS11C; (b) TS12C; (c) TS12S; (d) TS13C; and (e) TS13S.

Figure 9 shows the energy level diagram for the six reactions leading to H<sub>2</sub> elimination. All reactions are endothermic. The



**Figure 9.** Energy level diagrams for the 1,1-, 1,2-, and 1,3-H<sub>2</sub> elimination pathways of DSCB (Scheme 3). For each pathway, both stepwise and concerted mechanisms were investigated. Energy values represent the relative enthalpies in kcal/mol at 0 K (ZPE corrections included).

products for 1,1- and 1,2-elimination, i.e., 1,3-disilacyclobut-1-ylidene (V) + H<sub>2</sub> and DSCBE + H<sub>2</sub>, have similar energies. They are found to be 44.8 and 44.3 kcal/mol, respectively, higher in energy than 1,3-DSCB. We have shown that the concerted and stepwise 1,3-H<sub>2</sub> eliminations produce two different products: the cyclic *trans*-1,3-diradical (VI) and DSBCB. When examining the IRC of the concerted pathway, it is found that, when the two H atoms detach from the two diagonal Si atoms, the remaining two H's occupy the trans position due to the steric factors. Alternatively, in the stepwise pathway, the H radical approaches the 1,3-disilacyclobut-1-yl radical (VII) that has two H atoms in axial positions. This leads to the final conversion to the bicyclo-product. Orbital hybridization and the formation of a relatively stable Si–Si single bond (in the LB isomer) are the driving forces in forming DSBCB in the stepwise mechanism. The LB isomer of DSBCB is found to be 16.0 kcal/mol lower in energy than VI. Among the three transition states for the concerted routes, the energy of TS11C is the lowest at 62.2 kcal/mol relative to 1,3-DSCB. TS12C and TS13C lies, respectively, at 81.8 and 80.2 kcal/mol, above 1,3-DSCB. The first step in the stepwise mechanism requires an energy of 86.2 kcal/mol for the rupture of the Si–H bond to form two radicals from which a respective energy barrier of 0.0, 16.1, and 3.0 kcal/mol is needed for the second step in 1,1-, 1,2-, and 1,3-eliminations. Therefore, the concerted H<sub>2</sub> eliminations are favored kinetically over the stepwise ones as a whole, with concerted 1,1-elimination being the most favorable of all. Thermodynamically, 1,1- and 1,2-eliminations are almost equally less endothermic than the 1,3-elimination.

As mentioned in the Theoretical Methods section, an additional PES scan along the IRC using CCSD(T)/6-311++G(3d,2p) was performed to validate the structures of the transition states obtained at MP2/6-311++G(d,p) level of theory. It was found that the energy profiles of the transition states TS11C, TS12C, TS13C, TS-CR-C, TS1-H-shift, TS-i, TS2-H-shift, and TS3-CR-S at the CCSD(T) level were similar to the ones at the MP2 level in the sense that the highest point in the PES has the same geometry. On the contrary, the transition states TS1-CR-S, TS2a-CR-S, TS2b-CR-S, TS12S, and TS13S have shown deviation in the PES when using CCSD(T) as compared to MP2. It is noted that all transition states with deviation in the optimized geometry at the CCSD(T) level correspond to stepwise reactions and therefore relate to free radicals at one side of the reaction. MP2, being a perturbation method, is known to overestimate the bond lengths for species involving excitation into antibonding orbitals. This leads to overestimated bond lengths between H and heavy atoms. The CCSD(T) method avoids this enigma and calculates more accurate bond lengths, which lead to tighter transition states.

**Reaction Kinetics and Thermochemistry.** The activation enthalpies ( $\Delta H_0^\ddagger$ ) and reaction enthalpies ( $\Delta H_0$ ) for the various decomposition pathways of 1,3-DSCB studied in this work are listed in Tables 1 and 2, respectively. The subscript 0 indicates the enthalpy values calculated at 0 K. It is clear that the concerted ring-opening and 1,2-H shift to form the open-chain silylene (II-a) has the lowest activation barrier (59.9 kcal/mol) of all; this is followed closely by the concerted 1,1-H<sub>2</sub> elimination at 62.2 kcal/mol. The activation barrier for the stepwise 2 + 2 cycloreversion is 11.2 kcal/mol lower than the concerted one. The highest activation barrier of 86.2 kcal/mol is found for the stepwise 1,1-, 1,2-, and 1,3-H<sub>2</sub> eliminations and corresponds to the breaking of the Si–C bond. The concerted

**Table 1. Enthalpies, Entropies, and Gibbs Free Energies of Activation for the Various Decomposition Pathways of 1,3-DSCB**

	transition state	$\Delta H_0^\ddagger$ (kcal/mol)	$\Delta H_{298}^\ddagger$ (kcal/mol)	$T\Delta S_{298}^\ddagger$ (kcal/mol)	$\Delta G_{298}^\ddagger$ (kcal/mol)
concerted cycloreversion	TS-CR-C	77.3	78.5	3.7	74.8
stepwise cycloreversion <sup>a</sup>	TS1-CR-S	66.1	66.6	1.8	64.7
ring-opening with 1,2-H shift <sup>b</sup>	TS1-H-shift	59.9	59.9	0.6	59.3
concerted 1,1-H <sub>2</sub> elimination	TS11C	62.2	62.1	0.2	61.9
concerted 1,2-H <sub>2</sub> elimination	TS12C	81.8	81.7	0.3	81.4
concerted 1,3-H <sub>2</sub> elimination	TS13C	80.2	80.1	0.0	80.1
stepwise 1,1-, 1,2-, and 1,3-H <sub>2</sub> elimination <sup>c</sup>		86.2	86.1	0.5	85.6

<sup>a</sup>The first step in the stepwise cycloreversion to form the 1,4-diradical, I. <sup>b</sup>The first step in the ring-opening initiated by 1,2-H shift to form II-a. <sup>c</sup>The first step in the stepwise H<sub>2</sub> elimination involving Si-H bond cleavage to form VII and H radicals.

**Table 2. Reaction Ethalpies, Entropies, and Gibbs Free Energies for the Various Decomposition Pathways of 1,3-DSCB**

	products	$\Delta H_0$ (kcal/mol)	$\Delta H_{298}$ (kcal/mol)	$T\Delta S_{298}$ (kcal/mol)	$\Delta G_{298}$ (kcal/mol)
concerted/stepwise cycloreversion	two silenes	75.6	77.5	13.5	64.0
stepwise cycloreversion	SMS	27.4	28.4	3.1	25.2
ring-opening/1,2-H shift	II-a	28.2	29.1	3.0	26.1
concerted/stepwise 1,1-H <sub>2</sub> elimination	V + H <sub>2</sub>	44.8	46.6	9.2	37.5
concerted/stepwise 1,2-H <sub>2</sub> elimination	DSCBE + H <sub>2</sub>	44.3	46.1	9.0	37.1
concerted 1,3-H <sub>2</sub> elimination	VI + H <sub>2</sub>	67.5	69.2	8.8	60.4
stepwise 1,3-H <sub>2</sub> elimination	DSBCB (LB) + H <sub>2</sub>	51.5	53.2	8.3	44.8

1,3- and 1,2-H<sub>2</sub> eliminations are also hindered by relatively high barriers at 80.2 and 81.8 kcal/mol, respectively. All reactions studied in this work are endothermic in nature. A comparison of the reaction enthalpy values shows that the stepwise cycloreversion to form SMS, the newly discovered route, and concerted ring-opening and 1,2-H shift to form II-a are the least endothermic. The 2 + 2 cycloreversion to form two silenes has the highest positive reaction enthalpy of 75.6 kcal/mol.

In order to gain insights into the kinetic and thermodynamic competitions among the different decomposition channels, we calculated the activation enthalpies ( $\Delta H_{298}^\ddagger$ ) along with the entropies ( $\Delta S_{298}^\ddagger$ ) and free Gibbs energies ( $\Delta G_{298}^\ddagger$ ) of activation at room temperature (Table 1). The thermochemical parameters, including  $\Delta H_{298}$ ,  $\Delta S_{298}$ , and  $\Delta G_{298}$  (Table 2), were also calculated. An increase in temperature from 0 to 298 K does not change the sequence of the activation enthalpy and reaction enthalpy for the different decomposition pathways. It is noted that all the entropies of activation are positive since they are decomposition reactions. The concerted cycloreversion reaction shows a relatively high  $T\Delta S_{298}^\ddagger$  value of 3.7 kcal/mol due to the loose structure of the transition state. In contrast,  $T\Delta S_{298}^\ddagger$  for the H<sub>2</sub> elimination reactions have lower values originating from the tight nature of their transition states. Comparison of the values of  $\Delta H_{298}^\ddagger$  with  $T\Delta S_{298}^\ddagger$  suggests a clear dominance of the enthalpy term in the contribution to the free Gibbs energies of activation. The concerted ring-opening and 1,2-H shift to form II-a has the lowest  $\Delta G_{298}^\ddagger$ , in line with the results that it also has the lowest  $\Delta H_{298}^\ddagger$ .

In terms of the thermochemical parameters in Table 2, the  $T\Delta S_{298}$  values, in general, show increases as compared to the  $T\Delta S_{298}^\ddagger$  since one reactant molecule decomposes to form two species as products. Two exceptions are stepwise cycloreversion to form SMS and ring-opening/1,2-H shift to form II-a, which show the lowest  $T\Delta S_{298}$  of all. Therefore, the  $\Delta G_{298}$  values are lower than the  $\Delta H_{298}$  for all reactions studied. However, the relative comparison in the magnitude for the different reactions does not change. The stepwise cycloreversion to form SMS and ring-opening/1,2-H shift to form II-a are still the least endergonic. According to our calculations of the  $\Delta H_{298}^\ddagger$ /

$\Delta G_{298}^\ddagger$  and  $\Delta H_{298}/\Delta G_{298}$ , the ring-opening by 1,2-H shift is the most kinetically and thermodynamically favorable decomposition pathway at 298 K.

## CONCLUSIONS

The three main decomposition pathways of 1,3-DSCB, including 2 + 2 cycloreversion, ring-opening initiated by 1,2-H shift, and H<sub>2</sub> elimination, have been examined in this work using ab initio methods at the CCSD(T)/6-311++G(3d,2p)//MP2/6-311++G(d,p) level of theory. Both concerted and stepwise 2 + 2 cycloreversion mechanisms were explored. It is found that the structures of the transition states for the concerted and the stepwise pathways resemble closely those reported for the head-to-tail and head-to-head dimerization, respectively. This supports the previous conclusion drawn from the investigations of the 2 + 2 cycloaddition that the head-to-head dimerization occurs via a diradical intermediate whereas the head-to-tail dimerization is concerted in nature. The activation enthalpy at 0 K for the stepwise 2 + 2 cycloreversion determined at 66.1 kcal/mol is significantly lower than the corresponding value of 77.3 kcal/mol for the concerted route. Therefore, our calculations demonstrate unambiguously that the stepwise cycloreversion is favored over the concerted one. From the 1,4-diradical intermediate I formed in the stepwise mechanism, an alternative and new pathway was found to form 1-silylmethylsilene (SMS). This pathway is kinetically competitive with and thermodynamically much more favorable to the decomposition of I to form two silenes. Our study on the ring-opening/1,2-H shift has shown two isomers of 1,3-disilabut-1-ylidene, II-a and II-b, exist, and it is from II-b that cyclization occurs to form disilacyclopropane via  $\beta$ -insertion. It has also been demonstrated that both 1,3-disilabut-1-ylidene (II-b) and disilacyclopropane (III) decompose to silene/methyl-silylene or methylsilene/silylene with no energy barriers. For 1,1-, 1,2-, and 1,3-H<sub>2</sub> eliminations from 1,3-DSCB, we have shown that concerted H<sub>2</sub> eliminations are favored over the stepwise ones in general, with the concerted 1,1-H<sub>2</sub> elimination being the most favorable one of all ( $\Delta H_0^\ddagger = 62.2$  kcal/mol). Thermodynamically, 1,1- and 1,2-H<sub>2</sub> elimi-

nations are almost equally less endothermic than the 1,3-H<sub>2</sub> elimination.

A detailed kinetic and thermochemical analysis of all reactions studied in this work was performed by calculating the enthalpy ( $\Delta H^\ddagger$ ), entropy ( $\Delta S^\ddagger$ ), and Gibbs free energy ( $\Delta G^\ddagger$ ) of activation along with the reaction enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ), and free Gibbs energy ( $\Delta G$ ) both at 0 K and at the room temperature of 298 K. The ring-opening of 1,3-DSCB initiated by 1,2-H shift to form an open-chain silylene (II-a) is demonstrated to be the most kinetically and thermodynamically favorable decomposition pathway, both at 0 and 298 K. This agrees very well with the general experimental observations that this route was the main decomposition channel in the pyrolysis of 1,3-DSCB.<sup>3,14</sup>

This work provides a comprehensive model for the decomposition of 1,3-DSCB in the gas phase. This will shape the framework for future experimental and theoretical studies of the 1,3-DSCB decompositions at higher temperatures. The calculated thermochemical parameters, together with the enthalpy and Gibbs free energy of activation, can be used in building a model for kinetic simulations needed to understand the pyrolysis experiments and to optimize the CVD processes using 1,3-DSCB as a precursor gas to produce high-quality silicon carbide thin films.

## ■ ASSOCIATED CONTENT

### S Supporting Information

Structures of the transitions states and products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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