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Theoretical Studies on the Ene Reaction Mechanisms of Propene and Cyclopropene with Ethylene and Cyclopropene: Concerted or Stepwise

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The potential energy surfaces of the ene reactions of propene and cyclopropene with ethylene and cyclopropene were studied by ab initio molecular orbital (MO) methods. The reaction mechanisms were analyzed by CiLC method on the basis of CASSCF MOs. The concerted and stepwise reaction pathways of the ene reaction of propene with ethylene as the parent reaction were located. The energy barrier of the stepwise process is about 4 kcal/mol lower than that of the concerted one. The other reactions can be found only the stepwise mechanism. Although the endo-type reaction of propene with cyclopropene, where cyclopropene is the enophile, probably occurs through a one-step process, the mechanism is divided into the CC bond formations and the hydrogen migration as a stepwise reaction. The CiLC-IRC analysis of the concerted process of propene with ethylene shows the different patterns of the electronic state variation for the CC bond formation/breaking and the hydrogen migration.

1. Introduction

Pericyclic reactions may be the most important class of organic reactions. The mechanisms of the reactions have been the subject of the most heated and interesting controversies. The mechanisms of the concerted pericyclic path and the stepwise path, involving a diradical or a zwitterion, have been discussed. Although the Woodward−Hoffmann rules[1] defined the concept of a concerted reaction in which all bonds are made or broken around a circle, the rules served not to settle mechanistic questions but to raise the stakes on what were already lively controversies. The ene reactions are one of the most interesting pericyclic reactions, and also have been the subject of controversies.[2−11] Although the ene reaction of propene with ethylene as the simplest reaction has not been observed experimentally, the experimental activation energies[12] for the ene reactions of ethylene with *trans*-2-butene and *cis*-2-butene to form 3-methylpent-1-ene were measured as 37.0 and 36.5 kcal/mol, respectively. The ene reaction of propene and ethylene as the parent reaction has been studied by some theoretical methods. The concerted pericyclic mechanism[13−15] for the reaction of propene with ethylene was proposed by ab initio molecular orbital (MO) and density functional methods. However, the stepwise mechanisms of the reaction of propene with ethylene have not been proposed at theoretical calculation levels. Houk and co-workers[13,15] also proposed that the dimerization of cyclopropene occurs through the intermediate on the stepwise path by the UB3LYP calculation level, although the reactions of cyclopropene with propene and ethylene occur through concerted paths. The energy barrier height from the intermediate to the dimerization product was estimated to be only 1.0 kcal/mol at the UB3LYP calculation level. However, to understand the mechanisms well, the reaction systems including diradical character as the stepwise process should be treated by more appropriate methods.

In our previous papers, the mechanisms of some pericyclic reactions such as electrocyclic reactions,[16,17] Diels−Alder reactions,[18] and 1,3-dipolar additions[19−21] were characterized by a configuration interaction ((CI)/localized molecular orbital (LMO) CASSCF calculation along the IRC pathway (CiLC-IRC) method. From the analysis of these reactions by the CiLC-IRC method, the difference between the conrotatory and the disrotatory mechanisms for electrocyclic reactions was explained with the biradical character of the terminal atoms. For the Diels−Alder reactions, the characterization of the mechanisms of the concerted and the stepwise processes was proposed. Recently it has been shown that the mechanisms of 1,3-dipolar cyclic additions are classified into the concerted and the stepwise including diradical and polar cyclic processes.

In the present paper, we report the potential energy surfaces of the ene reactions of propene with ethylene as the parent reaction and of cyclopropene with ethylene, propene, and cyclopropene by the CASSCF and CAS-MP2 calculation levels. These reaction pathways are also analyzed by the CiLC-IRC method.

2. Computational Approch

All equilibrium and transition state geometries were determined with analytically calculated energy gradients at a complete active space self-consistent field (CASSCF) method[22] with the split-valence plus polarization 6-31G(d,p) set.[23,24] For the CASSCF calculation, six active orbitals relating to the reactions were included. All configurations in active spaces were generated. Frequency calculations were performed to determine the nature of each stationary point. Single-point energies were determined at a multiconfigurational second-order Møller−Plesset perturbation (CAS-MP2) method[25] with the 6-31G(d,p) and 6-311+G(d,p) basis sets[26] using the CASSCF-optimized structures. The intrinsic reaction coordinate (IRC)[27,28] 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,p) basis set.[29] The details of the CiLC-IRC can be found in previous papers.[16−18] Briefly, the CASSCF calculation was carried out to obtain a starting set of orbitals

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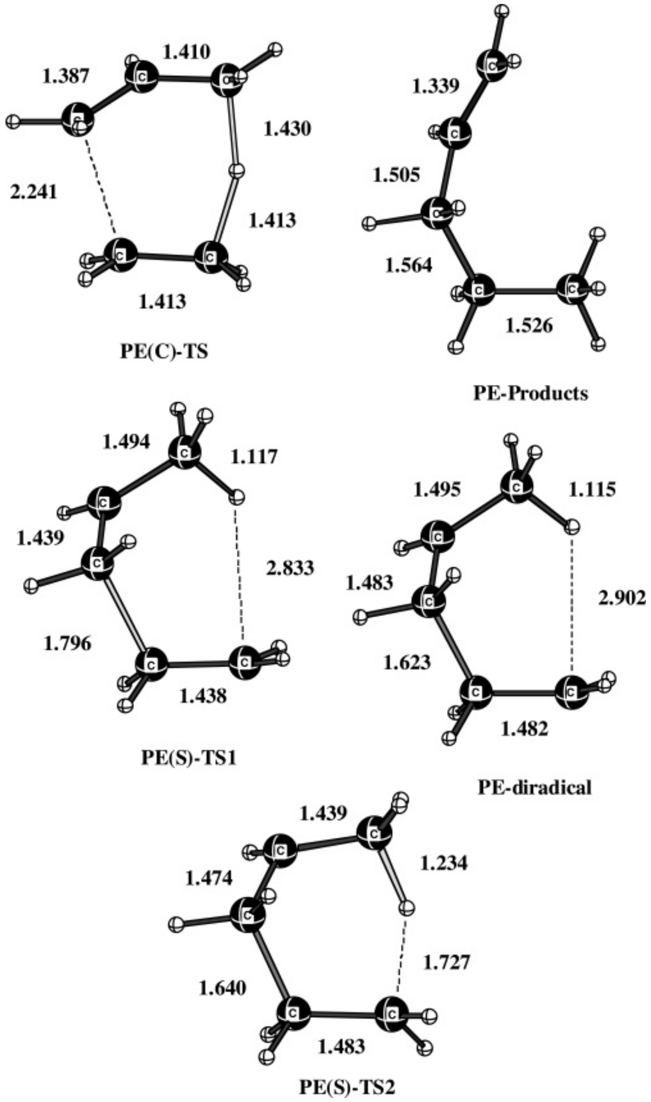
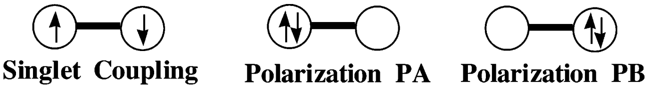


Figure 1. Geometric parameters of the transition states, intermediate, and products of the ene reaction of propene with ethylene using the CASSCF/6-31G(d,p) method. All bond lengths are in Å.

for the localization procedure. The Boys localization[30] 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 weights of configurations in the atomic-orbital-like wave functions. The total energy calculated by the CI procedure corresponds well with 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 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 to explain the bond formation and bond extinction along a chemical reaction path.



The calculations of the CiLC-IRC analysis were performed with the GAMESS program package,[31] and the others were made with the use of the Gaussian 98 program package.[32]

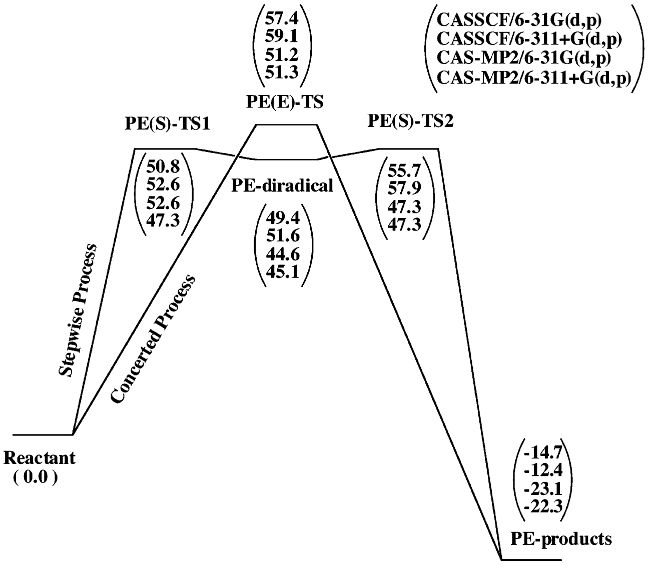


Figure 2. Potential energy diagram of the reactions of propene with ethylene. The units are kcal/mol.

3. Results and Discussion

3.1. Reaction Pathways.

3.1.1. Propene + Ethylene. The stationary points of the ene reaction of propene with ethylene are shown in Figure 1. The relative energies from the reactants are listed in Table 1. To understand easily the concerted and the stepwise processes, the potential energy diagram of the reactions of propene with ethylene is also shown in Figure 2. Although previous papers[13−15] proposed only the concerted transition state for the ene reaction of propene with ethylene, we found not only the concerted transition state but also the stationary points of the stepwise process. The obtained structure of the concerted transition state (PE(C)-TS) is similar to the B3LYP/6-31G* transition state in a previous paper,[15] except for the breaking and forming CH bond lengths. For the CASSCF calculation, the breaking CH bond is 0.017 Å longer than the forming CH bond. The breaking CH bond length obtained by the B3LYP calculation is 0.167 Å shorter than the forming CH bond length. The difference of the breaking and the forming CH bond lengths at the transition states may be important for the electronic mechanisms of the reactions.

On the other hand, the stationary points on the stepwise reaction pathway of the ene reaction of propene with ethylene are also shown in Figure 1. The first step of the stepwise reaction is the CC bond formation through the transition state (PE(S)-TS1), and leads to the diradical intermediate (PE(S)-diradical). The formatting CC bond length of PE(S)-TS1 is shorter by 0.445 Å than that of PE(C)-TS and is only 0.173 Å longer than that of PE(S)-diradical. The second step is hydrogen migration process through the transition state of PE(S)-TS2. For the transition state (PE(S)-TS2) of hydrogen migration, the breaking CH bond length is shorter by 0.493 Å than the forming CH bond length. The difference of the breaking and forming CH bond lengths of PE(S)-TS2 is very large in comparison with that of PE(C)-TS. The hydrogen migration through PE-(S)-TS2 has an earlier transition process than that through PE(C)-TS.

The energy barrier height at PE(S)-TS1 is 50.8 kcal/mol above the reactants at the CASSCF/6-31G(d,p) calculation level, and 47.3 kcal/mol at the CAS-MP2/6-311+G(d,p) level. The energy difference between PE(S)-TS1 and the diradical intermediate (PE-diradical) is only 1.4 and 2.2 kcal/mol by the CASSCF/6-31G(d,p) and CAS-MP2/6-311+G(d,p) methods, respectively.

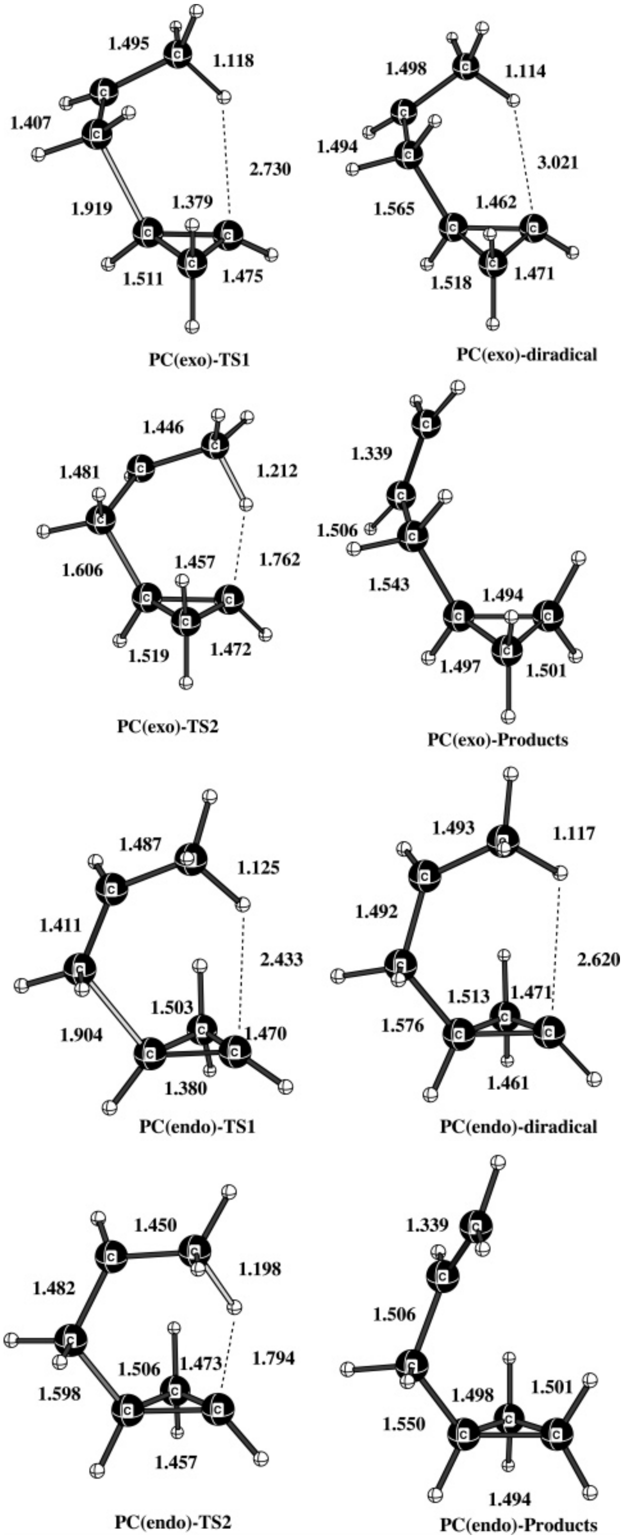


Figure 3. Geometric parameters of the transition states, intermediates, and products of the ene reaction of propene with cyclopropene using the CASSCF/6-31G(d,p) method. All bond lengths are in Å.

The hydrogen migration process through PE(S)-TS2 has the energy barrier height of 47.3 kcal/mol from the reactants of propene and ethylene, and the barrier is only 2.2 kcal/mol above the diradical intermediate at the CAS-MP2/6-311+G(d,p) method. The energy barrier height of the transition state of PE-(S)-TS1 is equal to that of PE(S)-TS2 and is 4.0 kcal/mol lower than that of PE(C)-TS of the concerted process. Consequently the ene reaction of propene with ethylene occurs through the stepwise process but not the concerted one. The detection of the diradical intermediates, however, may be hard experimentally, because of the very flat potential energy surface in the region between the transition states of PE(S)-TS1 and PE(S)-TS2 through the PE-diradical intermediate.

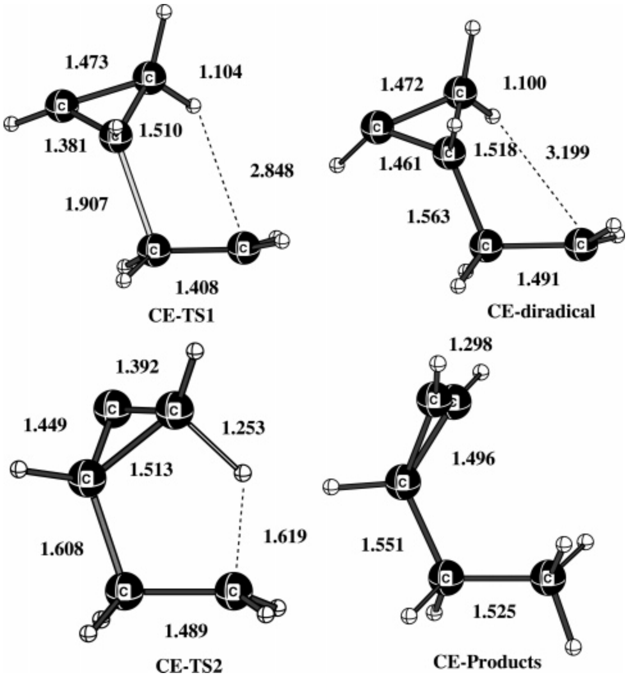


Figure 4. Geometric parameters of the transition states, intermediate, and products of the ene reaction of cyclopropene with ethylene using the CASSCF/6-31G(d,p) method. All bond lengths are in Å.

3.1.2. Propene with Cyclopropene. The ene reaction of propene with cyclopropene, where cyclopropene is the enophile, has both exo and endo transition structures. The stationary points of the reactions are displayed in Figure 3. The reactions of both exo and endo types occurs through the stepwise process at the CASSCF calculation level. The transition state on the concerted reaction path collapses to the stepwise energy surface at this calculation level. The first step is the formation of CC bond, and the second is the hydrogen migration via the breaking CH bond and the forming CH bond. The mechanisms are different from the concerted pathway obtained by the Hartree−Fock and the B3LYP calculations in the previous papers.[13,15] The forming CC bonds of the first-step transition states of the exo type (PC-(exo)-TS1) and the endo type (PC(endo)-TS1) are about 0.123 and 0.108 Å longer than that of PE(S)-TS1 of the reaction of propene with ethylene. Namely, the first step reactions of propene with cyclopropene have an earlier transition state than that of propene with ethylene. This reflects the high reactivity of cyclopropene in reactions involving additions to the highly strained double bond. The forming CC bond of the first-step transition state (PC(exo)-TS1) of the exo type is a little longer than that (PC(endo)-TS1) of the endo type. In the second step, the breaking CH bond length of the transition state (PC(exo)-TS2) of the exo type is longer than that of the endo type and the forming CH bond length of the exo type is shorter than that of the endo type. Namely, the breaking and formation processes of the CH bonds of the exo type are later than those of the endo type.

For the exo type, the energy barrier of the first-step transition state (PC(exo)-TS1) is about 8.7 kcal/mol higher than that of the second-step transition state (PC(exo)-TS2) at the CAS-MP2/6-311+G(d,p) level. The barrier height of PC(exo)-TS2 is about 2.7 kcal/mol above the intermediate (PC(exo)-diradical). For

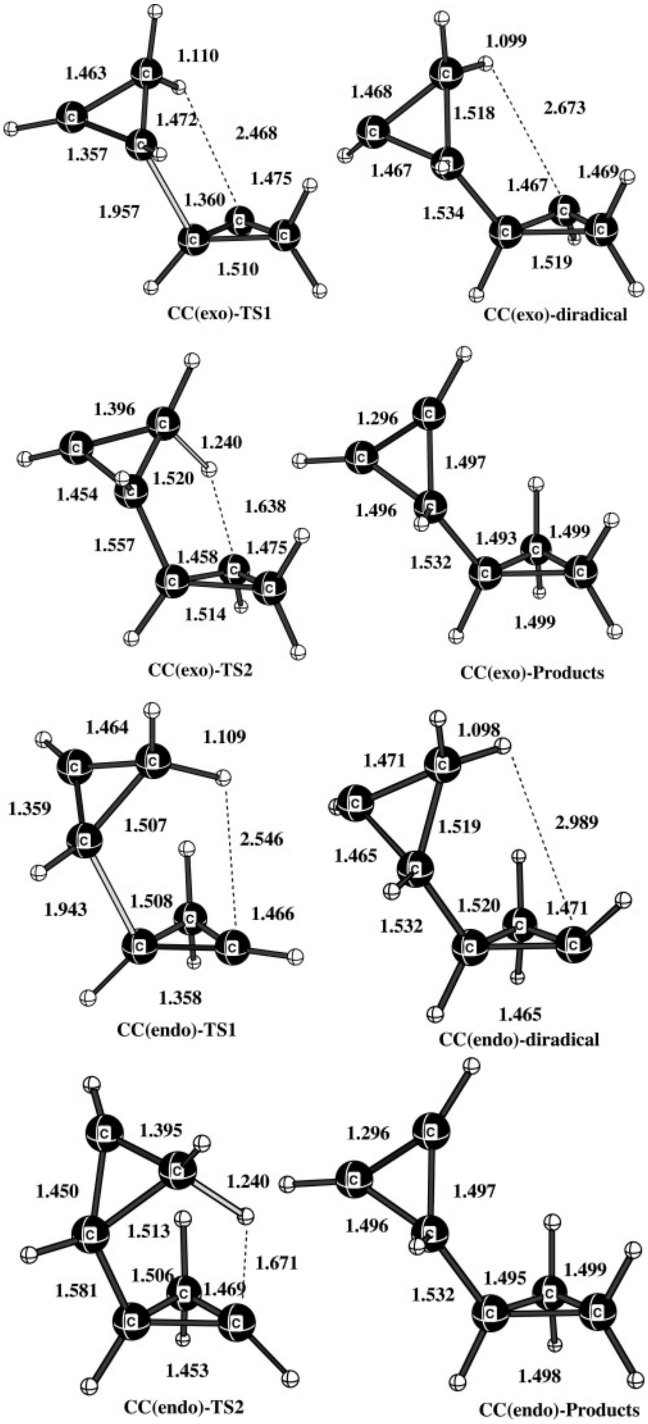


Figure 5. Geometric parameters of the transition states, intermediates, and products of the ene reaction of cyclopropene dimerization using the CASSCF/6-31G(d,p) method. All bond lengths are in Å.

the endo type, the energy barrier of the first-step transition state (PC(endo)-TS1) is higher by 8.7 kcal/mol than that of the second-step transition state (PC(endo)-TS2) at the CAS-MP2 calculation level. Although PC(endo)-TS2 is slightly higher in energy than the intermediate (PC(endo)-diradical) by the CASSCF method, at the CAS-MP2 calculation level the transition state is lower by 0.4 kcal/mol than the intermediate. Therefore, the endo-type reaction of propene with cyclopropene probably occurs at the one-step but not the concerted pathway (stepwise-like or a very strongly asymmetric reaction). The intermediate of the exo type is slightly lower by 1.3 kcal/mol than that of the endo type. The overall energy barrier of the exo type is about 1.8 kcal/mol higher than that of the endo type at the CAS-MP2 level. Consequently the endo-type pathway is slightly more favorable than the exo type.

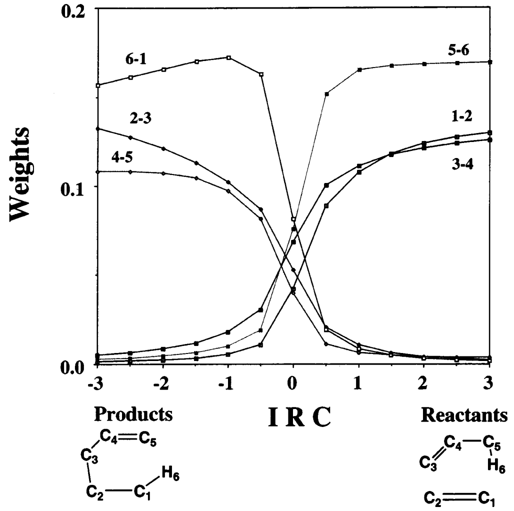


Figure 6. Weights of bonds of CiLC calculation along the IRC pathway of the concerted ene reaction of propene with ethylene. The units are bohr·amu$^{1/2}$.

3.1.3. Cyclopropene + Ethylene. The stationary points of the ene reaction of cyclopropene with ethylene are shown in Figure 4. The reaction occurs also through the stepwise process. The reaction pathway is also different from that of the parent reaction and/or the ene reaction of cyclopropene with ethylene obtained by the B3LYP calculation. The forming CC bond length of the first-step transition state (CE-TS1) is similar to that of the endo-type ene reaction of propene with cyclopropene and is different from that of PE(S)-TS1. Namely, the forming CC bond length of CE-TS1 is 0.174 Å longer than that of PE(S)-TS1 and only 0.003 Å longer than that of PC(endo)-TS1. The breaking CH bond of the second transition state (CE-TS2) is 1.253 Å, and is longer than those of the reactions of propene with cyclopropene. The forming CH bond length of the second transition state (CE-TS2) is shorter than those of the reactions of propene with cyclopropene.

The first-step transition state (CE-TS1) is about 5.3 and 0.4 kcal/mol lower in energy than the second transition state (CE-TS2) at the CASSCF/6-31G(d,p) and CAS-MP2/6-311+G(d,p) calculation levels, respectively. The first-step transition state (CE-TS1) is 12.6 kcal/mol higher in energy than the intermediate (CE-diradical). The energy barrier height of the second-step transition state is about 13.0 kcal/mol above CE-diradical at the CAS-MP2/6-311+G(d,p) method. The stability of CE-diradical comes from the highly strained double bond of cyclopropene.

The energy barrier of CE-TS1 is 0.9 and 2.7 kcal/mol higher than those of PC(exo)-TS1 and PC(endo)-TS1, respectively. The intermediate (CE-diradical) is 0.3 and 1.6 kcal/mol lower in energy than PC(exo)-diradical and PC(endo)-diradical, respectively. Therefore, the potential energy surface of the first step of the reaction of cyclopropene with ethylene is similar to that of propene with cyclopropene. However, the energy barrier of CE-TS2 is 10.0 and 11.8 kcal/mol higher than those of PC-(exo)-TS2 and PC(endo)-TS2, respectively. The difference of energy barriers of the second step comes from the stabilization energy of the π-bond formation.

3.1.4. Cyclopropene Dimerization. The stationary points of the dimerization of cyclopropene are shown in Figure 5. Both exo and endo reactions occur through the stepwise process. The first-step transition state structures (CC(exo)-TS1 and CC(endo)-

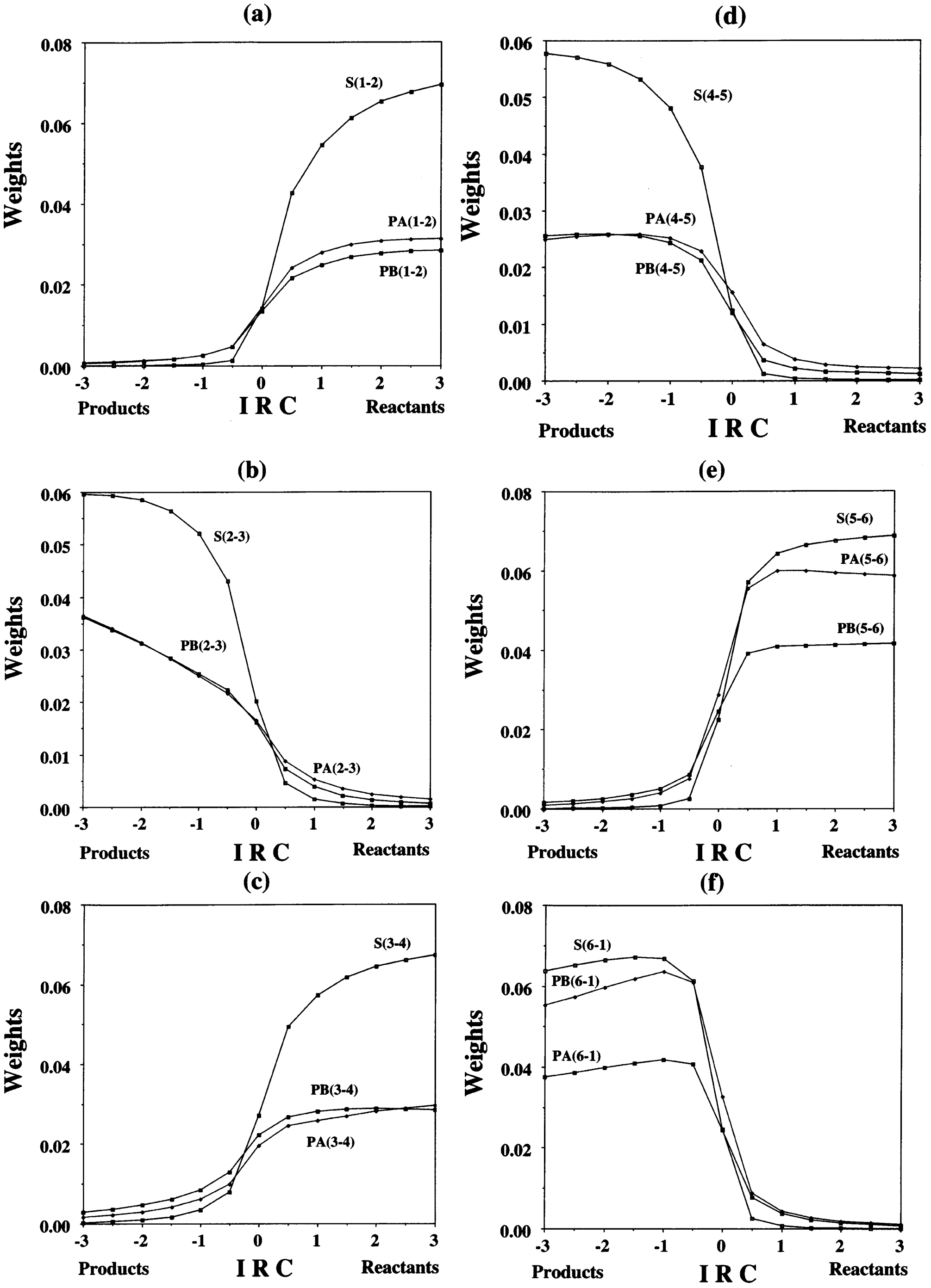


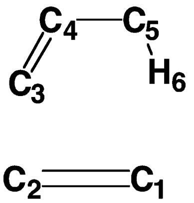
Figure 7. Weights of singlet and polarization terms for each bond of CiLC calculation along the IRC pathway of the concerted ene reaction of propene with ethylene. The units are bohr•amu$^{1/2}$.

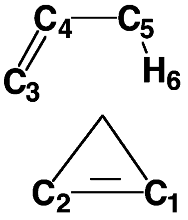
TS1) on both exo and endo pathways are similar to those obtained by the B3LYP calculation level. The forming CC bond lengths of CC(exo)-TS1 and CC(endo)-TS1 are 1.957 and 1.943 Å, respectively, and are a little longer than those (1.925 and 1.939 Å)[15] obtained by the B3LYP method. The forming CH bond lengths of CC(exo)-TS1 and CC(endo)-TS1 are 2.469 and 2.546 Å, respectively, and are also longer than those (2.035 and 2.201 Å) by the B3LYP method. Of course, the hydrogen migration does not occur on the first step of both exo and endo pathways.

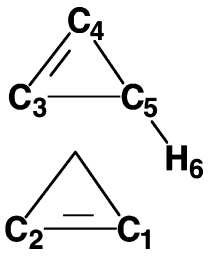
For the intermediate led along the IRC path from the first-step transition state, the direction of the expanse of the radical orbital of the enophile part of CC(exo)-diradical is inward and that of CC(endo)-diradical is outward. For the exo type, the radical orbital probably has a weak interaction with the active hydrogen atom at the first-step transition state. This is similar to other reactions. For the endo type, the radical orbital has a repulsive effect with the other cyclopropene part. Therefore, two diradical intermediates for the endo type are led along the IRC pathways of the first and the second processes, and their relative energies are listed as CC(endo)-diradical(1) and CC-(endo)-diradical(2) in Table 1, respectively. In Figure 5, only CC(endo)-diradical(1) is shown as CC(endo)-diradical.

For the second step from the intermediate to the products, the breaking CH bond lengths are 1.240 and 1.240 Å for the exo and endo transition states (CC(exo)-TS2 and CC(endo)-TS2), while the forming CH bond lengths are 1.638 and 1.671 Å, respectively. These transition state structures (CC(exo)-TS2 and CC(endo)-TS2) are a later transition state than those of the reaction of propene with cyclopropene and an earlier one than that of the reaction of cyclopropene with ethylene. The endo-type transition state (CC(endo)-TS2) is a little earlier than CC-(exo)-TS2.

In the first step, the energy barrier of the exo transition state (CC(exo)-TS1) is about 2.4 kcal/mol higher than that of the endo one (CC(endo)-TS1), and the exo intermediate (CC(exo)-diradical) is also higher by 2.0 kcal/mol than CC(endo)-diradical(1) and lower by 1.2 kcal/mol than CC(endo)-diradical-(2). The second-step transition state (CC(exo)-TS2) of the exo type is 14.6 kcal/mol lower in energy than CC(exo)-TS1 and 8.6 kcal/mol higher than the intermediate (CC(exo)-diradical-(1)) by the CAS-MP2 method, although Deng and co-workers were not able to locate the second-step transition state by the UB3LYP method. The second-step transition state (CC(endo)-TS2) of the endo type is about 13.8 kcal/mol higher in energy than the intermediate(CC(endo)-diradical(2)) by the CASSCF method and is about 10.3 kcal/mol higher than that by the CAS-MP2 method.







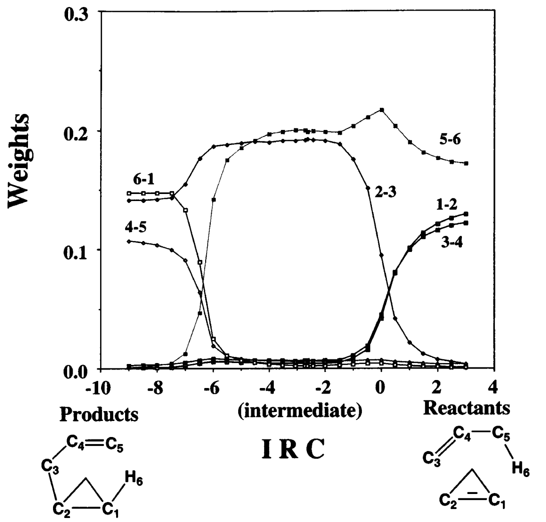


Figure 8. Weights of bonds of CiLC calculation along the IRC pathway of the endo-type reaction of propene with cyclopropene. The units are bohr·amu$^{1/2}$.

3.2. CiLC Analysis. As shown in the previous section, the ene reaction of propene with ethylene occurs through the stepwise pathway and/or the concerted pathway as a one-step process. Although the stepwise reaction is more favorable in energy by 4 kcal/mol than the concerted one, the mechanism of the concerted reaction is interested in the origin between the stepwise and the concerted processes. To study the electronic mechanism of the concerted reaction as a one-step process, the variations of the weights of the related bonds of the concerted reaction of propene with ethylene by the CiLC analysis along the IRC pathway are shown in Figure 6. In the figure, $x-y$ indicates the bond between x and y atoms (orbitals). The variations of the weights of the singlet coupling ($S(x-y)$) and the polarization terms ($PA(x-y)$ and $PB(x-y)$) of each bond are shown in Figure 7, where $PA(x-y)$ means the polarization term that the electron pairs polarized to x atom (orbital) and $PB(x-y)$ means the polarization term that the electron pairs polarized to y atom (orbital). The bond formations and the bond breaking occur almost symmetrically at the region of the transition state. This is similar to those[18] of the Diels−Alder reaction of butadiene and ethylene. For the reactant side, the weight of the π bond of C_1-C_2 decreases a little earlier than that of the π bond of C_3-C_4 along the IRC path. This corresponds to the bond formations of C_2-C_3 and C_4-C_5. Namely, the bond formation of C_2-C_3 occurs earlier than that of C_4-C_5. The bond breaking of C_5-H_6 and the bond formation of H_6-C_1 for the hydrogen migration occurs suddenly in the narrow region near the transition state. This sudden variation can be seen in the symmetry-forbidden reaction of the cyclic dimerization of ethylene as shown in a previous paper.[33] Thus the hydrogen migration part of the ene reaction is unfavorable in comparison with the bond formations of C_2-C_3 and C_4-C_5 and the bond breaking of C_1-C_2 and C_3-C_4. This comes from the electronic states of the C−C bonds and the C−H bonds. Namely, the C_1-C_2 and C_3-C_4 bonds for the reactant side and the C_2-C_3 and C_4-C_5 bonds for the product side consist of almost the same weights of two polarization terms, nonpolarized bonds, and these bonds at the region of the transition state have aromatic character[34,35] of almost equal weight of the singlet coupling and polarization terms (see Figure 6). On the other hand, one polarization term (PA of the C_5-H_6 bond for the reactant side and PA of the H_6-C_1 bond for the product side) of the CH breaking/forming bonds is larger than the other polarization terms (PB of the C_5-H_6 bond and PB of the H_6-C_1 bond). This means the polarization of each CH bond. These polarization terms are almost equal weights at the region of the transition state, and these bonds show the aromatic character at the transition state as the concerted mechanism. Thus the breaking and the forming CC bonds occur from nonpolar bonds to nonpolar bonds through the aromatic character at the transition state, whereas the hydrogen migration occurs from the polarized bond to polarized bond through the same aromatic character. This corresponds to the sudden mechanism of the hydrogen migration and may lead to the stepwise process of other ene reactions.

The weights of the relating bonds of the endo-type reaction of propene with cyclopropene by the CiLC-IRC analysis are shown in Figure 8. The weights of the singlet coupling and the polarization terms of each bond are also shown in Figure 9. Although the ene reaction of propene with cyclopropene may have only one energy barrier at the CAS-MP2 calculation level, the process is divided into two steps completely. This reaction mechanism is an absolutely stepwise-like process. The first step is the π-bond breakings of C_1-C_2 and C_3-C_4 and the C_2-C_3 bond formation, and the second is the hydrogen migration between C_5 and C_1 atoms and the π-bond formation of C_4-C_5. Accordingly the intermediates between the first and second processes have diradical character on the C_1 and C_4 atoms. Although the C_5-H_6 bond before the second process polarizes as a minus for C_5 and a plus for H_6, the H_6-C_1 bond after the second process polarizes as a minus for H_6 and a plus for C_1 atom (Figure 9e,f). Thus, the direction of polarization for the hydrogen atom (H_6) probably suffocates the smooth concerted process.

The weights of the bonds of the first and the second steps of the ene reaction of cyclopropene with ethylene by the CiLC-IRC analysis are shown in Figures 10 and 11, respectively. At the first step (Figure 10), the π-bond breakings of C_1-C_2 and C_3-C_4 and the σ-bond formation of C_2-C_3 occur smoothly

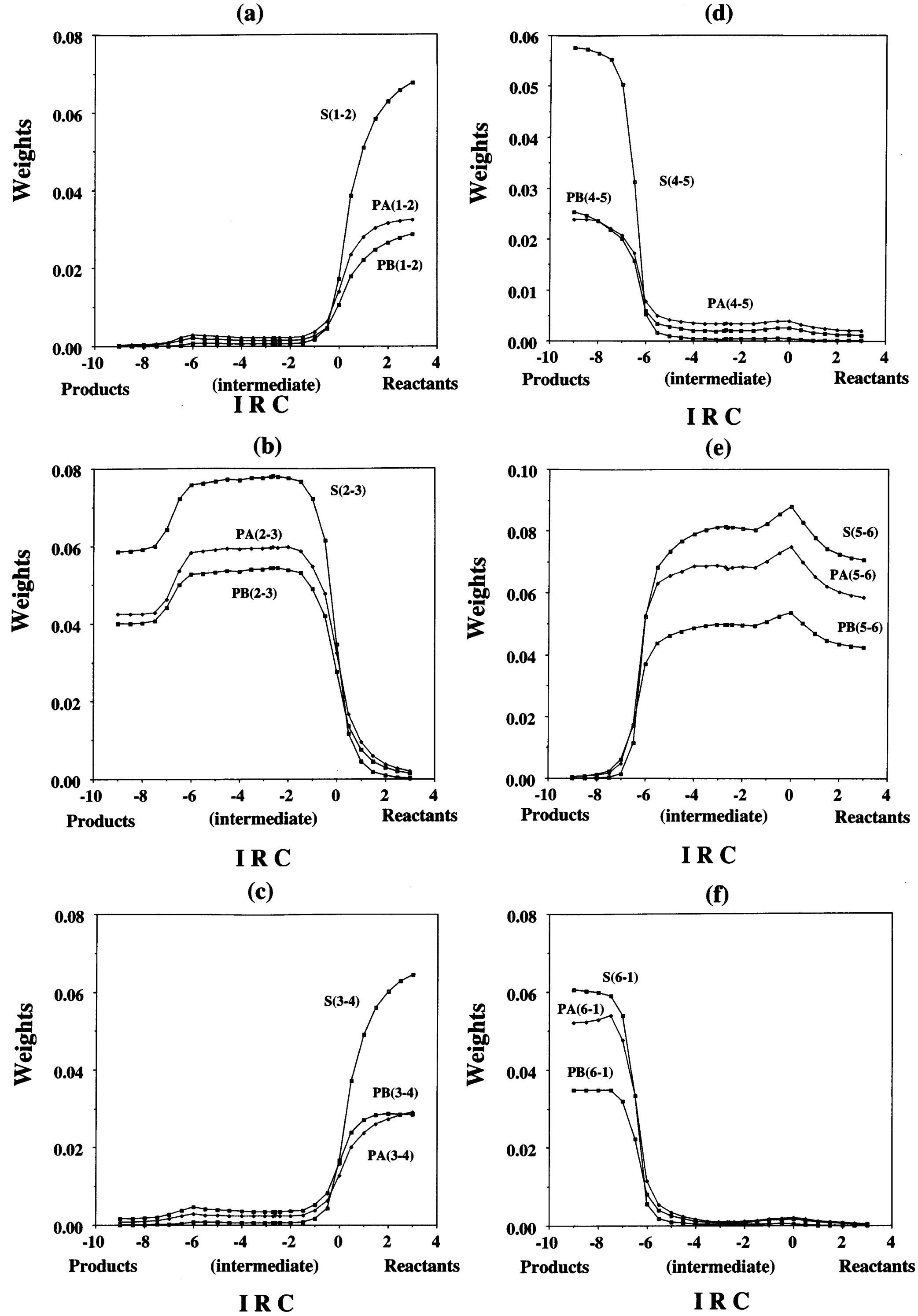


Figure 9. Weights of singlet and polarization terms for each bond of CiLC calculation along the IRC pathway of the endo-type reaction of propene with cyclopropene. The units are bohr•amu$^{1/2}$.

during the region between about 2.0 and −2.0 bohr•amu$^{1/2}$ of the IRC. For the second step (Figure 11), the C_5−H_6 bond breaking occurs from 1.0 to −1.0 bohr•amu$^{1/2}$ of the IRC and the H_6−C_1 bond formation occurs from 0.5 to −1.5 bohr•amu$^{1/2}$ of the IRC. Namely, the hydrogen migration occurs suddenly at the narrow region of the IRC. The π-bond formation of C_4−C_5 occurs smoothly from 0.5 to −2.0 (or −2.5) bohr•amu$^{1/2}$ of the IRC.

4. Conclusion

The ene reaction mechanisms of propene and cyclopropene with ethylene and cyclopropene were investigated by ab initio MO methods. For the reaction of propene with ethylene as the parent ene reaction, the concerted and stepwise pathways were located. The overall energy barrier height on the stepwise pathway is 4 kcal/mol lower than that on the concerted pathway. Although the concerted reaction occurs via a one-step process, the C−C bond formation/breaking and the hydrogen migration are distinguished: the former is the smooth process and the later is the sudden process. Thus, the concerted pathway of the ene reaction of propene with ethylene is not a smooth process in comparison with the concerted pathway of the Diels−Alder reaction of butadiene with ethylene.

TABLE 1: Relative Energies (kcal/mol) of Ene Reactions

	CASSCF		CAS-MP2	
	6-31G(d,p)	6-311+G(d,p)	6-31G(d,p)	6-311+G(d,p)
	Propene + Ethylene			
PE(E)-TS	57.4	59.1	51.2	51.3
PE(S)-TS1	50.8	52.6	52.6	47.3
PE-diradical	49.4	51.6	44.6	45.1
PE(S)-TS2	55.7	57.9	47.3	47.3
PE-products	−14.7	−12.4	−23.1	−22.3
	Propene + Cyclopropene			
PC(exo)-TS1	39.8	41.5	33.6	34.5
PC(exo)-diradical	29.2	31.6	22.3	23.1
PC(exo)-TS2	35.6	37.9	25.2	25.8
PC(exo)-products	−41.0	−39.1	−50.5	−50.0
PC(endo)-TS1	36.1	41.1	31.9	32.7
PC(endo)-diradical	31.0	33.5	23.4	24.4
PC(endo)-TS2	33.8	36.1	23.3	24.0
PC(endo)-products	−39.8	−37.7	−49.8	−49.0
	Cyclopropene + Ethylene			
CE-TS1	39.1	40.9	34.5	35.4
CE-diradical	28.5	30.8	22.1	22.8
CE-TS2	44.4	46.8	35.1	35.8
CE-products	−16.2	−14.0	−25.1	−24.3
	Cyclopropene + Cyclopropene			
CC(exo)-TS1	30.8	32.6	24.2	25.6
CC(exo)-diradical	9.5	12.3	0.7	2.4
CC(exo)-TS2	21.9	24.2	9.9	11.0
CC(exo)-products	−43.1	−41.0	−53.4	−52.7
CC(endo)-TS1	30.2	31.8	22.4	23.2
CC(endo)-diradical(1)	8.9	11.5	-0.7	0.4
CC(endo)-diradical(2)	11.0	13.6	2.3	3.6
CC(endo)-TS2	24.8	27.1	13.0	13.9
CC(endo)-products	−43.1	−41.0	−53.6	−52.8

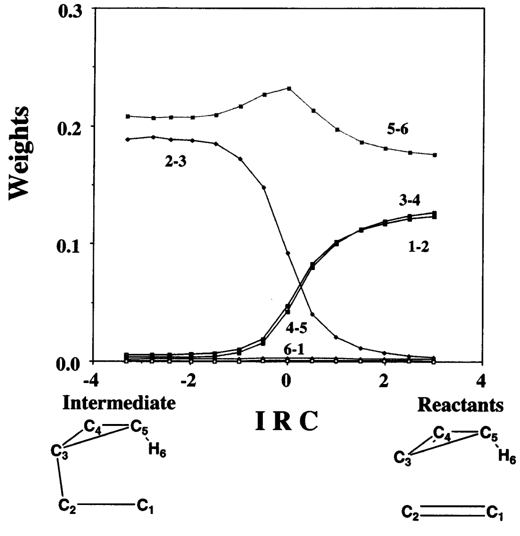


Figure 10. Weights of bonds of CiLC calculation along the IRC pathway of the first step reaction of cyclopropene with ethylene. The units are bohr·amu$^{1/2}$.

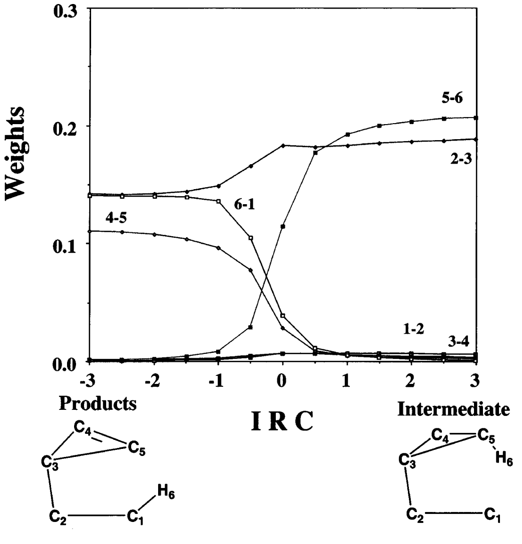


Figure 11. Weights of bonds of CiLC calculation along the IRC pathway of the second step reaction of cyclopropene with ethylene. The units are bohr·amu$^{1/2}$.

Experimentally the dimerization processes of propene and ethylene may occur in the reaction system of propene and ethylene. However, the overall energy barrier heights of the dimerization of propene are about 1−2 kcal/mol (not shown here) higher than that of propene with ethylene. The energy barrier of the dimerization of ethylene is about 10 kcal/mol higher[33] than that of propene with ethylene. Accordingly, the ene reaction of propene with ethylene occurs favorably in the system.

For the reaction of propene with cyclopropene, two reaction pathways of the exo and the endo types are found. Both reaction pathways occur through the stepwise process during the diradical intermediate at the CASSCF calculation level. The second transition state of the exo type is about 6.4 kcal/mol higher in energy than the intermediate by the CASSCF method, and about 2.7 kcal/mol higher by the CAS-MP2 method. Therefore, the ene reaction of the exo type of propene with cyclopropene occurs through the stepwise pathway. The concerted one-step transition state for the exo type could not be located. However, the second transition state of the endo type obtained by the CASSCF method is 0.4 kcal/mol lower in energy than the intermediate at the CAS-MP2 calculation level. Although the energy barrier at the second transition state of the endo type vanishes on the potential energy surface of the reaction, the electronic mechanism occurs through a stepwise-like process.

For the ene reaction of cyclopropene with ethylene, we also found only the stepwise process, not the concerted one. The second-step transition state is still higher in energy than the first-step transition state, and is about 13 kcal/mol energy barrier above the intermediate.

For the dimerization of cyclopropene, both reactions of exo and endo types occur through the stepwise pathway. The first transition state of the exo type is slightly higher by 2.4 kcal/mol than that of the endo type. The second transition state of the exo type is about 3 kcal/mol lower in energy than that of the endo type. The energy barrier height of the second transition state of the exo type is about 9 kcal/mol above the intermediate, and that of the endo type is about 10 kcal/mol above the intermediate.

Consequently, it is considered that the ene reactions treated here occur through the stepwise process, and some diradical intermediate could be detected experimentally.

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