J. Org. Chem. **2002,** *67,* 154−160

A Density Functional Theory Investigation of the Simmons−Smith Cyclopropanation Reaction: Examination of the Insertion Reaction of Zinc into the C−I Bond of CH_2I_2 and Subsequent Cyclopropanation Reactions

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Received July 30, 2001

The insertion reaction of zinc into the C−I bond of CH_2I_2 and subsequent cyclopropanation reactions with CH_2CH_2 have been investigated using B3LYP level density functional theory calculations. The Simmons-Smith cyclopropanation reaction of olefins does not proceed easily due to the relatively large barriers on the insertion and cyclopropanation pathways. The computed results indicate that the $IZnCH_2I$ molecule is the active reagent in the Simmons−Smith reaction. This is consistent with the $IZnCH_2I$ reactive species being generated from diiodomethane and a Zn−Cu couple as proposed by several other research groups. The Simmons−Smith $IZnCH_2I$ carbenoid and $CH_2I{-}I$ carbenoid cyclopropanation reactions with olefins are compared. The reactions of olefins with the radicals from the decomposition of the $IZnCH_2I$ and $CH_2I{-}I$ species were also compared. We found that the chemical reactivity of the carbenoid species is dependent on its electrophilic behavior, steric effects, the leaving group character and the mechanism of the cyclopropanation reactions.

Introduction

The cyclopropyl group has been found in many natural and unnatural products possessing interesting biological activities.[1−5] This has inspired chemists to find novel and diverse approaches to the synthesis of cyclopropyl moieties.[6−16] The reaction between diazoalkanes and olefinic substrates assisted by transition-metal complexes[12] provides important practical protocols for the cyclopropanation of electron-deficient and electron-rich double bonds. Dihalomethanes activated by ultraviolet photolysis in solution containing olefins can afford cyclopropanes with high stereospecificity.[13−15] The Norrish−Yang reaction, one of the best investigated photochemical reactions, was also used to synthesize cyclopropanes recently.[16]

Among the different cyclopropanation methods, the Simmons−Smith reaction[17] is the most widely used synthetic pathway for cyclopropanation of olefins. The Simmons−Smith reactive species is generated from diiodomethane and a Zn−Cu couple.[17] After this early study,[17] a great deal of work has been focused on the development of alternative methods to prepare active reagents that are capable of transforming olefins into cyclopropanes with high efficiency and stereoselectivity.[18−23] Some metal atoms (Ag, Zr, and Ti) and

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10.1021/jo0107655 CCC: $22.00

their halogenides, together with dihaloalkanes, were used to generate cyclopropanating reagents.[22,23] Furukawa[24] has developed a procedure that involves alkyl group exchange between diethylzinc and diiodomethane. Charette and Marcoux[21] have introduced an alternative procedure to prepare the Simmons–Smith reagent, which involves addition of CH_2I_2 to freshly prepared EtZnI. The nucleophilic displacement of Zn(II) salt by diazomethane was used by Wittig[25] to produce $XZnCH_2X$. Despite numerous experimental investigations on how to prepare the Simmons–Smith reagent, the structure and nature of the reagent are not unambiguously known up to date. Early studies[17] by Simmons, for example, suggested that $IZnCH_2I$ is the active cyclopropanating carbeniod, which has been used in textbooks[26] to elucidate the mechanism of the Simmons–Smith reaction. Recently, a range of possible intermediates, such as $ZnCH_2X$ (X = Cl, Br, I) and $Zn(CH_2X)_2$, have been proposed to be the active species that reacts with olefins to give cyclopropane products.[21,24,25,27]

The Simmons–Smith reaction has also been the subject of several theoretical investigations. Bernardi and co-workers[28] have studied the potential energy surface for the reaction between ethylene and (chloromethyl)zinc chloride, which represents a model system for the Simmons–Smith cyclopropanation reaction (using the B3LYP/6-311G** method). A relativistic core potential approach[29] has been used to investigate the Simmons–Smith cyclopropanation reaction. The reaction was predicted to be exothermic by 140–158 $kJ \cdot mol^{-1}$ with a barrier height of about 60 $kJ \cdot mol^{-1}$.[29] With the aid of density function theory (B3LYP) calculations, the effect of the $ZnCl_2$ molecules (as a Lewis acid) on the Simmons–Smith reaction was discussed in detail.[30] The mechanism of olefin cyclopropanation catalyzed by palladium dicarbonates[12] has been studied through density functional calculations with effective core potential for palladium atom. We have recently examined the reaction of isodihalomethanes ($CH_2X{-}X$, X = I, Br, Cl) with ethylene using density functional theory calculations.[31,32] These results showed that the $CH_2I{-}I$ isomer photoproduct species is most likely the methylene transfer agent for the cyclopropanation reaction of olefins via ultraviolet photoexitation of diiodomethane. Despite the numerous theoretical studies involving the Simmons–Smith reaction, a detailed understanding of the mechanism for formation of the reactive species and knowledge of the electronic and geometric structures of the species are still lacking. The factors that influence chemical reactivity of the carbeniod remain largely unknown. In this paper, we present a density functional theory investigation to help elucidate pathways for formation of possible active intermediates from CH_2I_2 and Zn. Meanwhile, the relationship between the reactivity and the structure of the carbeniod and the most probable pathway for formation of cyclopropane product are discussed on the basis of the calculated potential energy surfaces for reactions of ethylene with the possible active intermediates. The Simmons–Smith $IZnCH_2I$ carbenoid and $CH_2I{-}I$ carbenoid cyclopropanation reactions and the reactions with olefins of the radicals from the decomposition of the $IZnCH_2I$ and $CH_2I{-}I$ species were compared. We discuss factors found to influence the chemical reactivity of the $IZnCH_2I$ and $CH_2I{-}I$ carbenoid species: their electrophilic behavior, steric effects, nature of the leaving group, and the mechanism of the cyclopropanation reactions.

Computational Details

The density functional method of B3LYP has been used to investigate the potential energy surfaces of the insertion reactions of Zn into CH_2I_2 and subsequent processes, involving the dissociation of $IZnCH_2I$ and cyclopropanation of ethylene with $IZnCH_2I$ and $IZnCH_2$. The stationary structures in the potential energy surfaces are fully optimized at the B3LYP or UB3LYP level using C_1 symmetry. The analytic frequency calculations have been performed to confirm the optimized structure to be at a minimum or first-order saddle point and to carry out zero-point energy corrections. IRC calculations are used to confirm that the optimized transition state structure correctly connects reactants and products. Geometry optimization and frequency calculations are carried out with the 6-311G** basis set.[33] Energies of the stationary structures are refined by the single-point calculation at the B3LYP level of theory with a hybridized basis set, referred to as PVTZ, which is composed of the standard cc-pVTZ basis set for C and H atoms, the TZV basis set[34,35] for Zn atoms, and the Sadlej-PVTZ basis set[36] for I atoms. The hybridized basis set contains 368 basis functions contracted from 1082 primitive Gaussian functions for the $IZnCH_2I + C_2H_4$ system. Some structures are also optimized with the PVTZ basis set to see the influence of size of basis set on structural parameters. All calculations were carried out using Gaussian 98 program packages.[37]

Results

In the system of $Zn + CH_2I_2 + CH_2CH_2$, the possible reactions that are related to formation of cyclopropane

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(c-C_3H_6) are as follows:

$$Zn + CH_2I_2 \rightarrow ICH_2ZnI \tag{1}$$

$$ICH_2ZnI \rightarrow ICH_2 + ZnI \tag{2}$$

$$ICH_2ZnI \rightarrow CH_2 + ZnI_2 \tag{3}$$

$$ICH_2ZnI \rightarrow ICH_2Zn + I \tag{4}$$

$$ICH_2ZnI \rightarrow IZnCH_2 + I \tag{5}$$

$$CH_2 + CH_2CH_2 \rightarrow c\text{-}C_3H_6 \tag{6}$$

$$ICH_2 + CH_2CH_2 \rightarrow c\text{-}C_3H_6 + I \tag{7}$$

$$IZnCH_2 + CH_2CH_2 \rightarrow c\text{-}C_3H_6 + ZnI \tag{8}$$

$$ICH_2Zn + CH_2CH_2 \rightarrow c\text{-}C_3H_6 + ZnI \tag{9}$$

$$ICH_2ZnI + CH_2CH_2 \rightarrow c\text{-}C_3H_6 + ZnI_2 \tag{10}$$

$$IZnCH_2{+} + CH_2CH_2 \rightarrow c\text{-}C_3H_6 + ZnI^+ \tag{11}$$

The optimized stationary structures (minima and saddle points) on the potential energy surfaces of the preceding reactions are displayed in Figure 1 with key parameters also given. The computed total energies for the structures located in our study are collected in Table 1 with their relative energies given in Figure 2 where the potential energy profiles are plotted.

A. Insertion Reaction of Zn with CH_2I_2 and Its Product. A transition state, referred to as TS1, was found for the insertion of Zn into the C−I bond of CH_2I_2 and was confirmed to be the first-order saddle point on the ground-state potential energy surface of the reaction (**1**). TS1 has a C_s structure with the two H atoms locating above and below the plane of symmetry. In comparison with CH_2I_2, one C−I bond length is decreased a little in the TS1 structure, while the other C−I bond is elongated by about 1.0 Å. The C−Zn bond is actually formed in TS1, whereas the Zn−I distance is 4.132 Å. The reaction vector, which is associated with the imaginary vibrational mode of TS1, has been identified as $0.08R_{C-Zn} - 0.30R_{C-I} + 0.90R_{Zn-I}$. This shows that there is large change in the Zn−I distance accompanied by a small amount of change in Zn−C bond in going from TS1 to the insertion product of ICH_2ZnI. This is consistent with the Zn−C bond formation and long Zn−I distance in the TS1 structure. Starting from the TS1 structure, the IRC calculations are completed only after a few steps of optimization. The energy is unchanged in each step of the IRC optimization. We make relatively large changes of the TS1 geometry in both the reactant and product directions and then search for an energy minimum. In this case, the optimization procedure leads to formation of Zn + CH_2I_2 and $IZnCH_2I$ in reactant and product sides, respectively. The above calculations show that TS1 is relatively flat in the transition-state region that connects the corresponding reactants and product.

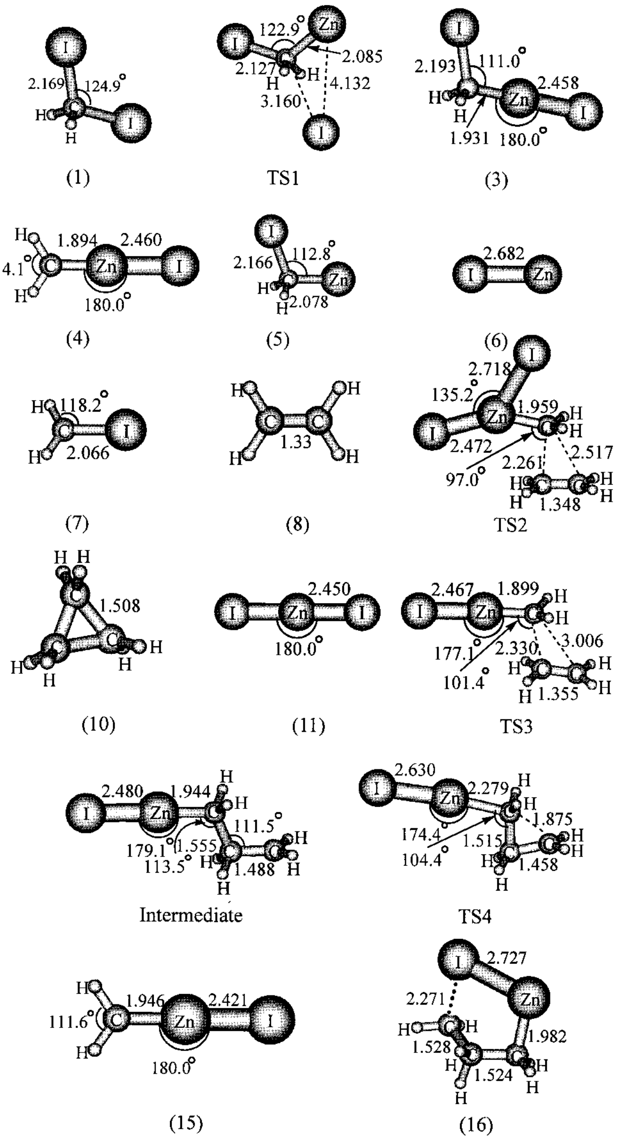

Figure 1. Stationary structures are schematically plotted with the selected key bond parameters (bond lengths in angstroms, bond angles in degrees), and the carbon atom numbering is given in CH_2CH_2 and $ZnCH_2I$, respectively.

Table 1. B3LYP Calculated Energies (Hartree) of the Stationary Structures

species	B3LYP/6311G**	zero-point energy	B3LYP/PVTZ
Zn	−1779.31208	0.00000	−1779.44512
CH_2I_2	−13878.37219	0.02708	−13880.22058
TS1	−15657.63616	0.02599	−15659.60989
$IZnCH_2I$	−15657.74254	0.02737	−15659.71617
$IZnCH_2$	−8738.14442	0.02273	−8739.19885
$ZnCH_2I$	−8738.10978	0.02325	−8739.16617
ZnI	−8698.84804	0.00033	−8699.90240
CH_2I	−6958.78353	0.02159	−6959.71077
CH_2CH_2	−78.61398	0.05081	−78.62316
TS2	−15736.32364	0.07903	−15738.30660
c-C_3H_6	−117.92995	0.08095	−117.94262
ZnI_2	−15618.46453	0.00138	−15620.43798
TS3	−8816.75023	0.07598	−8817.81169
$IZnCH_2CH_2CH_2$	−8816.79422	0.07906	−8817.85314
TS4	−8816.75890	0.07995	−8817.81898

Using the B3LYP/6-311G** calculated energies listed in Table 1, the insertion reaction of Zn into the C−I bond of CH_2I_2 is found to be exothermic by 36.4 kcal·mol^{-1} with the zero-point energy correction. With respect to Zn + CH_2I_2, the barrier to the insertion reaction is calculated to be 29.5 kcal·mol^{-1} at the B3LYP/6-311G** level of theory. The potential energy profile of the reaction is depicted in Figure 2. Although the barrier height is 29.5 kcal·mol^{-1} for the insertion reaction, the energy released by the reaction (36.4 kcal·mol^{-1}) is sufficient to compen-

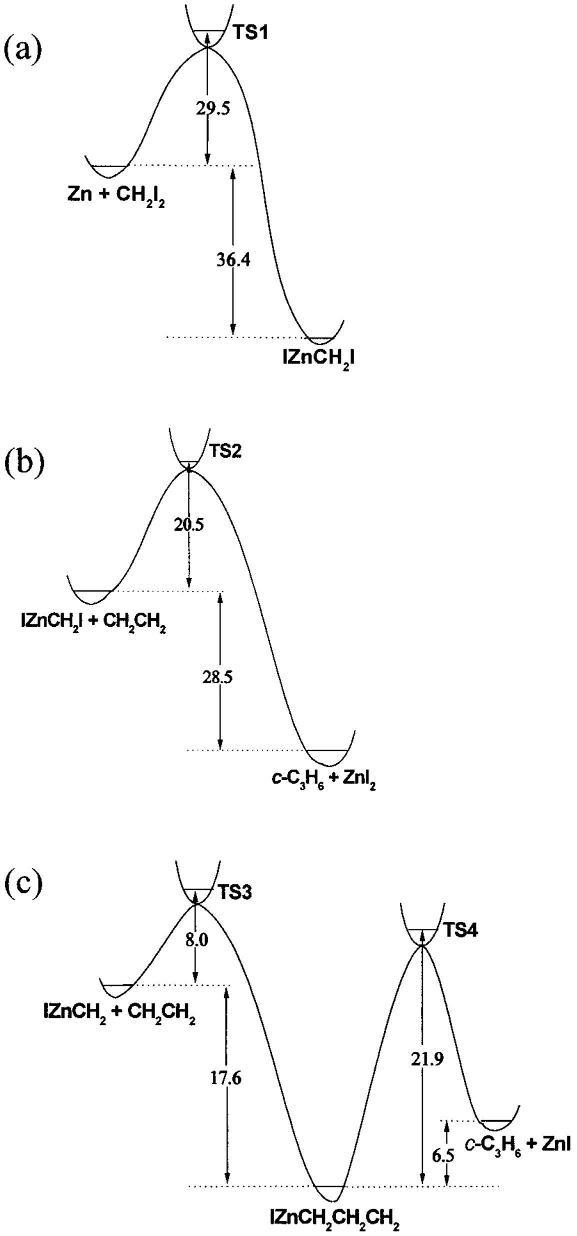

Figure 2. Schematic potential energy profiles for the reactions (a) Zn + CH_2I_2 → $IZnCH_2I$, (b) $IZnCH_2I$ + CH_2CH_2 → c-C_3H_6 + ZnI_2, and (c) $IZnCH_2$ + CH_2CH_2 → c-C_3H_6 + ZnI, along with the relative energies (kcal·mol^{-1}) of the stationary structures.

sate for the energy required to overcome the barrier. The present calculations show that the insertion reaction of Zn into the C−I bond of CH_2I_2 can occur, but not very easily.

The insertion reaction leads to formation of the $IZnCH_2I$ intermediate, which has a C_s-symmetry structure with all of the heavy atoms in the same plane and the two hydrogen atoms located above and below the plane of symmetry as shown in Figure 1. The I−Zn−C moiety adopts a linear arrangement with C−Zn and Zn−I bond lengths of 1.931 and 2.458 Å, respectively, at the B3LYP/6-311G** level of theory. The $IZnCH_2I$ structure is further optimized with the hybridized PVTZ basis set, and this gives C−Zn and Zn−I bond lengths of 1.930 and 2.468 Å, respectively. Increasing the size of the basis set from 6 to 311G** to PVTZ leads to only very small changes in the structural parameters of $IZnCH_2I$. A similar situation was found in our previous studies on the reaction of iso-CH_2X−X (X = Cl, Br, I) with C_2H_4.[31,32] The C−Zn and Zn−I bond lengths were reported to be about 1.95 and 2.21 Å, respectively, in X-ray crystallographic studies of bis(iodomethyl)zinc.[38] These values are consistent with the present calculations and indicate the calculations give a reasonable description on the $IZnCH_2I$ structure. The calculated molecular orbitals and their populations predict that the C−Zn and Zn−I bonds in $IZnCH_2I$ are partially of covalent and ionic character. The atomic charge on Zn is about +1.1, while the C atom has an atomic charge of about −0.95. The two H atoms have atomic charges of about +0.2 each and when added to the −0.95 charge of the C atom this gives the CH_2 moiety a charge of about −0.55. The same amount of atomic charge is distributed on the I atom bonded to the Zn atom. In discussions of the reaction between ethylene and $IZnCH_2I$ in the textbooks,[26] the $IZnCH_2I$ species is considered as a zwitterions with unit negative and positive charges distributed in the C and Zn atoms, respectively.

B. Dissociation of $IZnCH_2I$ into $IZnCH_2$+ I, $ZnCH_2I$ + I, ZnI + CH_2I, and ZnI_2 + CH_2. After the formation of the $IZnCH_2I$ molecule, it is possible for $IZnCH_2I$ to dissociate into $IZnCH_2$ + I, I + $ZnCH_2I$, ZnI + CH_2I, and ZnI_2 + CH_2. No transition states were found for these dissociation reactions. The UB3LYP/6-311G** calculations predict the reactions to be endothermic by 55.5, 66.2, 77.9, and 78.8 kcal·mol^{-1} for the $IZnCH_2I$ dissociation to I + $IZnCH_2$, ZnI + CH_2I, ZnI_2 + CH_2, and I + $ZnCH_2I$, respectively. The single-point B3LYP calculations with the PVTZ basis set give the corresponding dissociation energies of 55.4, 61.2, 74.4, and 77.5 kcal·mol^{-1} with the B3LYP/6-311G** zero-point energy correction. The distribution of atomic charges in the $IZnCH_2$ radical is similar to that in $IZnCH_2I$, with +1.1, −0.84, and −0.58 atomic charges on Zn, C, and I, respectively, in the radical. The nature of the Zn−C and Zn−I bonds in the $IZnCH_2$ radical are also very similar to the corresponding bond in the $IZnCH_2I$ molecule. As expected, one unpaired electron is mainly located on C atom of the $IZnCH_2$ radical.

It has been found experimentally that the Simmons−Smith reaction has high stereospecificity and insertion into the vinylic C−H bond does not take place with appreciable probability. This provides evidence that the singlet carbene is not the reactive species in the Simmons−Smith cyclopropanation reaction. The reaction of the singlet carbene and ethylene has been extensively investigated from the viewpoint of theory.[32,39−41] These calculations predicted that the addition reaction between singlet carbene and ethylene is continuously exothermic and thus without an activation barrier. Thus, the reaction of singlet carbene with CH_2CH_2 is not considered in the present work. In our previous paper, the cyclopropanation reaction between the CH_2I radical and CH_2CH_2 was investigated using the DFT method at the B3LYP level with two different basis sets. The reaction involves a two-step process with a considerable barrier height for the

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rate-determining step. These previous calculations indicated that the CH_2I radical is not the active species that reacts with ethylene in ultraviolet excitation of diiodomethane in the solution phase. The reaction between $ZnCH_2I$ and CH_2CH_2 may take place in the Zn + CH_2I_2 + CH_2CH_2 system. However, test calculations predict that the $ZnCH_2I$ radicals first isomerize to $IZnCH_2$, and then react with CH_2CH_2. Therefore, we mainly pay attention to the cyclopropanation reactions of $IZnCH_2I$ and $IZnCH_2$ with CH_2CH_2 in the following discussion.

Cyclopropanation Reaction between $IZnCH_2I$ and CH_2CH_2. When $IZnCH_2I$ and CH_2CH_2 approach each other, a complex may be formed between them. Previous calculations predicted that complexes between $ClZnCH_2Cl$ and CH_2CH_2 and between iso-CH_2I−I and CH_2CH_2 have stabilization energies of about 1 kcal·mol^{-1}.[28-32] One can expect that complex formation should not have a significant influence on the chemical reaction. A transition state was found on the way to the products c-C_3H_6 and ZnI_2, which is referred to as TS2 in Figures 1 and 2. The $IZnCH_2I$ molecules approach CH_2CH_2 in an asymmetric way. The C2−C3 distance in TS2 is 2.261 Å, and this is 0.256 Å shorter than the C1−C3 distance. The relatively large C3−C2 distance predicts that TS2 is closer to the reactants than products in structure. This structural feature agrees with Hammond's postulate:[42] the exothermic reaction has a transition-state geometry close to the reactant. The planar ethylene molecule has a significant pyramidalization of about 10° at C2 in the TS2 structure, indicating the onset of the $sp^2 \rightarrow sp^3$ rehybridization required for the cyclopropane formation. The C1═C2 and C3−Zn bond lengths are increased by 0.021 and 0.026 Å, respectively, in going from the reactants to the transition state. The interaction of the $IZnCH_2I$ moiety with the π olefin orbitals is mainly responsible for the slight lengthening of the C1═C2 and C3−Zn bonds. There are relatively large changes associated with the C3−Zn−I angle, C3−I and Zn−I distances that vary from 180.0°, 2.193 and 2.402 Å, respectively, in $IZnCH_2I$ to 152.3°, 2.474 and 2.718 Å in TS2. These structural changes are attributed to the ZnI_2 molecule being partially formed in the transition state (TS2). It is evident that TS2 is the transition state of the concerted reaction from $IZnCH_2I$ + CH_2CH_2 to c-C_3H_6 + ZnI_2. Similar transition state structures[28,29,31,32] were found in previous studies, and the transition state structure was confirmed to be the first-order saddle point connecting the corresponding reactants and products by IRC calculations.

Relative to the separated reactants of $IZnCH_2I$ and CH_2CH_2, the reaction has a barrier of 21.2 kcal·mol^{-1} and is exothermic by 21.2 kcal·mol^{-1} at the B3LYP/6-311G** level of theory. These values for the barrier height and the exothermicity of the reaction become 20.5 and 28.5 kcal·mol^{-1}, respectively, using further single point B3LYP calculations with the PVTZ basis set. BP calculations with the effective core potentials[29] for Zn and I atoms predicted the $IZnCH_2I$ + CH_2CH_2 reaction to have a barrier of about 14.6 kcal·mol^{-1} and to be exothermic by 34.0 kcal·mol^{-1}. These values are about 5.9 kcal·mol^{-1} lower about 5.5 kcal·mol^{-1} higher than the B3LYP/PVTZ calculated results presented here. The reaction of $ClZnCH_2Cl$ with CH_2CH_2 to give c-C_3H_6 and $ZnCl_2$ has been calculated with the B3LYP/6-311G** method and these computations predicted the reaction to be exothermic by 19.3 kcal·mol^{-1} with a barrier of 24.7 kcal·mol^{-1}. The single-point CCSD(T) calculations on the B3LYP optimized structures also provided a barrier of 19.5 kcal·mol^{-1} for the reaction of $ClZnCH_2Cl$ with CH_2CH_2. The Simmons−Smith cyclopropanation reaction takes place only at room temperature or above (and typically needs a higher temperature to proceed at a reasonable rate).[21] This is consistent with a reaction barrier of about 20 kcal·mol^{-1}.

C. Cyclopropanation Reaction between $IZnCH_2$ and CH_2CH_2. In the Zn + CH_2I_2 system, the $IZnCH_2$ radicals may be formed through dissociation of $IZnCH_2I$. Since there is about −0.85 atomic charge distributed on the C atom, the $IZnCH_2$ radical should be a nucleophilic agent. Similar to the $IZnCH_2I$ molecule, electrophilic behavior was observed experimentally for the MCH_2X (M = Li, Zn; X=Cl, I) radicals.[27] Unlike the cyclopropanation reaction of $IZnCH_2I$ with CH_2CH_2, a two-step process was predicted by the B3LYP/6-311G** calculations for formation of c-C_3H_6 + ZnI from $IZnCH_2$ + CH_2CH_2. The $IZnCH_2$ radical attacks preferentially one of the CH_2 group of CH_2CH_2 from above the CH_2CH_2 molecular plane. An intermediate of $IZnCH_2CH_2CH_2$ is formed in the first step via a transition state that is referred as TS3 in Figures 1 and 2. In TS3, the C3−C2 distance is 2.330 Å and this indicates the interaction between the $IZnCH_2$ and CH_2CH_2 moieties is not strong in the transition state. With respect to the CH_2CH_2 molecule the C1−C2 bond is elongated by 0.028 Å in TS3 and originates from the weak interaction of $IZnCH_2$ and CH_2CH_2 moieties. However, this interaction has little influence on the $IZnCH_2$ structure and this is quite different from the reaction between $IZnCH_2I$ and CH_2CH_2. The C3−C2−C1 angle of 106.3° in TS3 is close to that (111.5°) in the intermediate of $IZnCH_2CH_2CH_2$, but substantially different from the C−C−C angle of 60° in c-C_3H_6. This predicts that the reaction between $IZnCH_2$ and CH_2CH_2 is a two-step process for formation of c-C_3H_6 and ZnI. Further evidence for this comes from the IRC calculations.

In the second step of the reaction mechanism, the cyclopropane product is formed with the ZnI radical as the coproduct. A transition state, labeled TS4 in Figures 1 and 2, was found on the way from the $CH_2CH_2CH_2ZnI$ radical intermediate to the c-C_3H_6 + ZnI products. The C3−C2−C1 angle varies from 111.5° in $CH_2CH_2CH_2ZnI$ to 78.2° in TS4, which is closer to 60.0° in c-C_3H_6. Meanwhile, the C3−Zn distance is increased by 0.335 Å in going from $CH_2CH_2CH_2ZnI$ to TS4. The structural features of TS4 predict that it is the correct transition state for the corresponding reactant and products. Starting from the TS4 structure, the IRC calculations show that TS4 is the transition state located between the $CH_2CH_2CH_2ZnI$ intermediate and the c-C_3H_6 + ZnI products.

Relative to the separated reactants of $IZnCH_2$ and CH_2CH_2, the first step has a barrier of 6.7 kcal·mol^{-1} at the B3LYP/6-311G** level of theory. The barrier is predicted to be 8.0 kcal·mol^{-1} using single-point energy B3LYP/PVTZ calculations. The formed intermediate is 19.0 and 17.6 kcal·mol^{-1} in energy lower than the separated reactants at the B3LYP/6-311G** and B3LYP/PVTZ levels of theory, respectively. It is evident that the first step of the reaction proceeds very easily. However, the second step of the reaction mechanism is more difficult to take place. With respect to the intermediate, the

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[42] Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

second step has a barrier of 22.7 kcal·mol^{-1}, which is reduced a little (21.9 kcal·mol^{-1}) in the B3LYP/PVTZ single point calculations. The second step is the rate-determining step of the reaction from $IZnCH_2 + CH_2CH_2$ to c-C_3H_6 + ZnI.

E. Reaction of $IZnCH_2$+ with CH_2CH_2. $IZnCH_2$+ could be produced by heterolytic bond cleavage of the C−I bond in $IZnCH_2I$. As an electrophilic reagent, $IZnCH_2^+$ is expected to react easily with CH_2CH_2, and this is confirmed by the B3LYP/6-311G** computations. However, this reaction does not directly lead to formation of the cyclopropane product and initially produces a relatively stable $IZnCH_2CH_2CH_2^+$ cation intermediate. The $IZnCH_2CH_2CH_2^+$ cation intermediate is formed from the $IZnCH_2^+$ and CH_2CH_2 reactants with no barrier for the reaction and the $IZnCH_2CH_2CH_2^+$ cation has a stabilization energy of 62.8 kcal/mol with respect to the separated reactants at the B3LYP/6-311G** level of theory. The dissociation reaction of the $IZnCH_2CH_2CH_2^+$ cation into cyclopropane and a ZnI^+ leaving group is 35.7 kcal/mol at the B3LYP/6-311G** level of theory including the zero-point energy correction. This is a very high barrier to form a cyclopropane product and it is unlikely that the $IZnCH_2^+$ cation is the reactive intermediate in the Simmons-Smith reaction. Similarly, the ICH_2^+ reaction with CH_2CH_2 generates a $ICH_2CH_2CH_2^+$ cation intermediate that is very stable relative to the separated reactants (ICH_2^+ and CH_2CH_2) and products (cyclopropane and I^+).[31]

Discussion

The $IZnCH_2I$ molecule is thought to be the reactive intermediate in the Simmons-Smith cyclopropanation reaction and this suggests that atomic Zn inserts into the C−I bond. The Zn atom has a valence electron configuration of $3d^{10}4s^2$ and the Zn−Zn bonds in Zn clusters are expected to relatively weak. Test B3LYP/6-311++G(3df,3pd) calculations predict Zn−Zn distances of about 3.7 Å in small Zn clusters (n=1−4). The smaller Zn clusters appear similar to van der Waals systems and are not likely to have a large influence on the reaction rate of atomic Zn insertion into the C−I bond of CH_2I_2. Any influence of the clusters on the Zn insertion reaction is probably small to moderate. Since it is very difficult to do reliable DFT and ab initio calculations between Zn clusters and CH_2I_2, we have focused on atomic Zn insertion into the C−I bond of CH_2I_2 in our present work. We expect that the pathway reported here reflect the essentials of the Zn insertion reaction.

The insertion reaction of Zn into the C−I bond of CH_2I_2 is the initial step for the Simmons-Smith reaction and is predicted to have a barrier of about 30 kcal·mol^{-1}. The relatively large barrier on the insertion pathway is reasonable since it takes place via a three-membered transition state with a large ring strain. Once the reaction takes place, the energy released by the reaction (36.4 kcal·mol^{-1}) is sufficient to compensate for the energy required to get over the barrier. There are many possible pathways for $IZnCH_2I$ to dissociate, but none of them takes place easily due to their high endothermicity. The reaction between $IZnCH_2I$ and CH_2CH_2 is a concerted process with a potential barrier of about 20.5 kcal·mol^{-1}. In comparison with this concerted reaction, the initial reaction between $IZnCH_2$ and CH_2CH_2 occurs more easily. However, the rate-determining second step has a barrier of 21.9 kcal·mol^{-1}. The reaction of $IZnCH_2$ and CH_2CH_2 to form c-C_3H_6 is a two-step process. The cyclopropanation of CH_2CH_2 from $IZnCH_2I$ via a one step concerted reaction proceeds a little more easily than from the two step $IZnCH_2$ reaction. The dissociation energy of $IZnCH_2I$ to $IZnCH_2$ + I is about 55.4 kcal·mol^{-1} and this indicates that formation of $IZnCH_2$ is very difficult from the $IZnCH_2I$ dissociation. Thus, the $IZnCH_2I$ species is the active species in the Simmons-Smith reaction.

Table 2. Mulliken Atomic Charges on the C and Zn Atoms for Selected Species examined in this work

	CH_2I	$CH_2I{-}I$	$IZnCH_2$	$IZnCH_2^+$	$IZnCH_2I$
C	−0.30	+0.78	−0.84	−0.47	−0.95
Zn			+1.09	+1.17	+1.11

The CH_2CH_2 molecule has a pair of π electron and electrophilic reagents are expected to react with CH_2CH_2 relatively easily. The CH_2I^+ cation has been proposed to be the species that reacts with olefins in cyclopropanation reactions using ultraviolet photoexcitation of diiodomethane.[15] Table 2 presents the Mulliken atomic charges located on the C and Zn atoms for selected species investigated in this work. There is about −0.9 atomic charge distributed in the C atoms in $IZnCH_2I$ and $IZnCH_2$. From the viewpoint of static interaction, the reactions of $IZnCH_2I$ and $IZnCH_2$ with CH_2CH_2 do not proceed easily. The barrier to the reaction between CH_2CH_2 and iso-$CH_2{-}I{-}I$ was predicted to be about 3 kcal·mol^{-1} from similar B3LYP calculations[31] and this value is much lower than that (21.6 kcal·mol^{-1}) for the reaction of CH_2CH_2 and $IZnCH_2I$. The atomic charge distributed to the C atom of $IZnCH_2I$ is about −0.95 compared to the C atom atomic charge of about +0.78 in the $CH_2I{-}I$ isomer molecule.[43] Therefore, the large difference in atomic charge of the C atom is one of the reasons for the different reactivity of the $CH_2{-}I{-}I$ and $IZnCH_2I$ species toward olefins. The cation-like character of the CH_2I moiety of the $CH_2I{-}I$ species makes it a better electrophilic agent and a substantially lower barrier to react with olefins to give cyclopropanated products compared to the $IZnCH_2I$ species of the Simmons−Smith reagent.

A two-step process was found for the reaction of ICH_2 and CH_2CH_2.[31] The first step from $ICH_2 + CH_2CH_2$ to $ICH_2CH_2CH_2$ has a barrier of 5.2 kcal·mol^{-1}, which is a little lower than that found (6.7 kcal·mol^{-1}) for the first step of the $IZnCH_2 + CH_2CH_2$ reaction. However, the C atom in CH_2I carries about −0.3 atomic charges, while −0.84 atomic charges are distributed in the C atom of $IZnCH_2$. It appears that the static interaction does not play the dominant role in these reactions.

The $IZnCH_2I$ molecules attack the CH_2CH_2 molecules in a way similar to that of the $IZnCH_2$ radicals, although the radical reaction is a two-step process. As discussed previously, the charge distributions on the C atoms are similar for the $IZnCH_2I$ molecule and the $IZnCH_2$ radical. The initial reaction of $IZnCH_2$ with CH_2CH_2 has a barrier of 6.7 kcal·mol^{-1}, which is much lower than that (20.5 kcal·mol^{-1}) for the reaction between $IZnCH_2I$ with CH_2CH_2. Inspection of the structures of $IZnCH_2$ and $IZnCH_2I$ in Figure 1, one can see that the $IZnCH_2$ radical approaches CH_2CH_2 without or with less steric obstacle than the $IZnCH_2I$ species approaches CH_2CH_2. Therefore

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(43) Zheng, X.; Phillips, D. L. *J. Phys. Chem. A* **2000**, *104*, 6880−6886.

steric effects should be one of the important reasons for the large difference in reactivity of the $IZnCH_2I$ and $IZnCH_2$ species toward CH_2CH_2. Similar steric effects may be partially responsible for the reactivity difference between the $IZnCH_2I$ and $CH_2{-}I{-}I$ species toward olefins. When the $ZnCH_2I$ radical approaches CH_2CH_2 isomerization from $ZnCH_2I$ to $IZnCH_2$ takes place prior to the reaction between $ZnCH_2I$ and CH_2CH_2. This also indicates that steric effects of the carbenoid species play an important role in their chemical reactivity.

The cyclopropanation reaction between $CH_2I{-}I$ and CH_2CH_2 leads to formation of C−C bonds and only the weak C−I bond is broken in this reaction. We would expect that the cyclopropanation reaction between $CH_2I{-}I$ and CH_2CH_2 takes place relatively easily. However, the $IZnCH_2I + CH_2CH_2$ cyclopropanation reaction has ZnI_2 as the leaving group attached by two bonds to the carbon atom. The cyclopropanation process involves cleavage of the C−I and C−Zn bonds simultaneously and appears to be more energetically demanding. This probably accounts for a significant contribution to the high barrier on the pathway of the $IZnCH_2I + CH_2CH_2$ cyclopropanation reaction. This indicates that the leaving group has a significant influence on the reactivity of the carbenoid species toward olefins.

The initial step for the reactions of the CH_2I and $IZnCH_2$ radicals with CH_2CH_2 have barrier heights close to each other, and only a little higher than that for the $CH_2I{-}I$ reaction with CH_2CH_2. However, the CH_2I and $IZnCH_2$ radical cyclopropanation reactions require two steps and the second reaction step takes place with more difficulty (since a high barrier exists on the pathway from $ICH_2CH_2CH_2$ to c-C_3H_6 + I. or from $IZnCH_2CH_2CH_2$ to c-C_3H_6 + ZnI). Thus, the CH_2I and $IZnCH_2$ radical cyclopropanation reactions do not occur very easily. In contrast, the $CH_2I{-}I$ and $IZnCH_2I$ cyclopropanation reactions with CH_2CH_2 occur via a single reaction step and can proceed more easily (particularly the $CH_2I{-}I$ carbenoid). The CH_2I and $IZnCH_2$ radical carbenoid species and the CH_2I^+ and $IZnCH_2^+$ cation carbenoid species appear to react easily with CH_2CH_2 to give radical or cation intermediates that then have large and difficult reaction pathways on the second rate-determining step to form cyclopropanated product.[31,32] This suggests that radical and cation carbenoids have a tendency to form relatively stable radical or cation intermediates that may be more difficult to get to form a cyclopropanated product via a two step reaction process. Thus, it appears to be beneficial to use molecular carbenoid species with molecular leaving groups to carry out more efficient cyclopropanation reactions. The difference in the reaction mechanisms of $CH_2I{-}I$, $IZnCH_2I$, $IZnCH_2$ and CH_2I toward olefins appears related to their relative chemical reactivity for making cyclopropanated products.

Summary

The insertion reaction of Zn into the C−I bond of CH_2I_2 was found to proceed via a fairly large barrier of ~30 kcal mol^{-1} to give the $IZnCH_2I$ reactive species. The $IZnCH_2I$ species may then undergo reaction with CH_2CH_2 to give a cyclopropane product and ZnI_2 leaving group with a barrier to reaction of about 21 kcal mol^{-1}. The $IZnCH_2I$ species may also undergo further dissociation reactions to give $IZnCH_2$ + I, I + $ZnCH_2I$, ZnI + CH_2I, and $ZnI_2 + CH_2$ (no transition states were found for these dissociation reactions) and UB3LYP/6-311G** computations indicate these reactions to be endothermic by 55.5, 66.2, 77.9, and 78.8 kcal·mol^{-1} respectively. Investigation of the $IZnCH_2$ species reaction with CH_2CH_2 indicates that it reacts via a two step mechanism to give a cyclopropane product and ZnI leaving group with a barrier of about 22.7 kcal mol^{-1} on the second rate-determining step. Comparison of the $IZnCH_2I$, $IZnCH_2$, $CH_2I{-}I$ and CH_2I reactions with CH_2CH_2 to give cyclopropane product indicates the ease of the carbenoid species cyclopropanation reactions are noticeably influenced several things: the electrophilic nature (e.g., charge distribution on the methylene carbon atom), steric effects, nature of the leaving group and the type of reaction mechanism of the carbenoid species.

Acknowledgment. W.H.F. thanks the National Natural Science Foundation of China (Grant Nos. 20073005 and 29873008) for support of this research. D.L.P. thanks the Committee on Research and Conference Grants (CRCG) and the Research Grants Council of Hong Kong (HKU 7087/01P) for support of this research.

Supporting Information Available: Selected output from the B3LYP density functional theory calculations showing the Cartesian coordinates, total energies, and vibrational zero-point energies of the species shown in Figure 1. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0107655