Interaction between Ethylene and Silene and the Possible Existence and Stability of Intermediates in the Thermal Decomposition Reaction of Silacyclobutane

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CASSCF(4,4), MR-CI and CASSCF(4,4)+MP2 calculations using the basis sets 3-21G* and 6-31G* have been performed in a study of the reaction between ethylene and silene. A cyclic transition state for the interaction leading on one side to a planar silacyclobutane transition state (TS), which falls to ground-state puckered silacyclobutane, and on the other side to a trans diradical having strict C_s symmetry has been found in this multistep process. At the highest calculational level the energy of this TS is 26.9 kcal/mol above a supermolecule consisting of noninteracting ethylene and silene molecules. The trans diradical and its gauche form have about the same energy, viz., 15.8 and 16.7 kcal/mol, respectively, above the same reference. The TS for fragmentation of the trans form to ethylene and silene is 16.0 kcal/mol above this reference and is 2.4 kcal/mol lower than the barrier to interconversion between the trans and the gauche forms. Size-consistency corrections to the MR-CI results are of great importance for semiquantitative estimates of energies. A symmetry analysis of the potential surface shows our proposed reaction paths are consistent.

Introduction

The gas-phase pyrolysis of silacyclobutane produces ethylene, propene, silene ($H_2C{=}SiH_2$), silylene (SiH_2), and methylsilylene.[1] The presence of the reactive silicon intermediates has been confirmed by butadiene trapping. A mechanism for this reaction has been suggested on the basis of a pyrolysis study of 1,1-dideuteriosilacyclobutane.[2] The distribution of deuterium in the reaction products led to the suggestion that thermal decomposition is initiated by a 1,2-migration of D from Si to C, producing *n*-propylsilylene, which subsequently forms a silacyclopropane before decomposing to silylene and propene.

Prior to the deuterium migration mentioned above it is conceivable that diradicals may be formed as a result of homolytic cleavages of ring bonds, notwithstanding that very recent calculations by one of us[3,4] on silacyclopropanes indicated that a concerted ring opening and hydrogen migration have a lower energy than that of the diradicals formed by ring opening alone. Furthermore, a comparison of the behavior of these diradicals with tetramethylene is chemically interesting, since silicon is a congener of carbon. The potential surface for tetramethylene rearrangements and fragmentations has been studied extensively by theoretical methods,[5] in contrast to the species considered here for which no theoretical studies are available.

The decomposition reaction of silacyclobutane is also of interest, since one of its possible reverse channels is an addition of ethylene to silene. The related head-to-tail cycloaddition of two silene molecules has been studied in two recent papers.[6,7] According to the Woodward−Hoffmann orbital symmetry rules,[8] a $[2\pi_s + 2\pi_s]$ cycloaddition maintaining C_{2h} symmetry for this system is forbidden. This implies a substantial reaction barrier that would favor a diradical mechanism. However, in the study by Schaefer and co-workers[6] a transition state of C_{2h} symmetry was found at SCF, CISD, and CCSD levels. They interpreted their results in terms of a relaxation of the Woodward−Hoffmann symmetry rules caused by polarization of the silicon−carbon bond, a rationale also invoked in other contexts.[9−11] Their conclusion, however, is in conflict with results of Bernardi and co-workers[7] who find that in MCSCF calculations the C_{2h} stationary point is not a transition state and that the ring closure occurs along a multistep path involving diradicals. Thus, the topology of the potential surface and concomitantly the predicted mechanism for this reaction appears to depend qualitatively on the calculational approach chosen.

The addition of ethylene to silene investigated in the present study is different in the sense that it has a gradient path of C_s symmetry with no symmetry operation linking the two reacting units. Chemically, however, it is related to the system consisting of two silene units, since one of the two polarized Si−C bonds is retained.

The purpose of the present study is to scrutinize the potential surface for the gradient path addition of ethylene to silene, and to search for the diradicals mentioned above. Estimates of energy barriers along the reaction paths connecting the various stationary points on the potential surface will be made. To our knowledge these reactions have not been studied previously by theoretical calculations.

Computations

Geometry optimizations using CASSCF/3-21G* were carried out for all the species included in the study. For one test case discussed in the next section an optimization at the CASSCF/6-31G* level was also done. The active space consisted of the four electrons and the four orbitals constituting the supermolecular π system of the noninteracting fragments silene and ethylene. This choice secures a correct description of the dissociation to the two interacting units. Furthermore, it gives a sufficiently flexible description of the diradical nature of the intermediates studied. Except for the symmetry constraints as indicated for some of the species, all $3N - 6$ internal coordinates were relaxed in all optimizations. Analytical vibrational frequencies were evaluated for all stationary points using CASSCF/3-21G* calculations. Thus, all reported stationary points on the surface were properly characterized. One of the

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TABLE 1: Total Energies (in au) at Various Calculational Levels

molecule	CASSCF(4,4) 3-21G*	CASSCF(4,4) 6-31G*	MR-CI[a] 6-31G*	CASSCF(4,4)+MP2 6-31G*	ZPE[b]	imaginary frequency[b]
$H_2Si{=}CH_2/H_2C{=}CH_2$, **6**	−405.049 58	−407.122 82	−407.496 68	−407.550 51	60.85	
	6		−407.555 03(D)			
			−407.564 64(S)			
			−407.568 68(P)			
trans min, C_s, **2**	−405.030 55	−407.098 84	−407.465 47	−407.525 28	60.87	
			−407.531 27(D)			
			−407.543 30(S)			
			−407.549 34(P)			
gauche min, **1**	−405.028 95	−407.096 69	−407.46412	−407.523 43	60.51	
			−407.527 64(D)			
			−407.538 91(S)			
			−407.544 31(P)			
cyclic TS, C_s, **5**	−404.988 27	−407.058 94	−407.446 32	−407.505 74	62.08	997, a′
			−407.509 45(D)			
			−407.520 40(S)			
			−407.525 46(P)			
TS for fragm of trans form, C_s, **4**	−405.023 00	−407.092 66	−407.462 75	−407.524 63	61.08	721, a′
			−407.530 17(D)			
			−407.542 76(S)			
	4		−407.549 28(P)			
TS for trans−gauche reaction, **3**	−405.026 85	−407.096 45	−407.444 41	−407.520 99	60.73	80
			−407.517 88(D)			
			−407.532 83(S)			
			−407.541 57(P)			

[a] The symbols D, S, and P stand for size-consistency corrected values using corrections due to Davidson, Siegbahn, and Pople, respectively. [b] ZPE (unscaled, in kcal/mol) and imaginary frequencies (in cm^{-1}) by CASSCF/3-21G*.

transition states found, **5**, has a very complicated vibrational mode associated with the imaginary frequency. In this case the reaction was followed, in the CASSCF/3-21G* approximation, from transition state to neighboring stationary points along the intrinsic reaction coordinate (IRC)[12] defined in mass-weighted internal coordinates. At the stationary points, energies were calculated by CASSCF/6-31G* using the same active space.

To obtain energies corrected for dynamic electron correlation, we have also carried out multireference CI calculations (MR-CI) using the 6-31G* basis, including configurations having coefficients higher than 0.03 in the CASSCF calculations as reference configurations for the CI calculations. In the CI calculations the eight lowest orbitals, comprising 1s on carbon and 1s, 2s, and 2p on silicon and their virtual counterparts were excluded.

The MR-CI energies were corrected for size-consistency errors by using the three methods of Davidson,[13] of Siegbahn,[14] and of Pople.[15] To avoid problems related to the lack of size consistency of the MR-CI results and to gauge the different size-consistency corrections applied, CASSCF(4,4)+MP2 calculations using the 6-31G* basis were also carried out.

Predicted energy differences were corrected for zero-point vibrational energies obtained from CASSCF/3-21G* calculations using the same active space. These corrections were based on unscaled vibrational frequencies. The program systems Gaussian 92[16] and GAMESS-UK[17] were used throughout the calculations.

Computational Results

Total energies calculated at various levels are given in Table 1 where zero-point energies are also included. Table 2 gives energies relative to a supermolecule consisting of an ethylene and a silene molecule separated by a distance of 20 Å and indicated by $H_2C{=}CH_2/H_2Si{=}CH_2$ in the tables.

Figure 1 gives optimized geometries for all species included in the study.

1. Transition State 5. Transition state **5** with optimized geometry shown in Figure 1 lies on the multistep path from ethylene plus silene to silacyclobutane and has one imaginary frequency of a′ symmetry at 997 cm^{-1}. An optimization at the CASSCF(4,4)/6-31G* level gave a structure almost identical with that from the smaller basis (Figure 1) except that the one imaginary a′ frequency shifted to 1754 cm^{-1}. Accordingly, we decided to use the smaller basis in geometry optimizations of the remaining species in this study. The normal mode of the imaginary frequency appeared to be appropriate for a concerted ring closure. IRC following at the CASSCF(4,4)/3-21G* level confirmed a path toward a planar silacyclobutane ring **7**, itself a transition state (TS) having C_{2v} symmetry. The C_s symmetry of TS **5** was imposed on the gradient path, as required by the results of Pechukas.[18] The path following was terminated when the two C−C bond distances were 1.59 and 1.62 Å, and the two different Si−C distances were 1.89 and 1.93 Å, respectively. Further motion closer to C_{2v} symmetry would require an extension of the active space to CASSCF(8,8) to be consistent with the C_{2v} symmetry. An RHF optimization toward a stationary point starting at this point gave a smooth transition to the planar ring. The final structural parameters found for the heavy-atom skeleton of the ring were $R(C{-}C) = 1.59$ Å and $R(Si{-}C) = 1.89$ Å. This stationary point displayed one imaginary frequency of 94 cm^{-1}, the associated normal mode being a puckering of the ring. Thus, CASSCF calculations predict **5** to be a genuine transition state.

The one-electron density matrix associated with the active space gave the populations 1.98, 1.69, 0.32, and 0.02. These indicate that the electron distribution in the TS is somewhat distorted from one having doubly occupied orbitals. A Mulliken population analysis indicates a transfer of 0.32 electrons from silene to ethylene in the TS.

The energy of the transition state relative to the noninteracting complex chosen as reference (Table 2) confirms that inclusion of dynamic correlation reduces this energy from near 40 to 31.6 kcal/mol. The various size-consistency corrections applied agree rather well, the spread being about 1.5 kcal/mol. They all give a lowering of the barrier of approximately 4 kcal/mol. The CASSCF/MP2 combination, which is size-consistent, predicts

TABLE 2: Relative Energies (in kcal/mol) Obtained at Various Calculational Levels

molecule	CASSCF(4,4) 3-21G*	CASSCF(4,4) 6-31G*	MR−CI[a] 6-31G*	CASSCF(4,4)+MP2 6-31G*	ΔZPE[b]
$H_2Si{=}CH_2/H_2C{=}CH_2$, **6**	0.0	0.0	0.0 0.0(D) 0.0(S) 0.0(P)	0.0	0.0
trans min, C_s, **2**	11.94	15.05	19.58 14.91(D) 13.39(S) 12.14(P)	15.83	0.02
gauche min, **1**	12.94	16.40	20.43 17.19(D) 16.15(S) 15.29(P)	16.99	−0.34
cyclic TS, C_s, **5**	38.47	40.08	31.60 27.12(D) 27.76(S) 28.60(P)	28.09	−1.23
TS for fragm of trans form, C_s, **4**	16.68	18.92	21.29 15.60(D) 13.73(S) 12.17(P)	16.24	0.23
TS for trans−gauche reaction, **3**	14.26	16.55	32.80 23.31(D) 19.96(S) 17.01(P)	18.52	−0.12

[a] The symbols D, S, and P stand for size-consistency-corrected values using corrections due to Davidson, Siegbahn, and Pople, respectively. [b] ΔZPE (unscaled, in kcal/mol).

a value of 28.1 kcal/mol, in good agreement with the corrected CI values.

2. Trans Diradical $H_2C{-}H_2Si{-}CH_2{-}CH_2$ (2) and Its Fragmentation. Following the IRC from the transition state above led in the second direction to a *trans* diradical **2** having an equilibrium geometry of C_s symmetry and with two terminal CH_2 groups. The optimized structure of this species reveals a rather long internal Si−C bond of 1.95 Å. The bonds around the Si and the internal C atom are very close to tetrahedral.

The populations of the natural orbitals of the active space have the values 1.98, 0.02, 1.23, and 0.77, indicating an electron distribution characteristic of a diradical with the approximately singly occupied orbitals located at the terminal carbon atoms.

The relative energies given in Table 2 show that the dynamic correlation correction is less important in this species than in the reference complex, and the value increases from 15.1 to 19.6 kcal/mol using the 6-31G* basis. Energy corrections to the CI value all give sizable lowering of the relative energy. Furthermore, for this species the predicted lowering is found to be very dependent on the correction scheme chosen. The approach by Siegbahn based on many-body perturbation theory gives a value that is midway between those obtained by the methods of Davidson and of Pople. The CASSCF/MP2 method gives a value of 15.8 kcal/mol, which is slightly above the 14.9 kcal/mol from the Davidson correction.

Transition state **4** for fragmentation of this diradical to silene and ethylene has been located. Its optimized geometry, given in Figure 1, has a central Si−C bond length of 2.24 Å. The species shows C_s symmetry and one imaginary frequency of 721 cm^{-1}, which belongs to the a′ representation. The associated normal mode is dominated by a Si−C stretch. Populations of the natural orbitals, 1.98, 0.02, 1.23, and 0.77, of the active space demonstrate that the diradical character has been retained in the transition state.

The predicted barrier to fragmentation is 3.8 kcal/mol at the CASSCF(4,4)/6-31G* level. When corrected for dynamic correlation, the barrier is reduced to 1.7 kcal/mol. After introducing size-consistency corrections, we find TS **4** to be 0.7 kcal/mol above the trans minimum, using the Davidson correction. The alternative corrections lead to a virtually vanishing barrier, i.e., 0.3 kcal/mol using the Siegbahn approximation and 0.1 kcal/mol using the one due to Pople. The CASSCF/MP2 method predicts a value of 0.4 kcal/mol. By adding the ZPE correction to this value, we predict a final value of 0.6 kcal/mol. As shown in Table 1, the transition state maintains the C_s symmetry of the *trans* form with the single imaginary vibration having a′ symmetry. These calculations illustrate the problems connected with estimating small energy differences and lead us to the conclusion that if there is a barrier to fragmentation, it is very small.

In a recent paper[5f] the fragmentation barrier for the trans form of the tetramethylene diradical was calculated at the MCSCF/MP2 level, and a value of 1.33 kcal/mol was predicted. Considering the fact that the silicon−carbon bond is weaker than the carbon−carbon bond, our presumably best value of 0.6 kcal/mol appears to be reasonable.

3. Gauche Diradical (1) $H_2C{-}H_2Si{-}CH_2{-}CH_2$. A stationary point for a gauche form of the diradical **1** was also found. The optimized geometry, given in Figure 1, shows a dihedral angle of 62.5° and a central Si−C bond distance of 1.93 Å. Its diradical nature is revealed by the natural orbital populations of 1.98, 0.02, 1.13, and 0.87, the singly populated orbitals being located at the terminal carbon atoms.

At the CASSCF level the gauche form is predicted to be around 1.3 kcal/mol less stable than the trans form. For this species also the various corrections for dynamic correlation lead to a spread of values, although not as large as for the trans form. The Davidson-corrected energy of 17.2 kcal/mol is rather close to the 17.0 kcal/mol obtained by the CASSCF/MP2 calculation. By adding the ZPE correction to the latter, we obtain a final value of 16.7 kcal/mol, which is slightly above the corresponding 15.8 kcal/mol for the trans form.

4. Trans−Gauche Transition State (3) for $H_2C{-}H_2Si{-}CH_2{-}CH_2$. In the search for the TS **3** between the trans and the gauche forms, we found a stationary point having a dihedral angle for the heavy-atom skeleton of 109.6°. This parameter is rather uncertain, since the energy maximum for rotation is very flat. As seen from Figure 1 the other geometrical

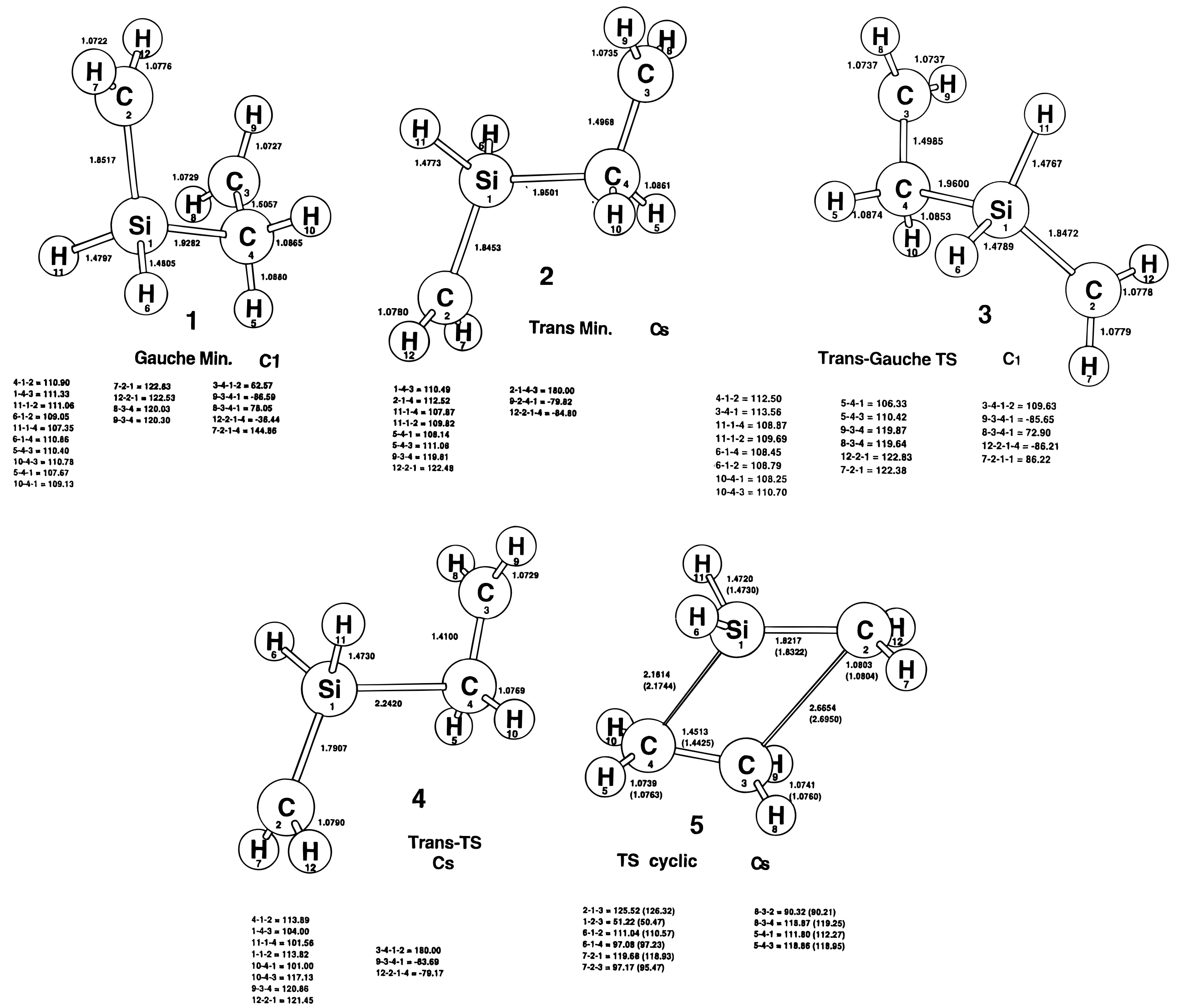

Figure 1. Optimized geometries from CASSCF(4,4)/3-21G* calculations. For the cyclic TS, CASSCF(4,4)/6-31G* values are in parentheses.

parameters are very similar to the corresponding ones of the local minima. The electron distribution in the active space indicates a typical diradical having the natural orbital populations of 1.98, 0.02, 1.20, and 0.80, respectively. The singly occupied orbitals are located at the terminal carbon atoms. It is worth noticing that the central Si−C bond in the TS is slightly longer than in the two minima connected by the TS. At the highest calculational level, CASSCF+MP2 with ZPE corrections, we find a relative energy of 18.4 kcal/mol for the TS, i.e., 1.9 kcal/mol above the TS for fragmentation of the trans form to ethylene and silene.

Symmetry Analysis of the Potential Surface

The following analysis was used to understand the computational reasults above, especially the interconnection among structures **5** and **7**−**9**. For clarity, this analysis, which used as yet unpublished techniques, is presented separately rather than at each point above where it was used.

McIver and Stanton,[19] and then more elegantly Pechukas[18] have shown how symmetries of reactant, product, and transition state must be interrelated in a nondegenerate concerted reaction (i.e., a one-step reaction where reactant and product are chemically distinct). More recently, Schaad and Hu[20] have extended this work to degenerate concerted reactions where reactant and product are chemically identical. We shall follow Balaban and Farcasiu[21] and call these reactions "automerizations". To discuss automerizations of a molecule with n_C carbon atoms, n_H hydrogen atoms, etc., it is often convenient to imagine numbering the atoms within each set so that the $n_C!n_H!$... automers, all chemically identical, can be distinguished. These automers, taking the labels into account, may or may not be superimposable by rotation. For example, the two automers of the water molecule are superimposable, but the two automers of silacyclobutane, **8** and **9** in Figure 3, are not.

It will be shown how these techniques helped in fitting together the computational data above. Although the results of the symmetry analysis may easily be given in terms of the usual point groups, the analysis itself is carried out using what we shall call "Pechukas Groups". These are modified point groups[18] in which each point symmetry operation, taken in the active sense, is followed by a permutation of identical nuclei that nullifies its effect. For example, the transition state **5** has C_s symmetry with the ring lying in a reflection plane that interchanges atoms 5 and 10, 6 and 11, 7 and 12, and 8 and 9

TABLE 3: Pechukas Groups of Structures 1−9

1 and **3**	$C_1 = \{E\}$
2, **4**−**6**	$C_s = \{E; (5,10)(6,11)(7,12)(8,9)\sigma\}$
7	$C_{2v} = \{E; (2,4)(5,12)(6,11)(7,10); C(2,4)(5,7)(10,12)\sigma_v; (5,10)(6,11)(7,12)(8,9)\sigma_v'\}$
8 and **9**	$C_s = \{E; (2,4)(5,7)(10,12)\sigma\}$

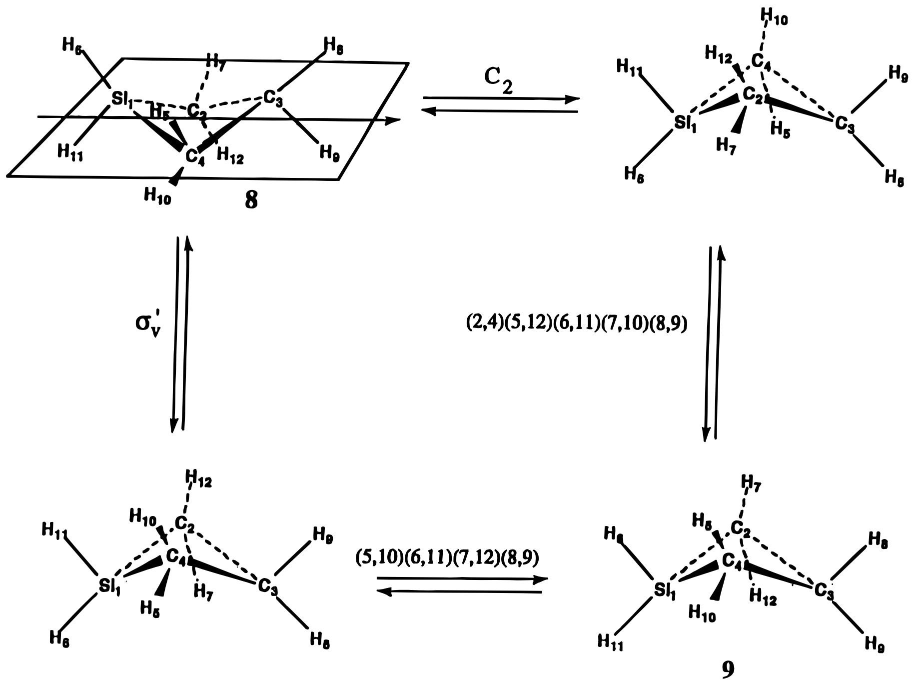

Figure 2. Interconversions of **8** (upper left) and **9** (lower right) by operations of the Pechukas group of **7** that are not common to those of 8 and 9.

using the automer shown in Figure 1. We indicate permutations using the cyclic notation so that (5,10) means atom 5 is replaced by 10, and 10 by 5. Each of these pair permutations is its own inverse, so in the Pechukas group of **5** the operation (5,10)(6,11)(7,12)(8,9)σ replaces σ of the point group. Pechukas groups of the systems studied here are in Table 3.

Two rules limiting possible transition-state symmetry will be used. The derivation of these rules depends on the validity of the Murrell−Laidler theorem,[22] which states that two and only two gradient paths lead down from each TS, on the assumption that there is no crossing of potential surfaces along the reaction path and that symmetry-breaking approximate wave funtions are not used (i.e., the electron density transforms like the totally symmetric irreducible representation of the point group of the nuclear framework).

Let G_R be the Pechukas group of reactant, G_P that of product, G_{TS} that of transition state, and G_0 the largest common subgroup of G_R and G_P. It can easily be shown that G_0 equals the set of all elements that G_R and G_P have in common ($G_0 = G_R \cap G_P$). Then the following holds.

Rule 1. For nondegenerate reactions G_{TS} must be either G_0 or a subgroup of G_0.[18,19]

Rule 2. For degenerate reactions G_{TS} must be either one of the symmetries allowed by rule 1 or a group obtained from one of these by adding elements to form a group of twice the order.[20] Any such additional elements must interconvert reactant and product structures.

It is important to note that these rules also hold for cases where either or both reactant and product are themselves transition states, that is, cases where a TS falls by either or both gradient paths down to other transition states.

Structure **5** of Figure 1 was found to be a true transition state early in the work, and the expensive process of reaction path following appeared to lead down from **5** to the trans diradical **2** in one direction. For the reasons mentioned in the previous section, the terminus in the opposite direction was not clear, and it was this that caused us to apply symmetry analysis to these related structures. Silacyclobutane **8** might at first glance be a possible product, since **2**, **5**, and **8** all have C_s symmetry, and hence, rule 1 appears to be obeyed for this nondegenerate reaction. However, the reflection plane is associated with the permutation (5,10)(6,11)(7,12)(8,9) in **2** and **5** but with (2,4)(5,12)(6,11)(7,10)(8,9) in **8**. The Pechukas groups of **2** and **5** are therefore not the same as the Pechukas group of **8,** and hence, **5** cannot be a TS in a concerted reaction from **2** to **8**. Further consideration suggested that **5** might fall instead to a C_{2v} transition state **7** that mediates the interconversion of the two automers **8** and **9** of the puckered ground state of silacyclobutane. From the general symmetry rules 1 and 2, the TS for this automerization must be of symmetry C_1, C_2, C_s, C_i, C_{2v}, or C_{2h}. The additional fact that this TS lies on the path of the nondegenerate reaction to TS **5** and thence to **2** requires that **7** has at least the C_s symmetry of **5**. Combining this with recent work by Bytautas[23] on rules for specific reactions leaves C_{2v} as the only possible symmetry of **7.** Further, as Figure 2 shows, the extra operations (2,4)(5,12)(6,11)(7,10)(8,9)C_2 and (5,1)(6,11)(7,12)(8,9)σ_v' in the Pechukas group of **7** but not in those of **8** or **9** do interconvert **8** and **9**, as required. After more extensive reaction path following, the last point on the IRC path had not yet reached the TS, but normal-mode analysis of this last CASSCF wave function showed two imaginary frequencies. One led to ring closure to **7** and the other to the two puckered silacyclobutane rings. In further support of this picture, geometry optimization of an RHF wave function starting at the last point on the CASSCF reaction path did give the C_{2v} structure **7**.

The entire reaction **7** → **5** → **2** with a C_{2v} symmetry for **7** does satisfy rule 1 for nondegenerate reactions. The Pechukas group of TS **5** is the largest common Pechukas group of reactant **7** and product **2**. In a nondegenerate concerted reaction the entire reaction path, excluding reactant and product themselves but including the TS, must all have the same symmetry. Therefore, the path from TS **5** to trans diradical **2** must retain the C_s symmetry of **5**. It follows that the reaction from TS **5** to the trans diradical must occur by the swinging of C_3 around C_4 in the C_s plane and not by rotation of C_3 out of that plane around the Si_1-C_4 bond. Inspection of the reaction path confirms this prediction.

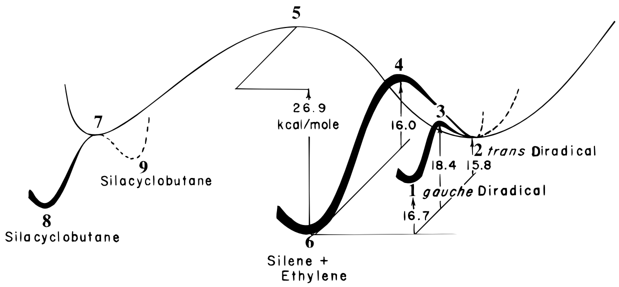

Figure 3. Perspective sketch of the relevant portion of the C_3H_8Si surface. Energies are shown in kcal/mol above the noninteracting ethylene + silene reference.

In the nondegenerate rearrangement of the C_s trans diradical **2** to the C_1 gauche form, the largest common subgroup is C_1, so the TS **3** must be of C_1 symmetry, as it is.

Direct formation of the C_s trans diradical from ethylene + silene **6** is found to have the C_s transition state **4**. Reactants must therefore approach each other with this same C_s symmetry.

Figure 3 is a sketch of the potential surface showing the interrelated structures **1**−**9**.

Conclusions

The main results of the present study are the following.

(1) There is a cyclic transition state in the multistep reaction of ethylene and silene to planar silacyclobutane, which is itself also a transition state. The first TS lies 26.9 kcal/mol above noninteracting ethylene and silene.

(2) There exist both trans and gauche forms of the diradical $H_2C-H_2Si-CH_2-CH_2$, the trans having an energy that is 0.9 kcal/mol below the gauche.

(3) Fragmentation of the trans diradical to ethylene and silene has a very low-energy barrier of 0.6 kcal/mol. The barrier to interconversion of the trans to the gauche diradical is estimated to be 2.6 kcal/mol.

(4) Size-consistency corrections to the energies obtained by MR-CI calculations are very important and lead to substantial corrections to the relative energies.

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