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Theoretical Analysis of Concerted and Stepwise Mechanisms of Diels−Alder Reactions of Butadiene with Silaethylene and Disilene

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The concerted and the stepwise mechanisms of the Diels−Alder reactions of butadiene with silaethylene and disilene were studied by ab initio MO methods. For the reaction of butadiene and silaethylene, an asymmetric concerted process that is almost stepwise and two stepwise processes were located. For the first step of the stepwise process, the C−Si bond formation is more favorable than the C−C bond formation. The activation energy barrier of the concerted transition state is only 0.89 kcal/mol lower than that of the first-step transition state of the C−Si bond formation for the stepwise process by the CASPT2 calculation level. For the reaction of butadiene and disilene, the activation energy barrier of the concerted-type transition state constrained with C_s symmetry is about 9 kcal/mol higher than that of the stepwise transition state by the CASSCF method. The energy barrier of the first step of the stepwise reaction disappears at the CASPT2/6-311++G(d,p) calculation level including the nondynamical correlation energy, although the reaction of the butadiene with disilene occurs through the stepwise-like process.

1. Introduction

The mechanisms of the Diels−Alder reactions have been the subject of the most heated and interesting controversies. The reactions of butadiene and ethylene have been extensively investigated using experimental[1−5] and theoretical[6−18] methods. Namely, the reaction mechanisms of the [4+2] cycloaddition have been controversial. Two competing alternative pathways have been debated: (i) a concerted mechanism in which the transition state is formed in one step either simultaneously or sequentially; (ii) a stepwise mechanism, involving forming either a diradical or a zwitterion as an intermediate step. However, it is not straightforward to ascertain which mechanism is favored in different situations, since the balanced description of closed shell and diradical species is very difficult by conventional quantum mechanical methods. Accordingly, reliable results can be obtained only by multireference correlation methods. Houk and co-workers[9] calculated the transition states of the concerted and stepwise paths for the Diels−Alder reaction between butadiene and ethylene by MCSCF/3-21G and density functional methods. We also studied[13] the concerted and stepwise mechanisms between butadiene and ethylene by CASSCF and CAS-MP2 methods with 6-31G(d,p) and 6-311+G(d,p) basis sets. Recently, Lischka and co-workers[18] showed that the energy barrier of the transition states of the concerted process for the Diels−Alder reaction of butadiene and ethylene is 6.5 kcal/mol lower than that of the stepwise process by the CASSCF and MRAQCC methods. Furthermore, the competition between the concerted and stepwise mechanisms was studied for hetero-Diels−Alder reactions. Barone and Arnaud[19] calculated the concerted transition states and the diradical intermediates between butadiene with formaldehyde and thioformaldehyde by the B3LYP density functional method. They did not calculate the transition states and the energy barriers for the stepwise pathways. The concerted transition state between butadiene and thioformaldehyde was calculated[20] by the semiempirical AM1 and PM3 methods. We also calculated[21] the concerted and stepwise transition states between butadiene with formaldehyde and thioformaldehyde by CASSCF and CAS-MP2 methods. For both reactions, the energy barriers of the concerted transition states were lower than those of the stepwise transition states. Although the energy barrier height of the concerted transition state between butadiene with formaldehyde is similar to that of the parent Diels−Alder reaction of butadiene and ethylene, the energy barrier height of the concerted reaction of butadiene with thioformaldehyde is about 20 kcal/mol lower than that of butadiene with formaldehyde and ethylene. The energy differences between the concerted and the stepwise transition states for the reactants of butadiene with formaldehyde and thioformaldehyde are larger by about 7 and 11 kcal/mol than that for the parent Diels−Alder reaction, respectively. For the hetero-Diels−Alder reaction of butadiene with dienophile as singlet oxygen, Liwo and co-workers[22] reported that the concerted cycloaddition transition state was the second-order saddle points and that the reaction occurred through the stepwise diradical mechanisms by the CASSCF and MCQDPT2 methods. Houk and co-workers[23] calculated the reaction paths of the concerted and stepwise transitions for the cyclic reactions of butadiene with nitroso by the B3LYP method. They indicated the concerted transition state was 3.5 kcal/mol lower in energy than the stepwise transition state leading to diradical intermediate. The concerted-type transition state of [4+2] additions of butadiene with formaldimine and diazene were calculated[24] by the HF/3-21G method. The obtained activation energy for the reaction of butadiene with formaldimine is almost similar to that of butadiene with ethylene, and the difference is about 2 kcal/mol. For the reaction of butadiene with diazene, the activation energy[25] is significantly smaller by slightly more than 10 kcal/mol (*cis*-HNNH-endo type) than that of butadiene with ethylene. The transition structure is quite unsymmetrical. Recently, we[56] calculated the concerted and the stepwise transition states of the [4+2] reactions of butadiene with diazene,

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and the activation energy of the stepwise transition state was lower in energy than that of the concerted state. Thus, for the reaction of butadiene with the dienophile including atoms with large electronegativity, the stepwise process is probably more favorable than the concerted one.

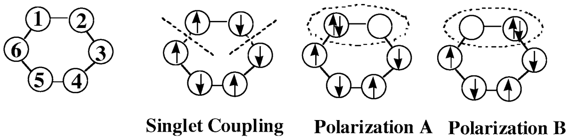
On the other hand, the Diels−Alder reactions of dienophile including atoms with small electronegativity were also studied. For the Diels−Alder reactions of diene and dienophile including silicon atoms, the reactions of butadiene with the Si(100) surface were studied experimentally[27,28] and theoretically.[29−31] Teplyakov et al.[27] showed the evidence for the formation of a Diels−Alder adduct of butadiene on the Si(100)-2 × 1 surface at room temperature by IR spectroscopy. The reaction of 1,3-cyclohexadiene on the Si(100)-2 × 1 surface was also observed[28] by a scanning tunneling microscopy. The Diels−Alder reaction of cyclohexadiene on the model of the Si(100)-2 × 1 surface was calculated[29] by the B3LYP/6-31G* level. They predicted a small energy barrier of 0.3 kcal/mol at the transition state constrained with C_s symmetry. Choi and Gordon[30] also calculated the [4+2] reaction of 1,3-cyclohexadiene on the silicon (001) surface by the SIMOMM calculation method. They obtained the third-order saddle point with barriers of 4.1 and 0.0 kcal/mol at the MP2 and MCQDPT2 levels. Recently, Minary and Tuckerman[31] calculated the reaction pathway of [4+2] adduct formation of butadiene on the Si(100)-2 × 1 surface by a molecular dynamic method with density functional theory, and pointed out a nonconcerted mechanism involving a well-defined reaction intermediate. However, the reaction mechanisms of the [4+2] cycloaddition on the silicon surface have continued to be controversial regarding the debate on two competing alternative pathways of the concerted and stepwise transitions. The mechanisms of the concerted and the stepwise transitions for the Diels−Alder reaction of dienophile molecules (not surface) including Si atoms are important for the understanding of criteria for distinguishing between the concerted and the stepwise mechanisms.

In the present paper, we report the potential energy surfaces for the concerted and the stepwise reactions of the [4+2] cycloadditions of butadiene with silaethylene and disilene by the CASSCF and CASPT2 calculation levels. To characterize the electronic behavior for these reactions, the reaction pathways are also analyzed by a CiLC-IRC method.

2. Computational Methods

All equilibrium and transition state geometries of the reactions treated here were determined with analytically calculated energy gradients at the complete active space self-consistent field (CASSCF) method[32] with the split-valence plus polarization 6-31G(d) set.[33,34] For the CASSCF calculation, six orbitals relating to the reactions were included in the active spaces to generate all configurations. Frequency calculations were carried out at the CASSCF level in order to determine the nature of the stationary point and evaluate the zero-point energy corrections. The CASPT2 single-point calculations[35] were performed with the 6-31G(d) and the 6-311++G(d,p) basis sets[36,37] using the CASSCF-optimized structures. The intrinsic reaction coordinate (IRC)[38,39] was followed from the transition state toward both reactants and products.

To interpret the mechanisms of reactions, a configuration interaction (CI)/localized molecular orbital (LMO)/CASSCF calculation along the IRC pathway (CiLC-IRC) was carried out with the 6-31G(d) basis set. The details of the CiLC-IRC can be found in previous papers.[13,40,41] Briefly, the CASSCF calculation was carried out to obtain a starting set of orbitals for the localization procedure. Boys localization[42] was then applied to give a localized orbital with a highly atomic nature. Using the localized MOs as a basis, a full CI with determinants level was used to generate electronic structures and to evaluate the relative weight of configurations in the atomic orbital-like wave functions. The total energy calculated by the CI procedure corresponds well to that obtained by the CASSCF calculation. These calculation procedures are repeated along the IRC pathway, which we call a CiLC-IRC for the procedure. In the notation of the valence bond-like model, the electronic structures of a bond on the basis of the CiLC calculation were presented roughly as one singlet coupling term and two polarization terms. The representation with the three terms (one singlet coupling and two polarization terms) for a bond has been successful[13,43−50] in explaining the bond formation and bond extinction along a chemical reaction path.



Singlet Coupling and Polarization terms for bond 1-2.

To study the aromaticity for a transition state, the IDA (index of deviation from aromaticity)[51] was calculated as proposed in the previous paper. The IDA was defined as the degree of equality of electronic structures for each of the bonds and by the narrowness of the gap between the weight of the singlet coupling and polarization terms for each bond. Therefore, the smaller IDA values mean larger aromaticity. The IDA showed an excellent correlation[52] with the stabilization energy for ring compounds.

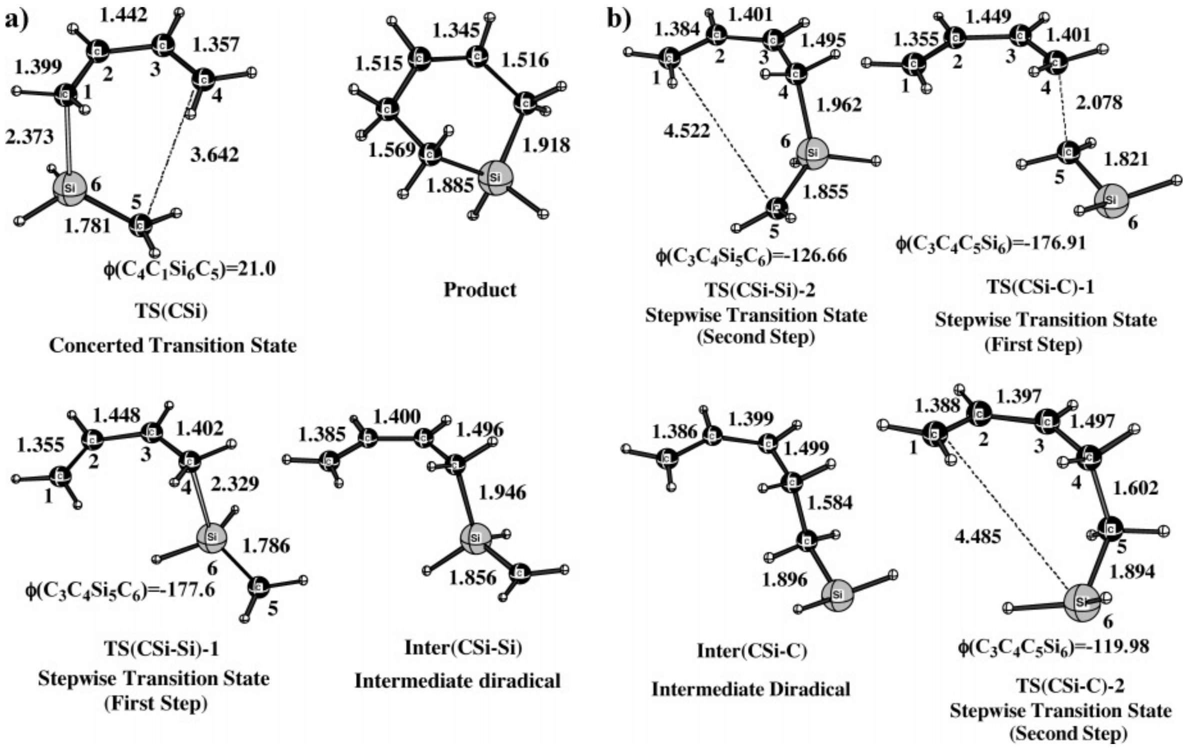
The calculations of the CiLC-IRC analysis were performed with the GAMESS program package,[53] the CASPT2 energies with the MOLCAS program package,[54] and the others with the GAUSSIAN03 program package,[55] respectively.

3. Results and Discussion

3.1. Reaction of Butadiene and Silaethylene. The geometries of the stationary points for the concerted and the stepwise pathways of the Diels−Alder reaction between butadiene and silaethylene are shown in Figure 1. The relative energies for their structures from the reactants of butadiene and silaethylene are also listed in Table 1. The values in the parenthesis of the table include the zero-point energy correction at the CASSCF/6-31G(d) level.

For the concerted reaction path (reaction (1)) of butadiene and silaethylene, the transition state is an asymmetric structure from the bond distances of C_1-Si_6 and C_4-C_5. But it is not a stepwise reaction, because an intermediate species cannot be located on the reaction pathway and the transition state leads to the product of cyclic adducts along the IRC pathway by the CASSCF level. The first process is the Si−C bond formation and leads to the product without an intermediate compound. The most interesting point at the transition state structure is the dihedral angle of 21.0 degrees for $\phi(C_4C_1Si_6C_5)$, and not zero degrees. This means that the C_4 and C_5 atoms probably avoid approaching each other.

For the stepwise reaction, there are two reaction paths. One (reaction (2)) is the Si−C bond formation in the first step, and the other (reaction (3)) is the C−C bond formation. The transition state (TS(CSi−Si)-1) of the Si−C bond formation in the first step of reaction (2) is 9.9 kcal/mol lower in energy



TS(CSi)
Concerted Transition State

Product

TS(CSi-Si)-2
Stepwise Transition State
(Second Step)

TS(CSi-C)-1
Stepwise Transition State
(First Step)

TS(CSi-Si)-1
Stepwise Transition State
(First Step)

Inter(CSi-Si)
Intermediate diradical

Inter(CSi-C)
Intermediate Diradical

TS(CSi-C)-2
Stepwise Transition State
(Second Step)

Figure 1. Stationary-point geometries (in angstroms and degrees) for the Diels−Alder reactions of butadiene with silaethylene at the CASSCF/6-31G(d) level.

TABLE 1: Relative Energies (kcal/mol) for the Reactions of Butadiene with Silaethylene and/or Disilene

	CAS/6-31G(d)	CASPT2/6-31G(d)	CASPT2/6311++G(d,p)
	Butadiene + Silaethylene Reactions		
reactants	0.0	0.0	0.0
TS(CSi)	14.96 (16.20)	3.41 (4.66)	0.85 (2.09)
TS(CSi−Si)-1	14.30 (15.55)	3.66 (4.91)	1.74 (2.99)
inter(CSi−Si)	5.24 (6.47)	−2.28 (−1.05)	−4.42 (−3.19)
TS(CSi−Si)-2	6.88 (8.13)	−0.56 (0.68)	−3.06 (−1.81)
TS(CSi−C)-1	23.10 (25.17)	12.19 (14.26)	10.82 (12.89)
inter(CSi−C)	6.62 (10.30)	−4.87 (−1.19)	−5.33 (−1.65)
TS(CSi−C)-2	9.59 (13.23)	−2.10 (1.54)	−2.92 (0.72)
product	−53.86 (−46.87)	−68.64 (−61.64)	−68.89 (−61.90)
	Butadiene + Disilene Reactions		
reactants	0.0	0.0	0.0
TS(SiSi)	18.45 (19.43)	1.83 (2.81)	−0.50 (0.48)
TS(SiSi)-1	9.44 (10.74)	−2.97 (−1.67)	−4.61 (−3.31)
inter(SiSi)	0.48 (2.23)	−11.06 (−9.31)	−13.92 (−12.17)
TS(SiSi)-2	2.07 (3.87)	−9.41 (−7.62)	−12.67 (−10.87)
product(C_s)	−53.28 (−48.16)	−68.29 (−63.17)	−71.86 (−66.74)
product(C_2)	−50.83 (−45.79)	−64.54 (−59.50)	−67.85 (−62.82)

than that (TS(CSi−C)-1) of the C−C bond formation of reaction (3). In a comparison of the structures of the concerted transition state (TS(CSi)) and the first-step transition state (TS(CSi−Si)-1), the difference of the new Si−C bond is only 0.044 Å length. The other remarkable difference between both transition state structures is only the dihedral angle of $\phi(C_4C_1Si_6C_5)$.

To study the electronic state of each bond for the concerted and the stepwise reactions of butadiene and silaethylene, the variations of the weight of the electronic states of the bonds along the reaction pathways by CiLC analysis are shown in Figures 2−7. From the results of the CiLC analysis for the concerted reaction as shown in Figure 2, the reaction occurs through the stepwise-like process from the viewpoint of electronic variation of each bond. The first process is the bond breaking of C_1-C_2 and Si_6-C_5, and is the bond formation of C_1-Si_6 near the transition state. Some part of the C_2-C_3 π-bond is formed near the transition state. The weight of the C_4-C_5 σ-bond is increasing only a little at this point. The small weight of the C_4-C_5 at this region is composed of only that of the singlet coupling term and no polarization terms (not shown here). This indicates the diradical-like state for C_4-C_5 bond. The second process, which is the formation of the C_2-C_3 π- and the C_4-C_5 σ-bonds, occurs at the region around −7.5 bohr amu$^{1/2}$ of the IRC pathway. The variations of the electronic states of the bonds in the region from −3 to −6 bohr amu$^{1/2}$ on the IRC pathway are very small. Accordingly, it is considered that the concerted transition state of butadiene and silaethylene is not the only asymmetric one. Simply considered, if two new bond formations occur only for the different order of the bond formations on the reaction pathways, the diradical angle of $\phi(C_4C_1Si_6C_5)$ at the concerted transition state will be zero degrees. But the dihedral angle is 21.0 degrees. This probably indicates the repulsion effects between the C_4 and C_5 atoms. In fact, the π-electrons of the C_3-C_4 bond at the concerted transition state

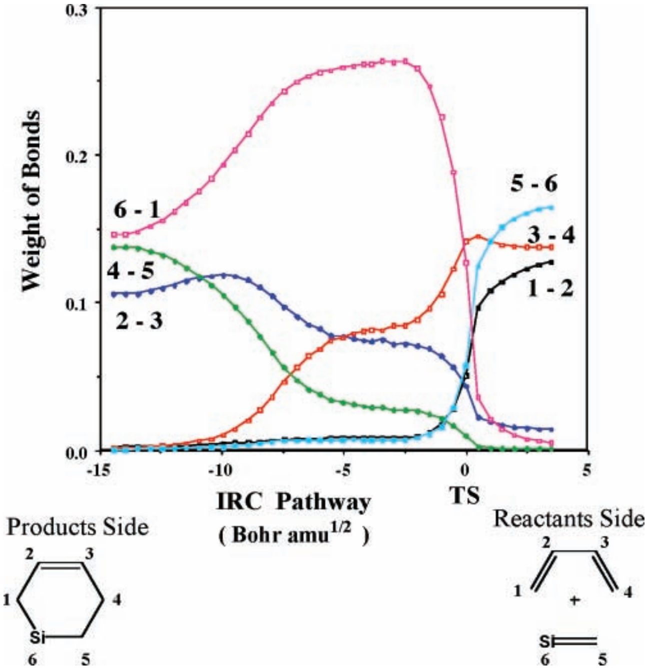


Figure 2. Weight of some bonds by CiLC analysis along the IRC pathway of the concerted reaction (1) between butadiene and silaethylene.

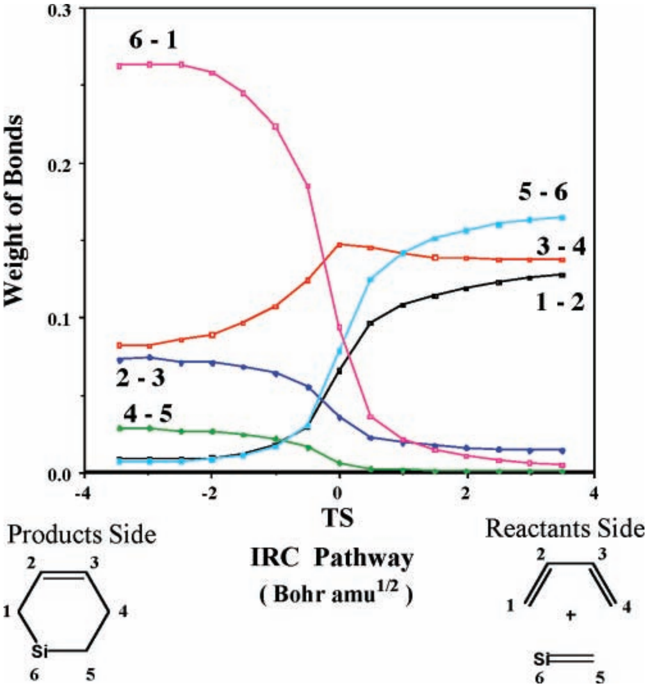


Figure 3. Weight of some bonds by CiLC analysis along the IRC pathway of the concerted reaction (1) between butadiene and silaethylene.

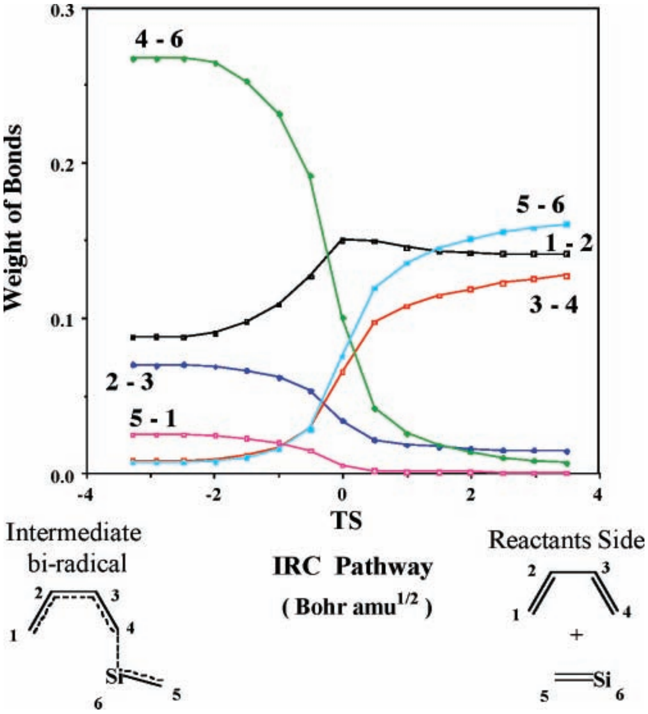


Figure 4. Weight of some bonds by CiLC analysis along the IRC pathway of the first step of the stepwise reaction (2) between butadiene and silaethylene.

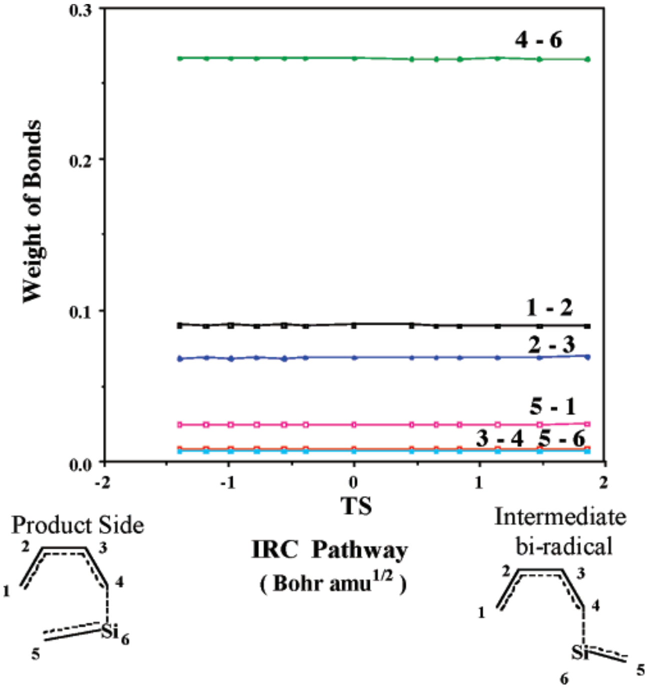


Figure 5. Weight of some bonds by CiLC analysis along the IRC pathway of the second step of the stepwise reaction (2) between butadiene and silaethylene.

polarize a little to the C_4 atom, and the π-electrons of the C_5-Si_6 bond polarize a lot to the C_5 atom. If the repulsion of C_4 and C_5 atoms becomes a lot by the electronic effects as substitution groups, the reaction might occur through the stepwise process.

The variations of the weight of the bonds along the reaction pathway of the first step of the stepwise reaction (2) are shown in Figure 4. The first step is the bond breaking of the C_5-Si_6 and C_3-C_4 and the C_4-Si_6 bond formation from Figure 4. Then the C_1-C_2 π-bond becomes weak, and the weight approaches that of the C_2-C_3 π-bond. The variation of the bonds for the first step of the stepwise reaction is similar to that of the first process of the concerted reaction as can be seen from a comparison of Figures 3 and 4; Figure 3 shows the variation of the weight of the bonds for the first process (from 3.5 to −3.5 bohr amu$^{1/2}$) of the concerted reaction. The variations of the electronic states of the bonds for the second step of reaction (2) are shown in Figure 5. From Figure 5, it can be seen that the variations of the electronic states of the bonds do not occur around the region of the second-step transition state. This means

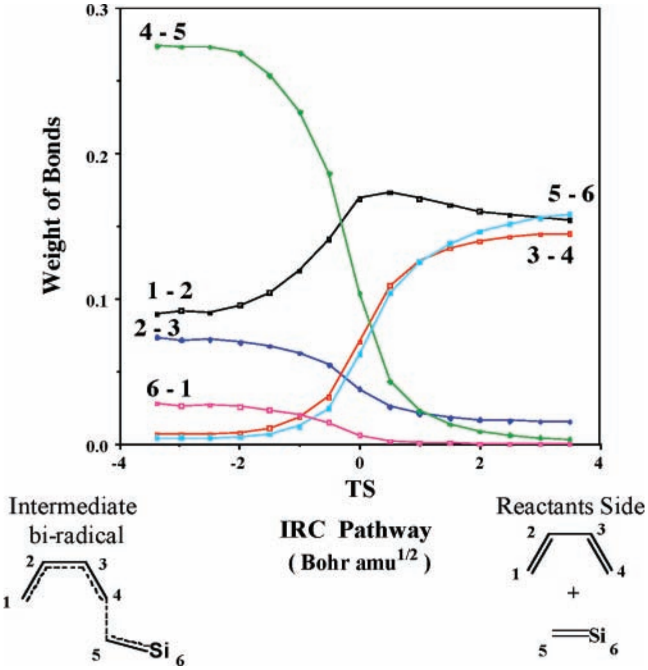


Figure 6. Weight of some bonds by CiLC analysis along the IRC pathway of the first step of the stepwise reaction (3) between butadiene and silaethylene.

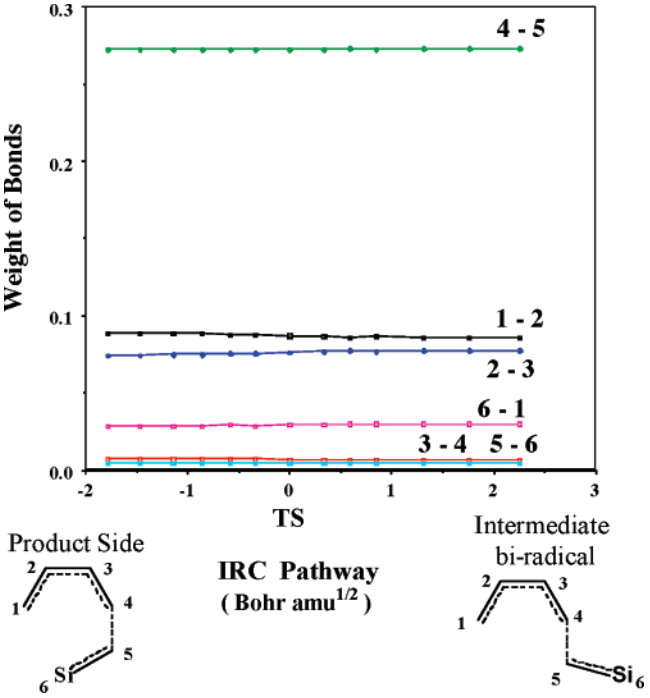


Figure 7. Weight of some bonds by CiLC analysis along the IRC pathway of the second step of the stepwise reaction (3) between butadiene and silaethylene.

the activation energy barrier of the second-step transition state comes from the steric effect, not the variation of the electronic state. This is similar to the second-step transition state of the stepwise reaction between butadiene and ethylene as shown in the previous paper.[13]

For the first-step transition state of the C_4-C_5 bond formation of the stepwise reaction (3), the activation energy is about 9.9 kcal/mol higher than that of reaction (2). Therefore, the stepwise process of reaction (3) does not occur for the reaction between butadiene and sialethylene. The variations of the electronic states of the bonds for the first step are shown in Figure 6. The variation of the weight of the bonds is roughly similar to that of the first step of reaction (2). From the variations of the electronic states of the bonds at the second step as shown in Figure 7, the energy barrier of the transition state of the second step results from the steric effects the same as that of reaction (2). The activation energy barrier of the second step is 2.4 kcal/mol above the intermediate diradical compound (Inter(CSi−C)), and it is 1.0 kcal/mol higher than that of reaction (2). The energy of 1.0 kcal/mol probably comes from the difference of the distances between the C_4-Si_6 and the C_4-C_5 bonds.

3.2. Reaction of Butadiene and Disilene. The stationary point geometries of the reactions of butadiene with disilene are shown in Figure 8. The transition state (TS(SiSi)) of the concerted reaction was obtained with the restriction of a C_s symmetry. The transition state has two negative eigenvalues for the force constant matrix. One (-439 cm^{-1}) corresponds to the reaction path of the C−Si bond formation, and the other (-149 cm^{-1}) corresponds to the inversion of the SiH_2 part. The new Si−C bond of the transition state (TS(SiSi)) is about 0.50 Å longer in length than that of the first-step transition state (TS(SiSi)-1) of the stepwise reaction, and it is also about 0.48 Å longer than that of the concerted transition state (TS(CSi)) between butadiene and silaethylene. Namely, the concerted transition state, TS(SiSi), is located on a very early stage for the reaction. The variations of the electronic states of the bonds along the concerted reaction pathway of butadiene and disilene by CiLC analysis are shown in Figure 9. From this figure, the crossing of the bond breaking and the bond formation occurs after the transition state (at the product side), although the crossing for the concerted reaction of butadiene with ethylene occurs[13] at the transition state. The crossing at the product side indicates the rearrangement of the electronic structure of disilene after the transition state. The stable structure of the isolated disilene has a C_{2h} symmetry, and the eigenvector of one negative eigenvalue of the force constant matrix of the concerted transition state corresponds to the mode of the inversion of the SiH_2 part. The energy difference between the C_{2h} and D_{2h} symmetry structures of isolated disilene is 2.87 kcal/mol at the CASPT2/6-311++G(d,p) level. The difference between the locations of the transition state and the crossing point at the product side indicates the decreasing of the stabilization energy as aromaticity at the transition state. In fact, the aromaticity of the transition state of TS(SiSi) is much less than that of the concerted transition state of butadiene with ethylene. The value of IDA (index of deviation from aromaticity) of TS(SiSi) is 1.18, and that[52] of the transition state of butadiene with ethylene is 0.27; the value of IDA at the crossing point of the bonds for the reaction of butadiene with disilene is 0.52. Although the activation energy barrier of the concerted transition state is higher by 9.0 kcal/mol than that of the first-step transition state of the stepwise reaction by the CASSCF calculations, the energy barrier (without the zero-point energy correction) of the concerted transition state disappears by the CASPT2 calculations. For the products, two structures with C_s and C_2 symmetries are located. Both structures are a real minimal point without negative eigenvalues for the force constant matrix. Although the stable structure of cyclohexene has only one with C_2 symmetry (no C_s symmetry), the C_s structure of the product is about 3.9 kcal/mol more stable than the C_2 structure.

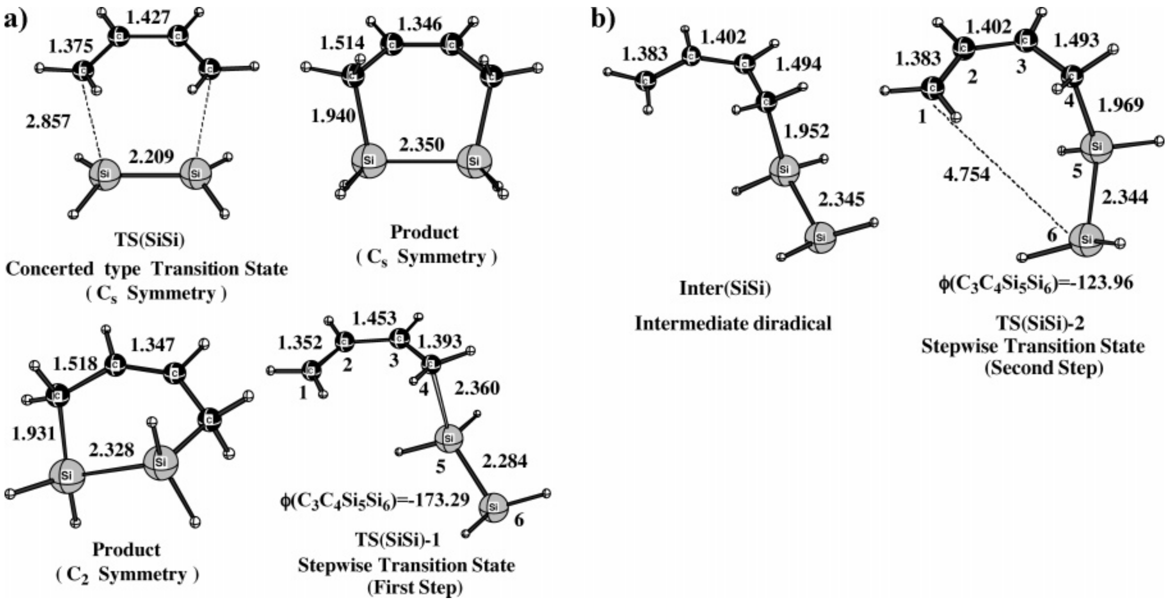


Figure 8. Stationary-point geometries (in angstroms and degrees) for the Diels−Alder reactions of butadiene and disilene at the CASSCF/6-31G-(d) level.

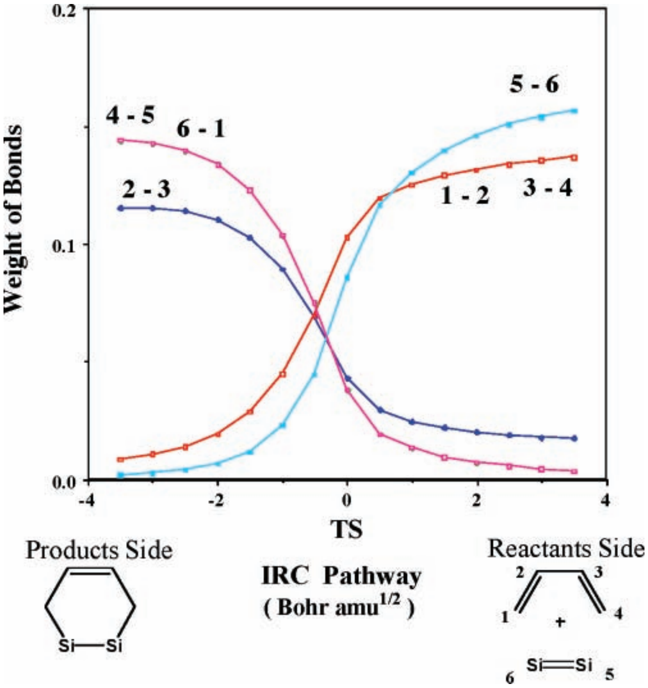


Figure 9. Weight of some bonds by CiLC analysis along the IRC pathway of the concerted reaction between butadiene and disilene.

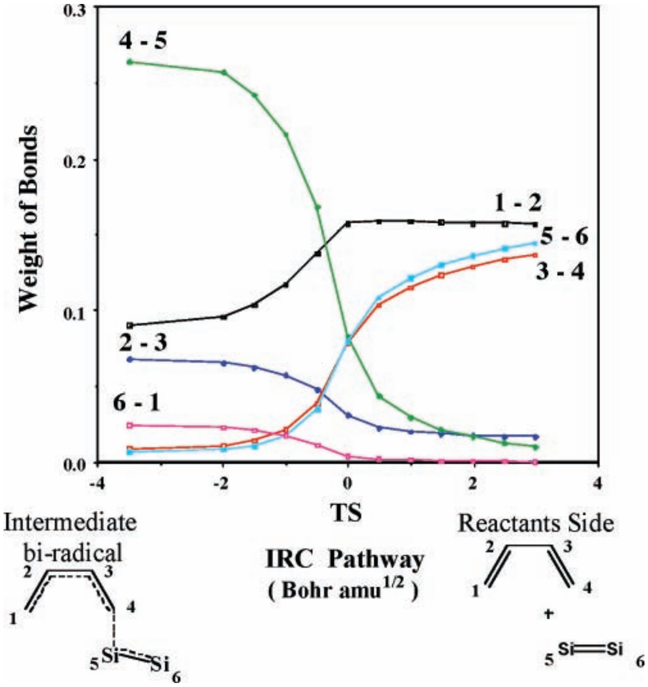


Figure 10. Weight of some bonds by CiLC analysis along the IRC pathway of the first step of the stepwise reaction between butadiene and disilene.

For the stepwise reaction, the C−Si bond of the first-step transition state, TS(SiSi)-1, is only 0.03 Å longer than that of TS(CSi−Si)-1. The intermediate compound, Inter(SiSi), is about 14 kcal/mol more stable in energy than the reactants. The second-step transition state, TS(SiSi)-2, has the energy barrier of 1.3 kcal/mol above the intermediate compound. The variations of the weight of the electronic states of the bonds of the first step and the second step for the stepwise reactions are shown in Figures 10 and 11, respectively. For the first step, the weight of the electronic states of the bonds of the C_3−C_4 and the Si_5−Si_6 is decreasing along the IRC pathway and that of the bond C_4−Si_5 is increasing, and these cross at the transition state region. Although the intermediate is a diradical state from the CI coefficients of the CASSCF calculation, the bond-exchange process occurs with ionic character as polarization of the C_3−C_4 and the Si_5−Si_6 bonds. The decreasing of the weight of the C_1−C_2 bond corresponds to the increasing of the C_2−C_3 bond. This indicates the resonance between the bonds of C_1−C_2 and C_2−C_3. For the second step as shown in Figure 11, the variations of the electronic state of the bonds cannot be seen near the transition state (TS(SiSi)-2). Therefore, the energy barrier of the transition state of the second step comes from the steric effects the same as the reactions of butadiene with ethylene and silaethylene.

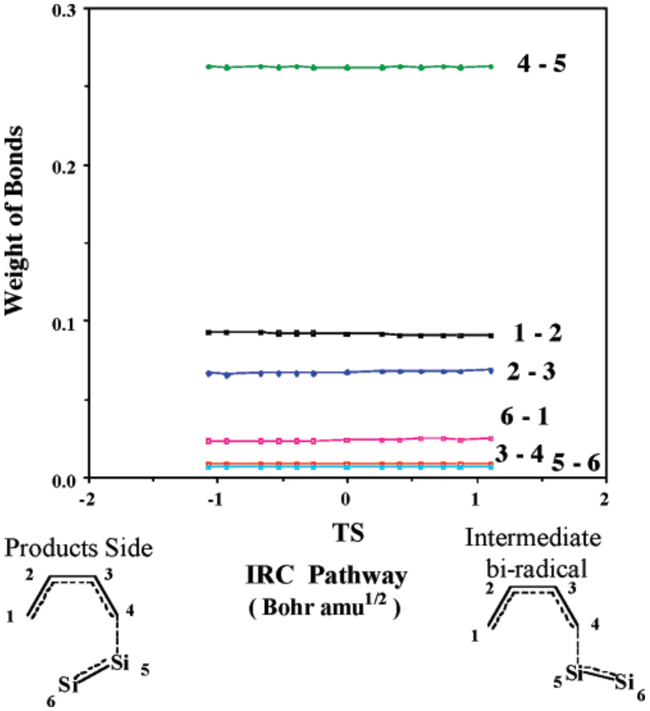


Figure 11. Weight of some bonds by CiLC analysis along the IRC pathway of the second step of the stepwise reaction between butadiene and disilene.

4. Conclusion

The potential energy surfaces of the concerted and the stepwise mechanisms of the Diels−Alder reactions between butadiene and silaethylene and disilene were calculated at the CASSCF and the CASPT2 calculation levels. The concerted reaction of butadiene and silaethylene occurs through an asymmetric process as almost a stepwise mechanism. The reaction leads to the product of cyclic addition without an intermediate. However, the variation of the electronic states of the bonds showed clearly the separated regions on the IRC pathway. The variations of the weight of the bonds at each separated region are similar to those of the stepwise reaction processes. For the stepwise reaction, the Si−C bond formation in the first step is more favorable than the C−C bond formation. The activation energy barrier height of the Si−C bond formation in the first step is lower by about 9 kcal/mol than that of the C−C bond formation. The activation energy barrier of the second step results from the steric effect, not the variation of electronic states of the bonds.

For the reaction of butadiene and disilene, the concerted-type transition state with a C_s symmetry is not a real transition state. The variation of the electronic state of the Si−Si bond occurs at the earlier stage along the reaction pathway than those of the other bonds. Accordingly, the transition state is located on the earlier stage than the crossing point of the weight of the breaking and the forming bonds along the IRC pathway. The activation energy barrier of the TS(SiSi) is higher by 9.0 kcal/mol than that of the first-step transition state of the stepwise reaction at the CASSCF method. At the CASPT2/ 6-311++G(d,p) level, the energy barrier of the concerted transition state is only 0.48 kcal/mol, and the activation energy barrier of the first-step transition state of the stepwise reaction disappears (−3.31 kcal/mol). The variations of the electronic states of the bonds of the stepwise reaction are similar to that of TS(SiC−Si)-1.

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