PAPER

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A theoretical study on the mechanism of the cycloaddition reaction between dichloroalkylidenesilylene and ethylene

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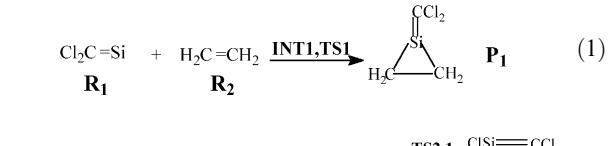
The mechanism of the cycloaddition reaction between singlet dichloroalkylidenesilylene and ethylene has been investigated with the MP2/6-31G* and B3LYP/6-31G* methods, including geometry optimization and vibrational analysis for the involved stationary points on the potential energy surface. The energies of the different conformations are calculated by CCSD(T)//MP2/6-31G* and CCSD(T)//B3LYP/6-31G* methods. From the surface energy profile obtained with the CCSD(T)//MP2/6-31G* method for the cycloaddition reaction between singlet dichloroalkylidenesilylene and ethylene, it can be predicted that the dominant reaction pathway for this reaction involves the initial formation of an intermediate through a barrier-free exothermic reaction (42.4 kJ mol^{-1}); this intermediate then isomerizes to an active four-membered ring product *via* a transition state, a second intermediate and a second transition state, for which the energy barriers are 31.2 and 32.2 kJ mol^{-1}, respectively.

1. Introduction

In recent years, silylene as an important active intermediate has attracted much attention in various fields of chemistry[1,2] and has led to a varied chemistry concerning silylenes. A silylene reaction is regarded as an effective method in the synthesis of new bonds and heterocyclic ring compounds with Si, which has long been one of the most interesting topics for organo-silicon chemists. There have been quite a lot of theoretical and experimental investigations on addition reactions to silylene,[3–9] For example, the rate constant for the reaction of SiH_2 ($\tilde{X}^1A_1$) and C_2H_4 is 9.7 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, measured by Inoue and Suzuki using the laser photolysis-laser-induced fluorescence method at 298 K and 1 torr.[6] The mechanism and kinetics of the reactions of silylene with ethylene and butadiene have been studied by the comparative rate technique.[3] The thermodynamics of the insertion reactions of SiH_2 and $CH_2{=}CH_2$ were predicted by using MP2/6-31G(d).[4] Schaefer *et al*. did an extensive analysis of the thermodynamic stability to fragmentation of the three-membered ring compounds *c*-$XH_2YH_2ZH_2$ (X, Y, Z = C, Si, Ge).[5] Time-resolved studies of silylene (SiH_2) have been carried out to obtain the rate constant for its bimolecular reaction with ethene over the pressure range 1–100 torr at five temperatures in the range of 298–595 K.[7] Time-resolved studies of the reaction of $SiH_2$with acetaldehyde have also been carried out over a wide temperature and pressure range.[8,9] *Ab initio* calculations at the G2 level indicates the initial formation of a silacarbonyl ylide, which can then either form the siloxirane by ring closure, rearrange to form siloxyethene or give ethoxysilylene. We also have performed some studies on this aspect.[10–13] However, the previous investigations usually focused on the cycloaddition reactions of saturated silylenes. There are still no reports on the cycloaddition reactions of unsaturated silylenes. In order to explore the rules of cycloaddition reactions between unsaturated silylenes and the symmetric π-bonded compounds, dichloroalkylidenesilylene and ethylene were selected as model species and the mechanism of this reaction was investigated and analyzed theoretically in terms of the two possible pathways for cycloaddition, shown below:



2. Calculation methods

MP2/6-31G*[14] and B3LYP/6-31G*[15,16] implemented in the Gaussian98 package are employed to locate all the stationary points along the reaction pathways. Full optimization and vibrational analysis are done for the stationary points on the reaction profile. Zero-point energy and CCSD(T) corrections are included for the energy calculations. In order to explicitly establish the relevant species, the intrinsic reaction coordinate (IRC)[17,18] was also calculated for all the transition states appearing on the cycloaddition energy surface profile.

3. Results and discussion

The theoretical calculations indicate that the ground state of dichloroalkylidenesilylene is a singlet. Major geometrical parameters obtained from the MP2/6-31G* and B3LYP/6-31G* methods for the intermediates (INT1, INT2), transition states (TS1, TS2, TS2.1, TS2.2) and products (P_1, $P_{2.1}$, $P_{2.2}$) that appear in the cycloaddition reaction between dichloroalkylidenesilylene and ethylene agree quite well with each other. The mechanism for the cycloaddition reaction between dichloroalkylidenesilylene and ethylene are also in good agreement from both MP2/6-31G* and B3LYP/6-31G* methods. Energies for the involved conformations from the MP2/6-31G*, B3LYP/

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Table 1 Total energies (E_T, a.u) and relative energies (E_R, kJ mol^{-1}) for the species obtained with different theoretical methods

	MP2/6-31G*		B3LYP/6-31G*		CCSD(T)//MP2		CCSD(T)//B3LYP	
Species	E_T[a]	E_R[b]	E_T	E_R	E_T	E_R	E_T	E_R
$R_1 + R_2$	−1324.332 85	0.0	−1326.425 97	0.0	−1324.428 03	0.0	−1324.429 15	0.0
INT1	−1324.360 22	−71.9	−1326.445 49	−51.2	−1324.444 16	−42.4	−1324.447 06	−47.0
TS1 (INT1–P_1)	−1324.337 96	−13.4	−1326.426 20	−0.6	−1324.425 83	5.8	−1324.427 83	3.5
P_1	−1324.347 80	−39.3	−1326.434 36	−22.0	−1324.435 99	−20.9	−1324.438 07	−23.4
TS2 (INT1–INT2)	−1324.347 98	−39.7	−1326.431 31	−14.0	−1324.432 31	−11.2	−1324.434 17	−13.2
INT2	−1324.395 34	−164.1	−1326.480 18	−142.3	−1324.481 73	−141.0	−1324.482 96	−141.3
TS2.1 (INT2–$P_{2.1}$)	−1324.377 17	−116.4	−1326.476 14	−131.7	−1324.469 47	−108.8	−1324.471 14	−110.2
$P_{2.1}$	−1324.436 69	−272.6	−1326.517 75	−241.0	−1324.517 39	−234.6	−1324.518 84	−235.5
TS2.2 (INT2–$P_{2.2}$)	−1324.325 48	19.4	−1326.420 22	15.1	−1324.420 29	20.3	−1324.422 41	17.7
$P_{2.2}$	−1324.376 25	−113.9	−1326.454 94	−76.0	−1324.459 95	−83.8	−1324.461 25	−84.3

[a] $E_T = E$(species) + ZPE, [b] $E_R = E_T - E(R_1 + R_2)$.

6-31G*, CCSD(T)//MP2 and CCSD(T)//B3LYP methods are listed in Table 1. According to Table 1, the relative energies for the involved conformations from the MP2/6-31G* and B3LYP/6-31G* methods do considerably differ, however, they agree quite well from the CCSD(T)//MP2 and CCSD(T)//B3LYP methods; The total energies from the B3LYP/6-31G* and CCSD(T)//B3LYP/6-31G* methods also considerably differ, but compared with these, the total energies from the MP2/6-31G* and CCSD(T)//MP2/6-31G* methods are closer. The following discussions for reactions 1 and 2 are therefore based on the results from CCSD(T)//MP2 and MP2/6-31G* with respect to the energies and geometrical parameters, respectively.

3.1 Reaction 1

The geometrical parameters for the intermediate INT1, transition state TS1 and product P_1 appearing in reaction path 1 are given in Fig. 1. (The geometrical parameters are listed in Table 2 at the B3LYP/6-31G* level.) The potential energy surfaces for the cycloaddition reaction between dichloroalkylidenesilylene and ethylene are given in Fig. 2.

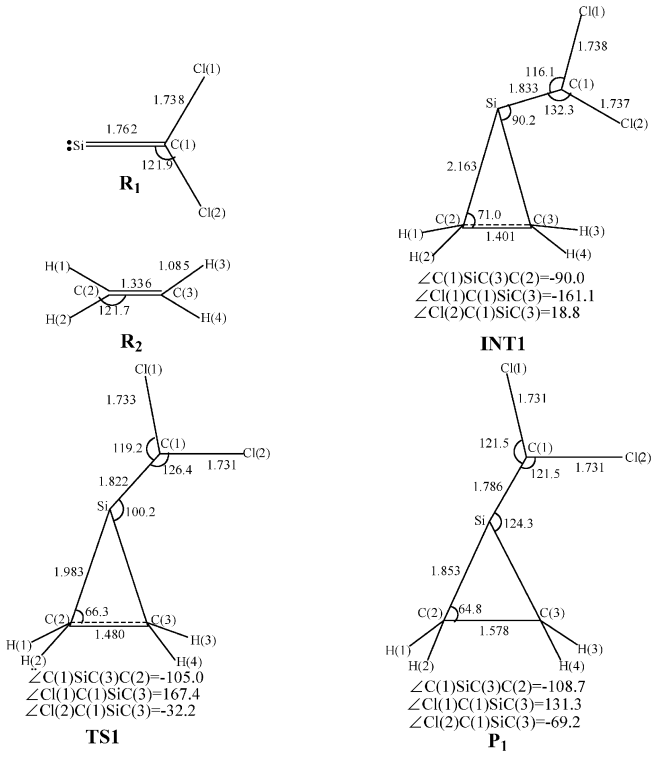

Fig. 1 Optimized MP2/6-31G* geometrical parameters and atomic numbering for the species in cycloaddition reaction 1. Bond lengths and angles are in Å and deg.

The unique imaginary frequency of the transition state TS1 is −283.4 cm^{-1} and the transition state can therefore be affirmed as the real one. According to the calculation of the IRC of TS1 and further optimization of the primary IRC results, TS1 connects INT1 and P_1. According to Fig. 2, it can be directly seen that reaction 1 consists of two steps: the first one is a barrier-free exothermic reaction of 42.4 kJ mol^{-1}, resulting in an intermediate INT1; Then INT1 isomerizes to product P_1 with a barrier of 48.2 kJ mol^{-1}.

3.2 Reaction 2

The geometric parameters for the intermediate INT2, transition states TS2, TS2.1, TS2.2 and products $P_{2.1}$, $P_{2.2}$ appearing on the reaction path 2 are given in Fig. 3. (The geometrical parameters are listed in Table 2 at the B3LYP/6-31G* level.) The potential energy surface for reaction 2 is illustrated in Fig. 2.

The unique imaginary frequencies of the transition states TS2, TS2.1 and TS2.2 are −198.0, −216.4 and −1040.7 cm^{-1}, respectively, and therefore these three transition states can be affirmed as the real ones. According to the calculations of the IRC of TS2, TS2.1 and TS2.2, and the further optimization of the primary IRC results, TS2 connects INT1 and INT2, TS2.1 connects INT2 and $P_{2.1}$, and TS2.2 connects INT2 and $P_{2.2}$.

Fig. 2 shows that reaction 2 consists of four steps (labelled a, b, c, and d). Similar to reaction 1, the first one is a barrier-free exothermic reaction of 42.4 kJ mol^{-1}, leading to intermediate INT1, which then isomerizes to intermediate INT2 *via* a transition state TS2 with a barrier of 31.2 kJ mol^{-1}, finally the intermediate INT2 isomerizes to products $P_{2.1}$ and $P_{2.2}$ *via* transition states TS2.1 and TS2.2, for which the energy barriers are 32.2 and 161.3 kJ mol^{-1}, respectively.

According to Fig. 2, step b of reaction 2 and the second step of reaction 1 compete with each other, with the energy barrier of the former being 17.0 kJ mol^{-1} lower than that of the latter. According to the exponential law of reaction velocity [$k = A\exp(-E_a/RT)$], the reaction velocity from TS2 to INT2 is approximately 954.9 times as fast as that from TS1 to P_1 at room temperature (298 K), thus reaction 2 will be the dominant reaction. Steps c and d of reaction 2 also compete with each other, with an energy barrier difference of 129.1 kJ mol^{-1}. According to the exponential law of reaction velocity, the reaction velocity of step c is approximately 4.2 × 10^{22} times as fast as that of step d at room temperature. It is obvious that step c is the dominant reaction pathway. The quite long separation between C(2) and Si (0.1959 nm) and short separation between C(2) and H(1) (0.1094 nm) in INT2 make it quite difficult for H(1) to transfer from C(2) to Si.

According to the above analysis, $P_{2.1}$ from reaction 2 will be the dominant product in the cycloaddition reaction between dichloroalkylidenesilylene and ethylene, with quite excellent

Table 2 The geometrical parameters for the various species in the cycloaddition reaction between dichloroalkylidenesilylene and ethylene at the B3LYP/6-31G* level (bond lengths in Å and bond angles in deg)

Species	C–Si	Cl–C	∠Cl–C–Si	∠Cl–C–Si–Cl	Species	C–C	H–C	∠H–C–C
$Cl_2C{=}Si$	1.754	1.755	122.0	180.00	C_2H_2	1.331	1.088	121.9

Species	C(2)–Si	C(3)–C(2)	C(1)–Si	Cl(1)–C(1)	Cl(2)–C(1)	∠C(3)–C(2)–Si	∠C(1)–Si–C(3)	∠Cl(1)–C(1)–Si	∠Cl(2)–C(1)–Si	∠C(1)–Si–C(3)–C(2)	∠Cl(1)–C(1)–Si–C(3)	∠Cl(2)–C(1)–Si–C(3)
INT1	2.298	1.379	1.811	1.763	1.760	72.5	91.6	114.9	133.8	−90.6	−162.5	17.6
TS1	1.990	1.485	1.850	1.742	1.743	66.6	100.4	118.8	126.9	−102.8	167.4	−33.2
P_1	1.860	1.585	1.790	1.746	1.746	64.8	124.4	121.6	121.6	−108.8	132.2	−70.1
TS2	1.991	1.459	1.851	1.761	1.777	77.7	67.8	117.1	132.0	−117.6	−120.8	71.5
INT2	1.979	1.553	1.960	1.764	1.925	93.7	35.7	134.8	81.9	−165.2	−142.3	106.5
TS2.1	1.997	1.551	1.959	1.703	2.510	94.1	34.4	139.9	60.0	−175.2	181.5	101.4
$P_{2.1}$	1.887	1.571	1.712	1.722	3.545[a]	84.0	41.4	145.0	22.0	−180.0	180.1	180.2
TS2.2	1.839	1.495	2.007	1.809	1.809	99.8	37.4	114.6	115.8	−174.2	−115.0	115.4
$P_{2.2}$	1.712	1.534	1.903	1.812	1.812	93.8	41.5	117.5	117.5	−180.0	−113.5	113.5

[a] No bond.

selectivity. The mechanism of reaction 2 can be explained with the frontier molecular orbitals (Fig. 4) and Figs. 1 and 3.

The combination of the unoccupied 3p orbital of the Si atom of dichloroalkylidenesilylene with the π orbital of ethylene gives a π → p donor-acceptor bond, forming a three-membered ring intermediate INT1 as dichloroalkylidenesilylene initially interacts with ethylene. INT1 is a quite loose and highly strained, energetic species, so the system reduces its energy by increasing the dihedral angles ∠C(1)–Si–C(3)–C(2) (INT1: −90.2°, TS2: −115.3°, INT2: −159.4°) and ∠C(3)–C(2)–Si (INT1: 71.0°, TS2: 76.6°, INT2: 93.1°) and decreasing ∠C(1)–Si–C(3) (INT1: 90.2°, TS2: 68.2°, INT2: 36.3°), and finally transforms INT1 into the twisted four-membered ring intermediate INT2 *via* the transition state TS2. In the conformation of INT2, the combination between dichloroalkylidenesilylene and ethylene has become the [2 + 2] cycloaddition reaction of the two π bonds. Since the sp lone electron pair on Si does not participate in bond formation, INT2 is still an active intermediate. So INT2 further reduces its energy by transferring Cl(2) from C(1) to Si, to change INT2 into the more stable four-membered ring $P_{2.1}$ *via* the transition state TS2.1. In the conformation of $P_{2.1}$, the Si atom changes to sp^2 hybridization and forms σ bonds with its three neighboring atoms, while simultaneously forming a π bond with C(1). There are no longer any sp lone pair electrons on the Si, which is now saturated; this is the main reason why the $P_{2.1}$ conformation is more stable than INT2 and it is also the original driving force that changes the INT2 into $P_{2.1}$.

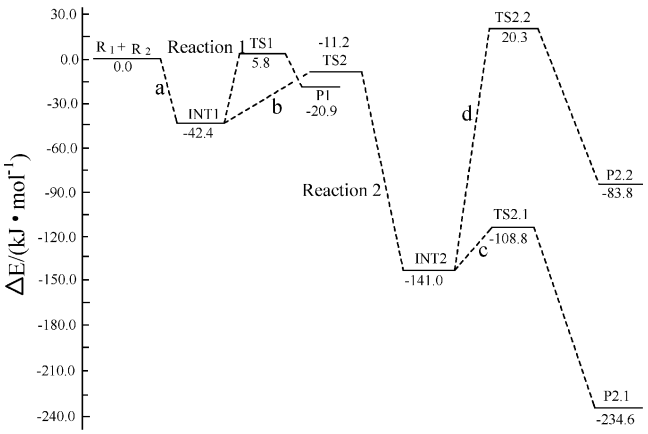

Fig. 2 The potential energy surface for the cycloaddition reactions between dichloroalkylidenesilylene and ethylene with CCSD(T)// MP2/6-31G*.

4. Conclusion

On the basis of the surface energy profile obtained with the CCSD(T)//MP2/6-31G* method for the cycloaddition reaction between singlet dichloroalkylidenesilylene and ethylene, it can be predicted that the dominant reaction pathway of this

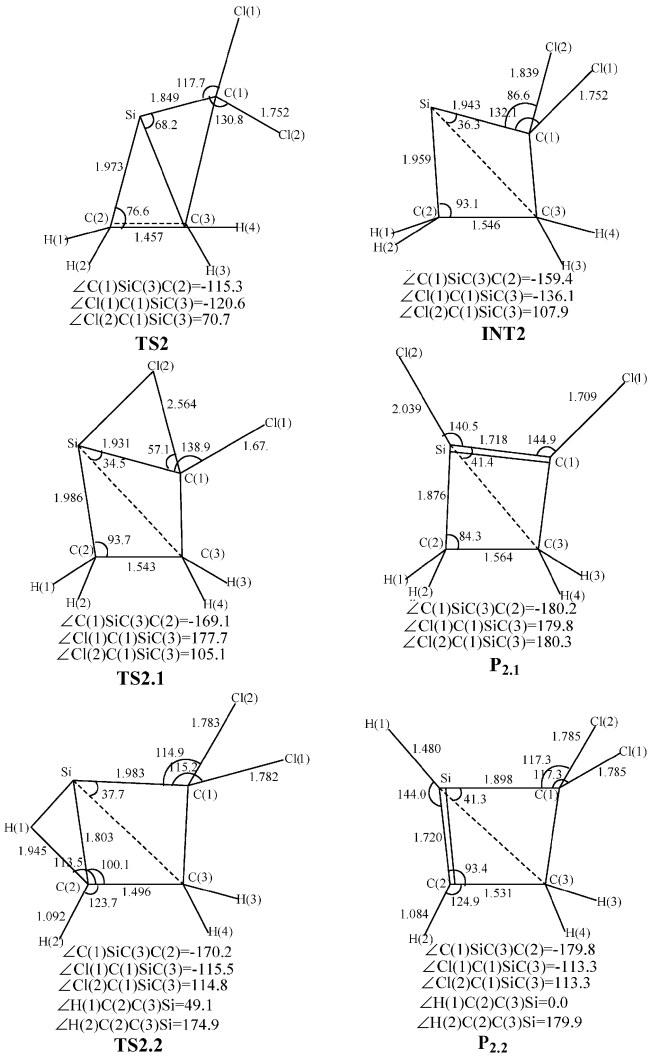

Fig. 3 Optimized MP2/6-31G* geometrical parameters of TS2, INT2, TS2.1, $P_{2.1}$, TS2.2, $P_{2.2}$ and the atomic numbering for cycloaddition reaction 2. Bond lengths and angles are in Å and deg.

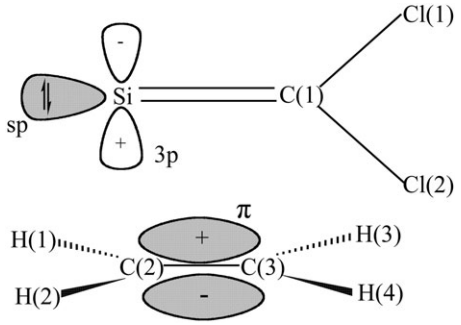

Fig. 4 Frontier molecular orbital (MO) symmetry-adaption of $Cl_2C{=}Si$: and C_2H_4.

reaction proceeds by initial formation of an intermediate INT1 through a barrier-free exothermic reaction (42.4 kJ mol^{-1}); INT1 then isomerizes to a four-membered ring $P_{2.1}$ *via* a transition state TS2, an intermediate INT2 and a second transition state TS2.1, for which the energy barriers are 31.2 and 32.2 kJ mol^{-1}, respectively. This reaction has an excellent selectivity.

Acknowledgements

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