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Theoretical Studies on Mechanisms of Cycloaddition Reaction between Dichlorovinylidene and Formaldehyde: Concerted and Stepwise?

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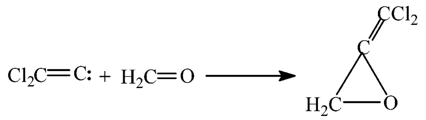
The mechanism of cycloaddition reaction between singlet dichlorovinylidene (R1) and formaldehyde (R2) has been investigated with MP2 and B3LYP /6-31G* methods, including geometry optimization, vibrational analysis, and energy for the involved stationary points on the potential energy surface. Energies from both methods are also further corrected by CCSD(T)/6-31G* single-point calculations. Although the relative energies do differ especially for the loose conformations such as transition states and intermediates, generally the geometries predicted by MP2 and B3LYP are in good agreement. CCSD(T) relative energies for the stationary points predicted by MP2 and B3LYP agree quite well, and they are more comparative to those from B3LYP than those from MP2. The results also show that both three-centered and [2+2] cycloadditions can happen in concerted pathways. The former leads to a stable three-membered ring product (P1), while the two intermediates (INT1c and INT1d) from the latter are not so stable and will rearrange into either P1 or a more stable four-membered ring product (P2). The orbital interactions are also discussed for the leading intermediates and products.

1. Introduction

Cycloaddition has long been widely used and rapidly advanced in organic chemistry. Especially since Woodward and Hoffmann put forward the orbital symmetry rule, the understanding of this kind of reaction has been strongly enhanced, and the mechanism investigation with the rule has been one of the most interesting topics for experimentalists as well as theoreticians. Since unsaturated carbene was recognized as an active intermediate in 1960s, it has not only attracted much attention from theoretical chemist but also been practically applied to organic chemistry.[1,2] For example, it provides simple and direct synthesis for small-ring, highly strained compounds, as well as those that are difficult to synthesize through conventional ways.[2] Apeloig et al.[3,4] extensively studied the mechanisms and stereoselectivity of alkylidene cycloadddition to olefins using experimental as well as theoretical methods. Rearrangement of vinylidene and fluoro/difluorovinylidene (carbene) and identification of relevant species were also intensively studied.[5,6] We have investigated the cycloaddition reaction between vinylidene carbene and asymmetric π systems, like formaldehyde.[7] Because of the important application of the chloro-substituted carbene in medicine synthesis,[8] in the present paper we choose dichlorovinylidene and formaldehyde as model molecules to further explore the cycloaddition of singlet dichloro-substituted carbene to asymmetric π systems. The results indicate that cycloaddition of dichlorovinylidene to formaldehyde has two leading reactions, as shown below. Similarly to the experimental findings of the cycloaddition between alkylidene carbene and olefin,[3,4] one of the leading products of the cycloaddition between dichlorovinylidene and formaldehyde is a three-membered ring compound; however in contrast to the cycloaddition of vinylidene and formaldehyde, for which only the first one is the leading reaction, reaction 2 also become a major channel.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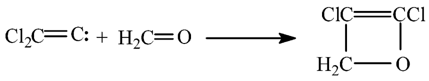
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2. Calculation Methods

MP2/6-31G*[9] and the hybrid density functional theory B3LYP/6-31G*[15,16] implemented in the Gaussian98 package[12] are employed to locate all the stationary points along the reaction pathways. Full optimization and harmonic vibrational analysis are done for the stationary points on the reaction profile. Zero-point energy correction is included for energy calculations. All minima and transition sates have the proper number of imaginary frequencies. To explicitly establish the relevant species, IRC[10,11] is also run for all the transition states appearing on the cycloaddition energy surface profile. CCSD(T)/6-31G single-point calculations are also performed for all the stationary points obtained from the MP2 and B3LYP methods, denoted as CCSD(T)//MP2 and CCSD(T)//B3LYP, respectively.

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TABLE 1. Relative Energies (E_R, kJ/mol) for the Species of the Cycloaddition Reaction between Dichlorovinylidene and Formaldehyde

species	MP2[a]	B3LYP	CCSD(T)//MP2[b]	CCSD(T)//B3LYP
R1+R2	0.0	0.0	0.0	0.0
TS1a (R ↔ P1)	3.1	0.8	11.7	9.1
P1	−301.4	−275.7	−260.2	−260.5
INT1b1	−57.5	−64.5	−39.4	−37.4
TS1b1 (INT1b1↔ INT1b2)	−54.7	−61.6	−39.9	−36.8
INT1b2	−71.9	−74.9	−46.0	−50.8
TS1b2 (INT1b2 ↔ P1)	13.4	−6.4	35.1	2.4
INT1c	−45.7	−18.8	−14.2	−17.7
TS1c (INT1c ↔ P1)	6.8	28.3	44.4	43.3
INT1d	−163.7	−143.0	−144.4	−145.7
TS1d (INT1d ↔ P1)	−19.7	3.4	15.9	14.8
TS2a (INT1c ↔ P2)	−27.1	−17.5	−13.6	−14.0
P2	−344.3	−308.3	−300.2	−300.6
TS2b (INT1d ↔ P2)	−24.1	−33.9	−10.8	−8.0

[a] $E_R = E(\text{species}) - E(R_1+R_2) + \Delta ZPE$; E, total energy of electronic structure; ZPE, zero-point energy correction. [b] $E_R = \Delta E(\text{CCSD}) + \Delta ZPE(\text{MP2})$.

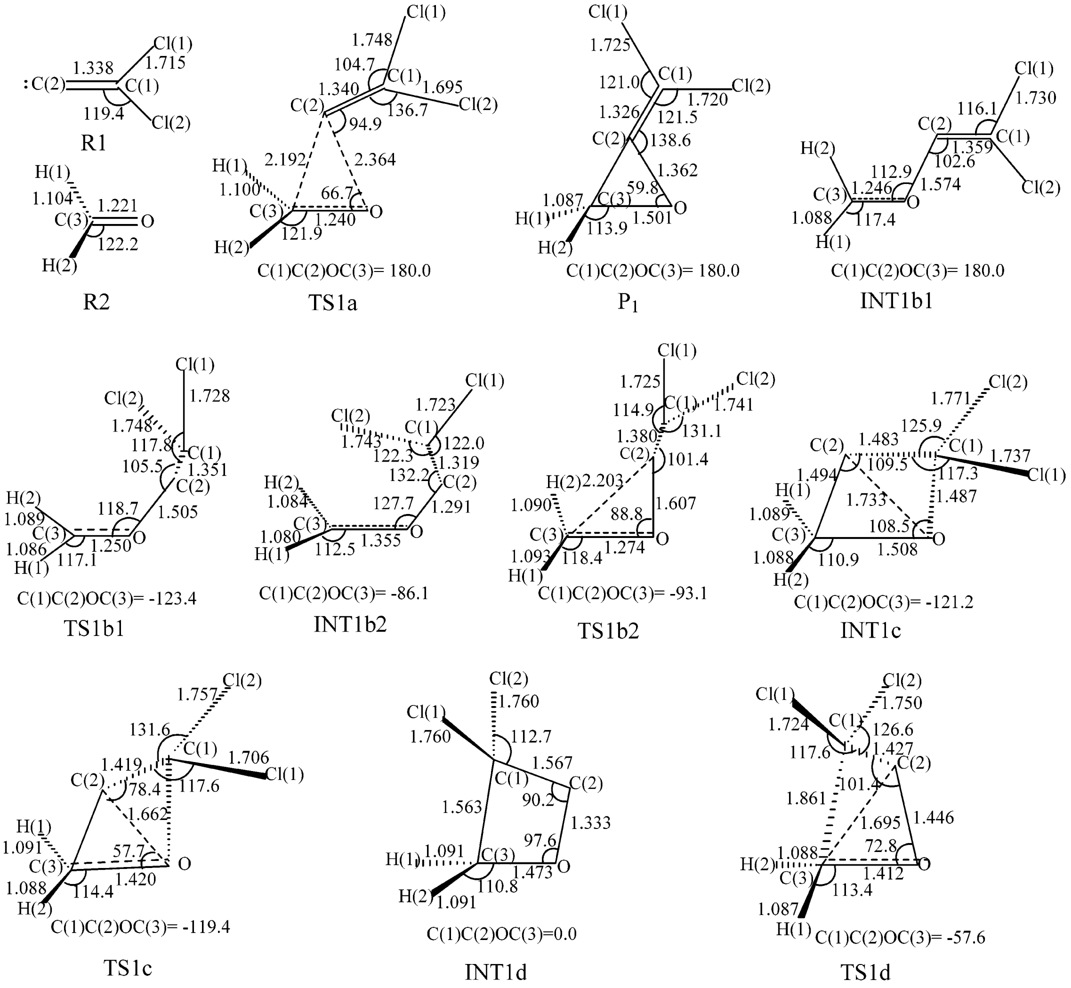


Figure 1. Optimized structures with MP2/6-31G* of the involved species of reaction 1 for the cycloaddition reaction between dichlorovinylidene and formaldehyde. Bond lengths and angles are in Å and deg.

3. Results and Discussions

The present calculations indicate that the ground state of dichlorovinylidene is a singlet state that has much lower energy than the triplet state by approximately 152.0 kJ/mol at the MP2/6-31G* level. Some geometric parameters, closely related to the reaction pathways, from both MP2/6-31G* and B3LYP/6-31G* methods for the two reactants, intermediates (INT1b1, INT1b2, INT1c, and INT1d), transition states (TS1a, TS1b1, TS1b2, TS1c, TS1d, TS2a, and TS2b), and products (P1 and P2) are listed in Table 2 for comparison. Optimized structures with parameters from MP2/6-31G* are given in Figures 1 and 5. The relative energies from MP2/6-31G*, B3LYP/6-31G*, CCSD(T)//MP2, and CCSD(T)//B3LYP methods for all the involved stationary points are summarized in Table 1. Overall reaction pathways are given in Figure 2.

According to Table 1, the relative energies of MP2/6-31G* and B3LYP/6-31G* do considerably differ, especially for some loose geometries such as transition states TS1b2 (13.4 vs −6.4

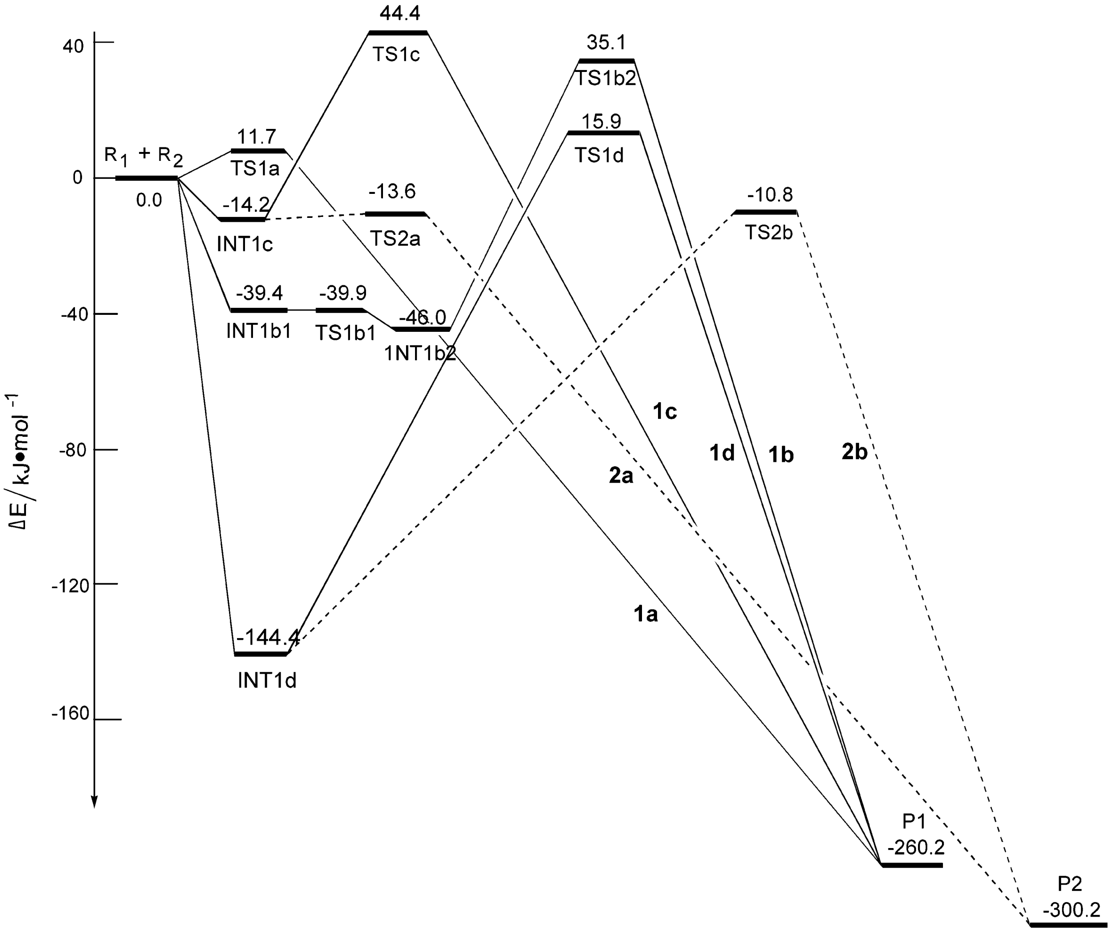


Figure 2. Potential energy surface for the cycloaddition reaction between dichlorovinylidene and formaldehyde with CCSD(T)//MP2/6-31G*.

kJ/mol) and TS1d (−19.7 vs 3.4 kJ/mol) and the intermediate INT1c (−45.7 vs −18.8 kJ/mol). However, two methods predict very similar trends such as dominant reaction pathways and the relative stability of the products, and as illustrated in Table 2, the leading parameters closely related to bond forming and breaking are in good agreement. Additionally, the relative energies predicted by CCSD(T)//MP2 and CCSD(T)//B3LYP agree within 5.0 kJ/mol except for TS1b2, which may be due to the relatively large difference of the C(2)O bond. Close inspection of Table 1 also indicates that CCSD(T) relative energies are closer to those from B3LYP than those from MP2. The below discussions therefore are based on the results from CCSD(T)//MP2 and MP2/6-31G* with respect to relative energies and geometries, respectively.

3.1. Reaction 1: Three-Membered Ring Product Channel. As illustrated in Figure 2, reaction 1 between dichlorovinylidene (R1) and formaldehyde (R2) generating a three-membered ring product (P1) has four paths, 1a, 1b, 1c, and 1d.

3.1.1. Concerted Pathway: *1a*. Three-centered cycloaddition of vinylidene occurs along the pathway 1a via a rather small barrier of 11.7 kJ/mol. TS1a has a C_s symmetry, R1 and the C═O group of R2 being in the same plane. As shown in Figure 1, the distances from C(2) to O and C(3) in TS1a are 2.364 and 2.192 Å, and the bond lengths of C(1)C(2) and C(3)O are only slightly stretched (1.340 vs 1.338, 1.240 vs 1.221 Å) as compared with the reactants. The smoothness of the full IRC shown in Figure 3 further indicates that TS1a connects reactants (R1 and R2) and the three-membered ring product P1 and that pathway 1a is indeed a concerted, three-centered cycloaddition of vinylidene. The IRC trajectory also shows that C_s symmetry is maintained along the cycloaddtion path. A similar path was also reported by Birney et al.[13] for the decarbonylation of a cyclopropanone.

According to the geometric evolution along path 1a and frontier molecular orbital (MO) analysis as illustrated in Figure 4, orbital interactions are supposed as follows for the three-centered cycloaddition. The unoccupied p orbital (main component of LUMO) of the C(2) end of dichlorovinylidene overlaps with the π electron highly polarized at the O end of formaldehyde, while the lone pair σ electrons of vinylidene overlap with the antibonding π^* (LUMO) orbital mainly located at C(3) of formaldehyde, consequently forming $\pi \rightarrow p$ of O−C(2) and $\sigma \rightarrow \pi^*$ of C(2)−C(3) donor−acceptor bonds, which change the reactants into the product P1 via the transition state TS1a. The electron slightly migrates from dichlorovinylidene (Mulliken charge: +0.233*e*) to formaldehyde. The angle of C2−O−C3 is very comparable to that in ethylene oxide (60.4° vs 61.8° with B3LYP/6-31G*).

3.1.2. Stepwise Pathways: *1b*, *1c*, *and 1d*. Figure 2 also indicates that P1 can be generated by the stepwise pathways, 1b, 1c, and 1d, where an intermediate is formed first and then rearranges into P1. Path 1b consists of three steps: the first one is an exothermic reaction of −39.4 kJ/mol, giving the intermediate INT1b1 that can be considered as a result of a donor−acceptor bond of $\pi \rightarrow p$ between O and C(2); then INT1b1 isomerizes to INT1b2 via a small barrier (2.8 kJ/mol, MP2/6-31G*; −0.5 kJ/mol, CCSD(T)//MP2); finally the intermediate INT1b2 cyclizes to product P1. The barrier of the last step is 81.1 kJ/mol, and it is a rate-determining step of path 1b.

Path 1c is completed by two steps: the intermediate INT1c is formed via a [2+2] cycloaddition reaction between the reactants, with an energy release of 14.2 kJ/mol, and then

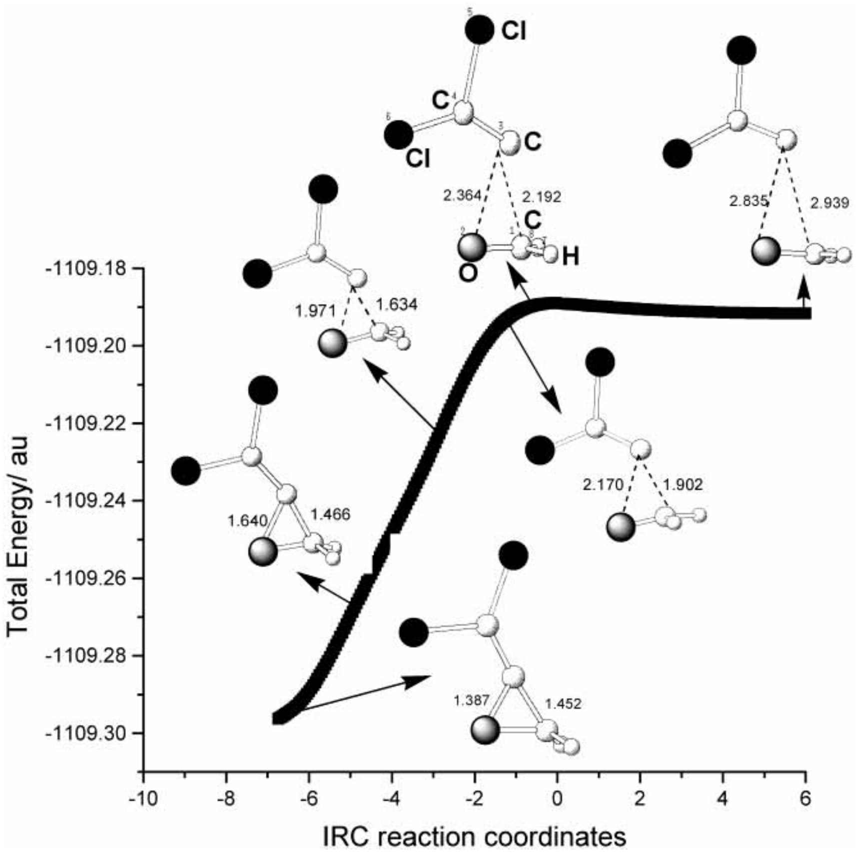


Figure 3. IRC of pathway 1a and geometry evolution.

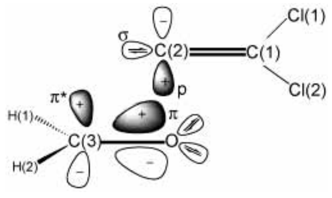


Figure 4. Frontier molecular orbital (MO) symmetry-adaption of $Cl_2C{=}C{:}$ and CH_2O.

isomerizes to the product P1 via transition state TS1c with a barrier of 58.6 kJ/mol. Regarding path 1d, it also consists of two steps: one is the generation of an intermediate, INT1d, due to [2+2] cycloaddition reactions between the reactants, releasing a quite high amount of energy (144.4 kJ/mol), and the other one is the isomerization of INT1d to the product P1 via transition state TS1d with a barrier of 160.3 kJ/mol. INT1c and INT1d are regioisomers, resulting from the two regioisomeric approach modes for the attack of R1 to R2. Since there is a lone-pair donation from the oxygen to the vacant p orbital on C(2) that is impossible in INT1c, INT1d is more stable than INT1c.

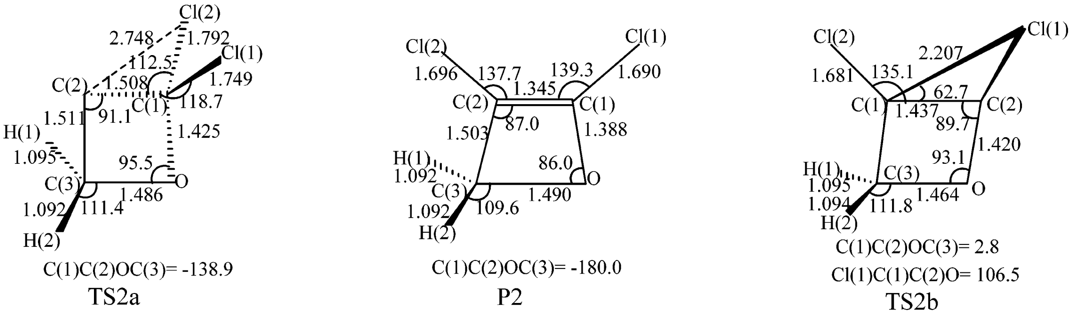
It is interesting to mention that even after careful potential surface scanning transition states have not been located for the two direct [2+2] cycloadditions between dichlorovinylidene and formaldehyde, leading to the intermediates INT1c and INT1d. This indicates that it is most likely that they are pseudopericyclic reactions, which usually exhibit barrierless or quite low barriers.[13] The two cycloadditions are comparable to the pericyclic and/or pseudopericyclic pathways in conjugated ketenes.[14]

A comparison among the four pathways indicates that the total energies of the transition states TS1b2 and TS1c of pathways 1b and 1c are quite higher than that of the two reactants by 35.1 and 44.4 kJ/mol, respectively; however the relative energies of the transition state TS1d of pathway 1d and TS1a of path *1*a are only 15.9 and 11.7 kJ/mol higher than the reactants. Hence it can be predicted that pathway 1d and the concerted pathway 1a should be the leading pathways of reaction 1.

3.2. Reaction 2: Four-Membered Ring Product Channel. According to Figure 2, INT1c and INT1d are isomerized into the more stable four-membered ring product P2. Figure 5 shows the geometric parameters of P2 and two transition states, TS2a and TS2b. The unique imaginary frequencies of TS2a and TS2b are −373.6 and −717.4 cm^{-1}, respectively, and the their IRC analysis shown in Figure S2 confirms that TS2a connects INT1c and P2, and TS2b connects INT1d and P2.

In pathway 2a, INT1c isomerizes to the four-membered ring product P2 by the migration of the Cl(2) atom via transition state TS2a with a quite small barrier of 0.6 kJ/mol. Because neither lone-pair σ electrons nor the unoccupied p orbital of C(2) participates in bond formation, intermediate INT1c has relatively high energy compared with the other three intermediates, INT1b1, INT1b2, and INT1d. Starting from the intermediate, Cl(2) gradually migrates to C(2) via the transition state TS2a, which is a very early transition state in which Cl(2) is still strongly bonded with C(1) (bond lengths: C(1)−Cl(2), 1.792 Å; C(1)−Cl(1), 1.749 Å). After the transition state, C(1) restores its sp^2 character from somewhat sp^3 in INT1c and TS2a, while C(2) maintains sp^2 character and C(3) sp^3. Hence, a covalent σ bond is formed between Cl(2) and C(2) in product P2, a σ bond exists between C(2) and C(3) through $sp^2{-}sp^3$ orbital overlap, and the π bond between C(1) and C(2) is restored.

INT1d rearranges to P2 via the transition state TS2b with a barrier of 133.6 kJ/mol in pathway 2b. In path 2b, INT1d similarly isomerizes to the four-membered ring product P2;



TS2a P2 TS2b

Figure 5. Optimized geometries for the species TS2a, TS2b, and P2 with MP2/6-31G*.

TABLE 2. Comparisons of Some Geometric Parameters (bond lengths, Å; bond angles, deg) from MP2/6-31G* and B3LYP/6-31G*

species	property	MP2	B3LYP
R1	C1−C2	1.338	1.330
R2	C3−O	1.221	1.206
TS1a	C2−O	2.364	2.527
	C2−C3	2.192	2.302
	C2−O−C3	66.7	65.3
P1	C2−O	1.362	1.354
	C2−O−C3[a]	59.8	60.4
TS1b1	C2−O	1.505	1.467
	C3−O	1.250	1.253
INT1b2	C2−O	1.291	1.357
	C3−O	1.355	1.274
TS1b2	C2−C3	2.203	2.025
	C2−O−C3	88.8	97.8
INT1c	C2−O	1.733	1.811
	C1−O	1.487	1.453
TS1c	C2−O	1.662	1.644
	C1−O	1.957	1.936
	C2−O−C3	57.7	57.9
INT1d	C1−C3	1.536	1.580
	C2−C3	2.113	2.117
	C2−O−C3	97.6	98.3
TS1d	C1−C3	1.861	1.905
	C2−C3	1.695	1.729
	C2−O−C3	72.8	72.8
TS2a	C1−C2	1.508	1.518
	C2−Cl(2)	2.748	2.700
	C1−O	1.425	1.418
P2	C1−C2	1.345	1.340
	C1−O	1.388	1.384
	C2−C3	1.503	1.516
TS2b	C1−C2	1.437	1.457
	C1−Cl(1)	2.207	2.110

[a] The angle of C1−O−C2 in ethylene oxide is 61.8° with B3LYP/6-31G*.

however the transition state (TS2b) of Cl(1) migration is very late, which is reflected by quite long distance between C(1) and Cl(1) (2.207 Å) and a clear bond between C(2) and Cl(1). The four-membered ring product (P2) is more stable by approximately 40 kJ/mol than the three-membered ring product (P1). It is likely that a delocalized $\pi_3{}^4$ is present in the four-membered ring product among C(1)−C(2)−O, which could be evidenced by drawing resonance structures involving one of the lone electron pairs of the oxygen with the C=C double bond. However, a similar delocalized $\pi_3{}^4$ bond also exists in P1. The energy difference between P1 and P2 therefore is most probably due to the increased strain of the three-membered ring relative to the four-membered ring.

According to Figure 2, pathways 2a and 1c, both starting from INT1c, compete with each other; however the former (2a) is a favorable pathway because of its much lower energy barrier (0.6 vs 58.6 kJ/mol). Since the energy barrier (TS1d) of pathway 1d is 26.7 kJ/mol higher than that (TS2b) of pathway 2b, it is believed that pathway 2b is a favorable path starting from INT1d. Both pathways 2a and 2b are leading paths for reaction 2 because their total energies, TS2a and TS2b, only differ by 2.8 kJ/mol.

In brief, pathways 1a, 1d, 2a, and 2b in Figure 2 are major competition reactions of cycloaddition between dichlorovinylidene and formaldehyde. The former two (1a and 1d) result in a three-rembered ring product (P1), and the latter two lead to the four-membered ring product (P2).

Conclusion

On the basis of the surface energy profile obtained with MP2/6-31G* and B3LYP/6-31G* methods for stationary location and CCSD(T)//MP2 and CCSD(T)//B3LYP methods for energy correction for the cycloaddition reaction between singlet dichlorovinylidene and formaldehyde, it can be predicted that this cycloaddition has two major reactions. The first one gives rise to a three-membered ring product (P1), via a concerted three-center cycloaddition pathway (1a) as well as a stepwise pathway (1d). In the case of 1d, an intermediate (INT1d) is formed through a barrierless exothermic [2+2] cycloaddition of 144.4 kJ/mol and then isomerizes to P1, dichloromethylene ethane oxide, with an energy barrier of 160.3 kJ/mol. The second reaction results in a four-memberd ring product (P2) via pathways 2a and 2b, in which the two unstable intermediates (INT1c and INT1d) are first formed and then isomerize to the more stable product P2. P2 has approximately 40 kJ/mol lower energy than P1.

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Supporting Information Available: Figures S1 and S2 show IRC curves of the involved transition states with MP2/6-31G* for the first and second reaction channel of cycloaddition between dichlorovinylidene and formaldehyde, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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