J. Am. Chem. Soc. **2001,** *123,* 4197−4203

Isodiiodomethane Is the Methylene Transfer Agent in Cyclopropanation Reactions with Olefins Using Ultraviolet Photolysis of Diiodomethane in Solutions: A Density Functional Theory Investigation of the Reactions of Isodiiodomethane, Iodomethyl Radical, and Iodomethyl Cation with Ethylene

David Lee Phillips,*,† Wei-Hai Fang,*,‡ and Xuming Zheng†

Contribution from the Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong S. A. R., P. R. China, and Department of Chemistry, Beijing Normal University, Beijing 100875, P. R. China

Received August 18, 2000. Revised Manuscript Received February 20, 2001

Abstract: We examine the chemical reactions of the isodiiodomethane (CH_2I-I), $\cdot CH_2I$ and CH_2I^+ species with ethylene using density functional theory computations. The CH_2I-I species readily reacts with ethylene to give the cyclopropane product and an I_2 product via a one-step reaction with a barrier height of ∼2.9 kcal/mol. However, the $\cdot CH_2I$ and CH_2I^+ species have much more difficult pathways (with larger potential barriers) to react with ethylene via a two-step reaction mechanism. Comparison of experimental results to our present calculation results indicates that the CH_2I-I photoproduct species is most likely the methylene transfer agent for the cyclopropanation reaction of olefins via ultraviolet photoexcitation of diiodomethane.

Introduction

Cyclopropanation reactions are very important in organic and organometallic chemistry, but their reaction mechanisms are not well understood. In this paper we investigate the long utilized cyclopropanation reaction that makes use of ultraviolet photolysis of diiodomethane to better understand the reaction mechanism and the nature of the methylene transfer agent. Diiodomethane is commonly used as a reagent for cyclopropanation reactions with olefins where diiodomethane is activated by either a Zn−Cu couple in the Simmons−Smith reaction[1] or by ultraviolet photolysis.[2−5] The ultraviolet excitation of diiodomethane in solutions containing olefins affords cyclopropanes with high sterospecificity.[2−5] This high stereospecificity and the lack of an appreciable C−H insertion reaction indicates that the reactive species is not a free carbene. A range of possible intermediates have been proposed (e.g., an excited diiodomethane state, an iodocarbenium-iodide ion pair, and others) as the species that reacts with olefins to give cyclopropane products.[1−5] Efforts to elucidate the key reaction intermediates and mechanism of the cyclopropanation reactions that use ultraviolet excitation of diiodomethane have been hampered by the lack of direct observation of the reaction intermediates with experiments that can reveal detailed structural information about the identity and properties of the reaction intermediates.

Excitation of diiodomethane in condensed phases (liquids and solid-state matrixes) by ultraviolet light,[6−9] direct photoionization,[10] and radiolysis[11,12] all generate products that exhibit characteristic absorption bands ∼385 nm (strong) and ∼570 nm (weak). These product absorption bands have been attributed to several possible species such as trapped electrons,[6] the cation of diiodomethane,[10,12] and the isomer of diiodomethane (CH_2I-I).[8,9] Femtosecond transient absorption studies[13−15] have also been done in the solution phase to examine the initial photodissociation of diiodomethane and the formation of the photoproduct species. These ultrafast transient absorption experiments all showed similar results: a fast rise of several hundred femtoseconds which was agreed to be due to the initial C−I bond cleavage to give $\cdot CH_2I$ and I• or I•* fragments; this was then followed by a fast decay of several hundred femtoseconds and then a slower rise in the transient absorption on the 5−20 ps time scale. However, three different interpretations of these experiments were put forward, depending on which product species was attributed to the transient absorption signal being

---

* Authors to whom correspondence should be addressed.

† The University of Hong Kong.

‡ Beijing Normal University.

(1) Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256−4264.

(2) Blomstrom, D. C.; Herbig, K.; Simmons, H. E. *J. Org. Chem.* **1965**, *30*, 959−964.

(3) Pienta, N. J.; Kropp, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 655−657.

(4) Kropp, P. J.; Pienta, N. J.; Sawyer, J. A.; Polniaszek, R. P. *Tetrahedron* **1981**, *37*, 3229−3236.

(5) Kropp, P. J. *Acc. Chem. Res.* **1984**, *17*, 131−137.

(6) Simons, J. P.; Tatham, P. E. R. *J. Chem. Soc. A* **1966**, 854−859.

(7) Mohan, H.; Rao, K. N.; Iyer, R. M. *Radiat. Phys. Chem.* **1984**, *23*, 505−508.

(8) Maier, G.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 819−822.

(9) Maier, G.; Reisennauer, H. P.; Hu, J.; Schaad, L. J.; Hess, B. A., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 5117−5122.

(10) Andrews, L.; Prochaska, F. T.; Ault, B. S. *J. Am. Chem. Soc.* **1979**, *101*, 9−15.

(11) Mohan, H.; Iyer, R. M. *Radiat. Eff.* **1978**, *39*, 97−101.

(12) Mohan, H.; Moorthy, P. N.; *J. Chem. Soc., Perkin Trans. 2* **1990**, 277−282.

(13) Schwartz, B. J.; King, J. C.; Zhang, J. Z.; Harris, C. B. *Chem. Phys. Lett.* **1993**, *203*, 503−508.

(14) Saitow, K.; Naitoh, Y.; Tominaga, K.; Yoshihara, K. *Chem. Phys. Lett.* **1996**, *262*, 621−626.

(15) Tarnovsky, A. N.; Alvarez, J.-L.; Yartsev, A. P.; Sundström, V.; Åkesson, E. *Chem. Phys. Lett.* **1999**, *312*, 121−130.

10.1021/ja003090g CCC: $20.00

monitored in each particular experiment. The differing assignments and controversy over which photoproduct species is responsible for the characteristic intense ∼385 nm absorption band observed in both the photochemistry experiments[6−12] and the ultrafast transient absorption experiments[13−15] prompted us to investigate this photoproduct species using transient resonance Raman spectroscopy.[16] The vibrational frequencies observed in the transient resonance Raman spectra were compared to the calculated frequencies obtained from density functional theory (DFT) computations for several of the proposed photoproduct species. This vibrational frequency comparison and comparison to the computed electronic absorption transition energies and oscillator strengths for the proposed photoproduct species clearly demonstrated that the CH_2I-I species is mainly responsible for the intense ∼385 nm transient absorption band observed following ultraviolet excitation of diiodomethane in room-temperature solutions.[16] In this paper, we examine the chemical reactivity of the CH_2I-I, $\cdot CH_2I$, and CH_2I^+ species toward olefins (alkenes) using density functional theory (DFT) computations. We find that CH_2I-I readily reacts with ethylene to give formation of the cyclopropane product and an I_2 product via a one-step reaction with a barrier height of ∼2.9 kcal/mol (after the initial formation of a very weak CH_2I-I/ethylene complex). The $\cdot CH_2I$ and CH_2I^+ species have much more difficult routes to react with ethylene via a two-step reaction mechanism that contains much larger barriers to reaction. Comparison of our present computational results with experimental observations in the literature leads us to conclude that the CH_2I-I photoproduct species is most likely the methylene transfer agent (i.e., carbenoid species) for the cyclopropanation reaction of olefins (alkenes) via ultraviolet excitation of diiodomethane. We discuss the implications of this carbenoid behavior observed for the CH_2I-I species for related cyclopropanated reactions that use ultraviolet photoexcitation of polyhalomethanes or a Zn(Cu) couple in the Simmons−Smith reaction.

Computational Details

Density functional theory (DFT) was used to investigate the potential energy surfaces of addition reactions of ethylene with isodiiodomethane and related species (the $\cdot CH_2I$ and the CH_2I^+ species). The stationary structures on the surfaces were fully optimized at the B3LYP or UB3LYP level of theory using C_1 symmetry.[17−21] In our present work, only the isodiiodomethane dissociation to $\cdot CH_2I + \cdot I\cdot$ or $CH_2\!: + I_2$ were calculated using the complete active-space SCF (CASSCF) approach.[22−26] Ten electrons originating from the 5p orbitals of the two iodine atoms were employed as active electrons for the dissociation reaction to give $CH_2I + I$. For the dissociation reaction to give $CH_2\!: + I_2$ (which involves the C−I σ bond cleavage) the C−I σ bond electrons were also used as active electrons with one lone pair of the terminal I atom excluded from the active space. To obtain proper configurations, two low-energy virtual orbitals (chosen automatically by the Gaussian program) were added to the active space. Finally, the dissociation pathways were optimized with 10 electrons in eight orbitals, denoted by CAS(10,8) hereafter in the paper. At the CAS(10,8) optimized structures, the dissociation energy to $CH_2I + I$ was further calculated with a larger active space (14,10) that includes 5s and 5p electrons of the two I atoms. The dissociation energy to $CH_2\!: + I_2$ was also computed at the CAS(14,10) level, but the C−I σ electrons were used as active electrons by excluding the two 5s electrons of the I atom. Since the Gaussian 98W suite only allows a maximum of 10 electrons, the CAS(14,10) single-point calculations were performed using the MOLPRO program suite.[27] Analytical frequency calculations were performed to confirm the optimized structure to be a minimum or a first-order saddle point as well as to carry out zero-point energy correction. The transition states were confirmed to connect the related reactants and products by using IRC calculations.[28] After a preliminary search was done using the 6-311G** basis set, all of the stationary structures were further optimized with the Sadlej-PVTZ basis set to assess the dependence of the structure and energy on the basis set employed for the computations. The Sadlej-PVTZ basis set was contracted as (6s4p//3s2p),[29] (10s6p4d//5s3p2d),[30] and (19s15p12d4f//11s9p6d2f),[31] for the H, C, and I atoms, respectively. For the $CH_2I-I + CH_2{=}CH_2$ system investigated here, this basis set was composed of 290 basis functions contracted from 996 primitive Gaussian functions. All calculations except the CAS(14,10) were carried out using the Gaussian 98 program packages.[32]

We note that relativistic effects may have considerable influence on the calculated energy of systems that contain heavy atoms (such as bromine and iodine atoms). However, we are concerned about the relative energies (i.e., barrier heights and reaction energies) in our chemical reaction computations, and the energy errors originating from relativistic effects will partially be canceled out in the calculated relative energies. Thus, we expect that relativistic effects will have little influence on the reaction processes investigated here. We note the caveat that relativistic effects due to spin−orbit coupling may be noticeable and may modestly affect the results. We have not considered spin−orbit relativistic effects since they are beyond the scope of the present study.

Results

A. Reaction of Isodiiodomethane and Ethylene. The isodiiodomethane molecule approaches $CH_2{=}CH_2$ in an asymmetric way, preferentially attacking one of the CH_2 groups of ethylene from above the molecular plane. A complex may be formed when the two molecules approach each other. Since the binding energy is very small, the formation of this complex has little influence on the chemical reaction. A transition state (TS1) was found on the way to the products cyclopropane (C_3H_6) and I_2. The TS1 structure is shown in Figure 1 along

---

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

(17) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372−1377.

(18) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513.

(19) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211.

(20) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.

(21) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *58*, 785−789.

(22) Roos, B. O.; Taylor, P. R. *Chem. Phys.* **1980**, *48*, 157−173.

(23) Siegbahn, P. E. M.; Almof, J.; Heiberg, A.; Roos, B. O. *J. Chem. Phys.* **1981**, *74*, 2384−2396.

(24) Bernardi, F.; Bottini, A.; McDougall, J. J. W.; Robb, M. A.; Schlegel, H. B. *Faraday Symp. Chem. Soc.* **1984**, *19*, 137−147.

(25) Frisch, M. J.; Ragazos, I. N.; Robb, M. A.; Schlegel, H. B. *Chem. Phys. Lett.* **1992**, *189*, 524−528.

(26) Yamamoto, N.; Vreven, T.; Robb, M. A.; Frisch, M. J.; Schlegel, H. B *Chem. Phys. Lett.* **1996**, *250*, 373−378.

(27) MOLPRO is a package of ab initio programs written by H.-J. Werner and P. J. Knowles with contributions from J. Almlof, R. D. Amos, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, E. Eclert, S. T. Elbert, C. Hampel, R. Lindh, A. W. Lloyd, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schutz, H. Stoll, and T. Thorsteinsson.

(28) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys*. **1989**, *90*, 2154; *J. Phys. Chem.* **1990**, *94*, 5523−5527.

(29) Sadlej, A. J. *Collect. Czech. Chem. Commun.* **1988**, *53*, 1995−2016.

(30) Sadlej, A. J. *Theor. Chem. Acta* **1992**, *79*, 123−140.

(31) Sadlej, A. J. *Theor. Chem. Acta* **1992**, *81*, 339−354.

(32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

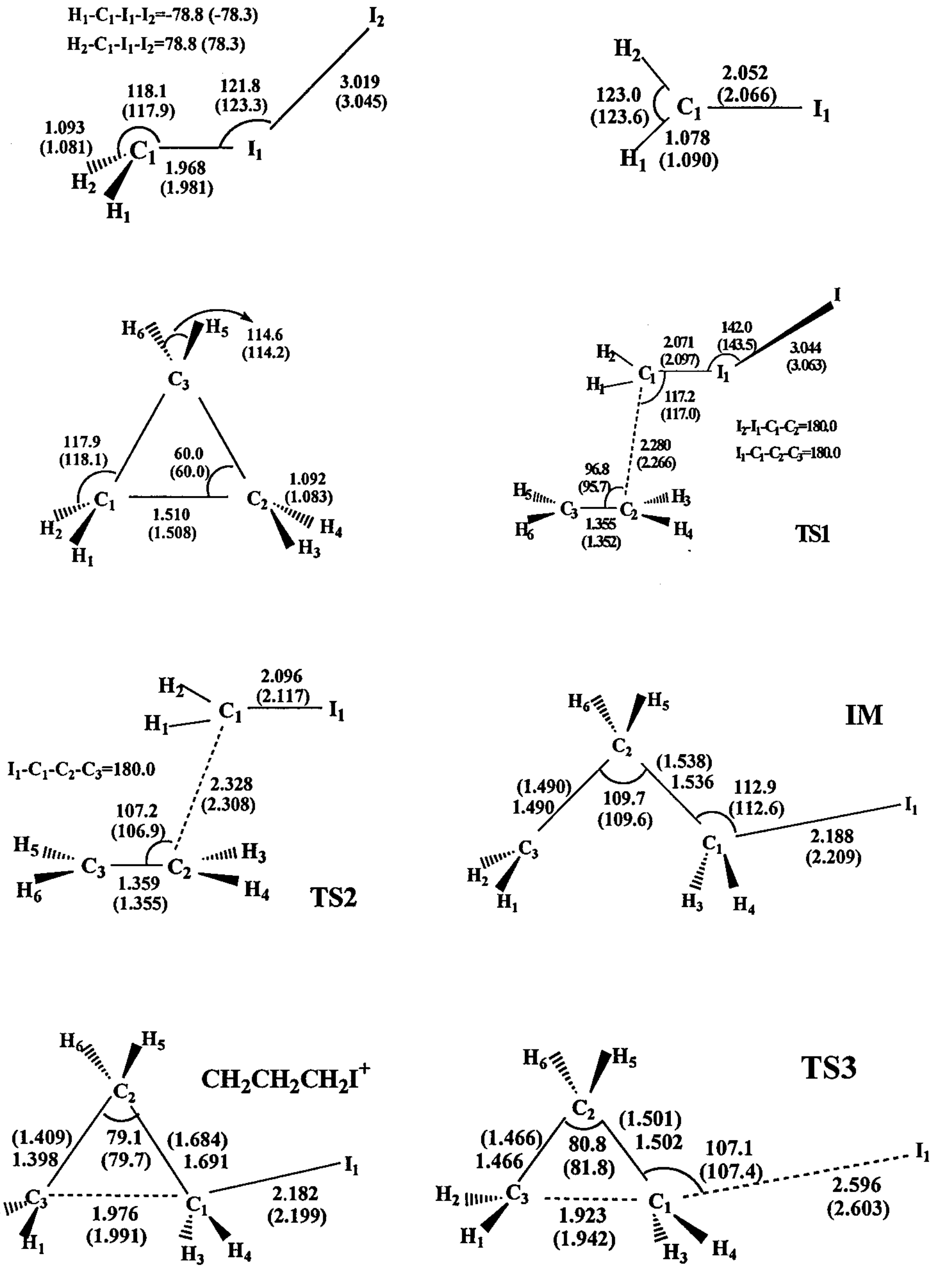

Figure 1. Schematic diagram showing the optimized geometry for selected reactants, transition state(s), intermediates, and reaction products for the reactions of $CH_2I{-}I$, $\cdot CH_2I$, CH_2I^+ with ethylene. The numbers present selected key structural parameters from the DFT/sadlej-PVTZ computations (bond lengths in Å and bond angles in degrees) for the species shown ($CH_2I{-}I$, TS1, cyclopropane, $\cdot CH_2I$, TS2, IM, $CH_2CH_2CH_2I^+$, and TS3). The key structural parameters shown in parentheses were found using a 6-311G** basis set as described in the text.

with selected key bond parameters. The C═C and C−I bonds in the TS1 structure are increased by 0.025 and 0.116 Å, respectively, compared to those found for the reactants. The largest change is associated with the I−I−C angle that varies from 123.3° in $CH_2I{-}I$ to 143.5° in the TS1 structure. The structural changes are consistent with the fact that the C−C bond between $CH_2{=}CH_2$ and $CH_2I{-}I$ is partially formed in TS1, which weakens the intramolecular C═C and C−I bonds. The I−I and I−C bond lengths are reduced by about 0.02 Å, while the C−C and C−H bond lengths are increased a little on going from the 6-311G** basis set to the Sadlej-PVTZ basis set. The increase in the size of the basis set has almost no influence on the bond angles.

An imaginary frequency of 246.8*i* cm^{-1} was found for the TS1 structure by vibrational analysis. The eigenvector corresponding to the negative eigenvalue of the force constant matrix indicates that the internal coordinate reaction vector is mainly composed of changes in the $C_1{-}C_2$ bond lengths and the $I_2{-}I_1{-}C_1$ bond angle. The reaction vector has been identified as $0.44\ R_{C1-C3} + 0.55\ R_{C1-C2} - 0.19\ A_{I2-I2-C1}$. On the basis of the reaction vector and the structure (the $C_1{-}C_2{-}C_3$ angle = 96.8°) of TS1, it at first appears possible that an intermediate radical like $\cdot CH_2CH_2CH_2I_2\cdot$ or $\cdot CH_2CH_2CH_2I + I\cdot$ is formed starting from the TS1 structure. However, the IRC calculations at the B3LYP/6-311G** level confirm the transition state to connect the reactants of $CH_2{=}CH_2 + CH_2I{-}I$ and the products of $C_3H_6 + I_2$. A transition state was found for the reaction of $CH_2Br{-}Br$ and $CH_2{=}CH_2$, and this was confirmed to be the first-order saddle point governing formation of products of $C_3H_6 + Br_2$ by IRC calculations at the UB3LYP/6-31+G* level.[33]

---

[33] Zheng, X.; Fang, W.-H.; Phillips, D. L. *J. Chem. Phys.* **2000**, *113*, 10934−10946.

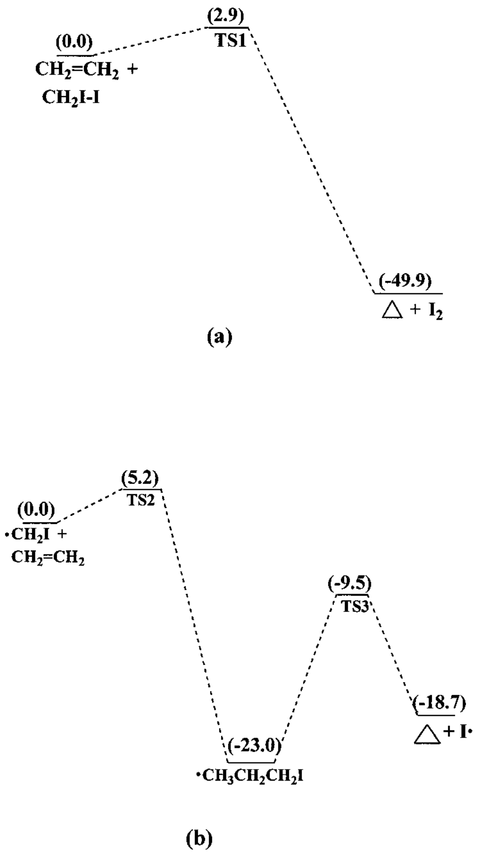

Figure 2. Schematic diagram showing the computed relative energies (in kcal/mol) for the reactants, transition state(s), intermediates, and reaction products for the reactions of $CH_2I{-}I$ with ethylene (a) and $\cdot CH_2I$ with ethylene (b). All energies are from B3LYP computations except for the relative energies of the $CH_2{:}\ + I_2$ and $\cdot CH_2I + I$ products which were obtained from CASSCF (CAS(10,8)) calculations. See text for more details.

The transition state for the reaction of $CH_2Br{-}Br$ and $CH_2{=}CH_2$ is structurally very similar to that found for the reaction of $CH_2I{-}I$ and $CH_2{=}CH_2$. Thus, we conclude that the reaction of $CH_2I{-}I$ or $CH_2Br{-}Br$ and $CH_2{=}CH_2$ is a one-step process, namely, an elementary reaction. Inspection of the TS1 for the reaction of $CH_2I{-}I$ with ethylene shows that the barrier to reaction is in the entrance channel.

Relative to the separated reactants, the barrier height was calculated to be 3.2 kcal/mol at the B3LYP/6311G** level. It becomes 4.5 kcal/mol with zero-point energy correction. The barrier height is lowered to 1.6 kcal/mol when the Sadlej-PVTZ basis set is used. Inclusion of the B3LYP/6311G** zero-point energy correction gives us an estimate of the barrier height to be ~2.9 kcal/mol. The potential energy profile of the reaction is shown in Figure 2a. It is evident that the reaction between $CH_2{=}CH_2$ and $CH_2I{-}I$ proceeds easily, due to a very small barrier on the way to cyclopropane and I_2.

We also used B3LYP/6-311G** computations to examine the reaction of singlet carbene and ethylene to form cyclopropane as a benchmark system. The B3LYP/6-311G** calculated potential energy surface of the reaction of singlet $CH_2{:}$ with $CH_2{=}CH_2$ is downhill from the reactants to the cyclopropane product. This is in good agreement with conclusions from previous calculations that showed the energy along the reaction pathway from the $CH_2{=}CH_2$ and $CH_2{:}$ reactants to cyclopropane product decreases montonically without a barrier.[34,35] This leads us to expect that the B3LYP calculated barrier for the reaction of $CH_2I{-}I$ and $CH_2{=}CH_2$ to give cyclopropane and I_2 is reasonable.

B. Reaction of Iodomethyl Radical and Ethylene. Similar to $CH_2I{-}I$, the $\cdot CH_2I$ radical preferentially attacks one of the CH_2 groups of $CH_2{=}CH_2$ from above the molecular plane. However, the reaction of $\cdot CH_2I$ and $CH_2{=}CH_2$ to form cyclopropane and iodine atom is a two-step process, which is distinctly different from the one-step reaction between $CH_2I{-}I$ and $CH_2{=}CH_2$ described in the preceding section. The first step involves a transition state (referred to as TS2 in Figure 1) in which the C−C bond between $\cdot CH_2I$ and $CH_2{=}CH_2$ is partially formed with the $C_1{-}C_2$ separation of 2.328 Å at the B3LYP/sadlej-PVTZ level of theory. The $C_3{-}C_2{-}C_1$ angle in TS2 is about 107°, which suggests that cyclopropane is not formed from TS2 but instead leads to formation of an intermediate like $\cdot CH_2CH_2CH_2I$. The evidence for this comes from the IRC calculations. The optimized geometry of the intermediate (IM) is shown in Figure 1, together with selected key parameters from the 6-311G** and Sadlej-PVTZ calculations. The heavy atoms are in the same plane with the $C_3{-}C_2{-}C_1{-}I_1$ dihedral angle of 180.0°, while the six hydrogen atoms lie above and below the heavy-atom plane symmetrically. In fact, the intermediate has C_s symmetry, despite the initial-guess geometry with C_1 symmetry. An analogous situation takes places for the transition state of TS2, which also has C_s symmetry. As noted before and discussed further in this section, the 6-311G** calculated structural parameters are close to those found from Sadlej-PVTZ calculations.

There exist two possible pathways from the intermediate $\cdot CH_2CH_2CH_2I$ to cyclopropane and I atom products: first a sequential process where the C−I bond cleavage occurs followed by cyclopropanation and second a concerted process where the breaking of the C−I bond is accompanied by the cyclopropanation. A transition state, labeled TS3 in Figure 1, was found on the way from IM to the products. The reaction vector associated with the imaginary frequency ($525i$ cm^{-1}) of TS3 has been mainly identified as $0.52\ R_{I1-C1} - 0.57\ A_{C3-C2-C1}$. It is obvious that TS3 is the transition state, governing the direct reaction from $\cdot CH_2CH_2CH_2I$ to cyclopropane and I atom. To provide additional evidence for the two-step mechanism of the reaction from $\cdot CH_2I$ and $CH_2{=}CH_2$ to cyclopropane and I atom, the reaction of $\cdot CH_2Br$ and $CH_2{=}CH_2$ was also investigated at the B3LYP/6-31+G* level.[33] A similar two-step process was traced and confirmed by the IRC calculations at the UB3LYP level. All of these results provide strong evidence that the reaction of $\cdot CH_2I$ and $CH_2{=}CH_2$ to cyclopropane and I· atom proceeds via a two-step mechanism.

Figure 2b schematically shows the potential energy surface of the reaction of $\cdot CH_2I$ and $CH_2{=}CH_2$, obtained from the UB3LYP/Sadlej-PVTZ calculations with the UB3LYP/6-311G** zero-point energy correction included. The first step of the reaction has a barrier of 7.4 kcal/mol at the UB3LYP/6-311G** level. Increasing the size of the basis set to Sadlej-PVTZ, the barrier is reduced to 5.2 kcal/mol, as shown in Figure 2b. The barrier height for the second step of the reaction is 12.1 kcal/mol from the 6-311G** calculations, and this is increased to 13.5 kcal/mol upon changing the basis set from 6 to 311G** to Sadlej-PVTZ. Since the barrier of 5.2 kcal/mol on the first step is much lower than that on the second step, cyclopropanation from the intermediate is the rate-determining step of the reaction from $\cdot CH_2I + CH_2{=}CH_2$ to cyclopropane + I·.

---

(34) Zurawski, B.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1978**, *100*, 2654−2659.

(35) Sakai, S. *Int. J. Quantum Chem.* **1998**, *70*, 291−302.

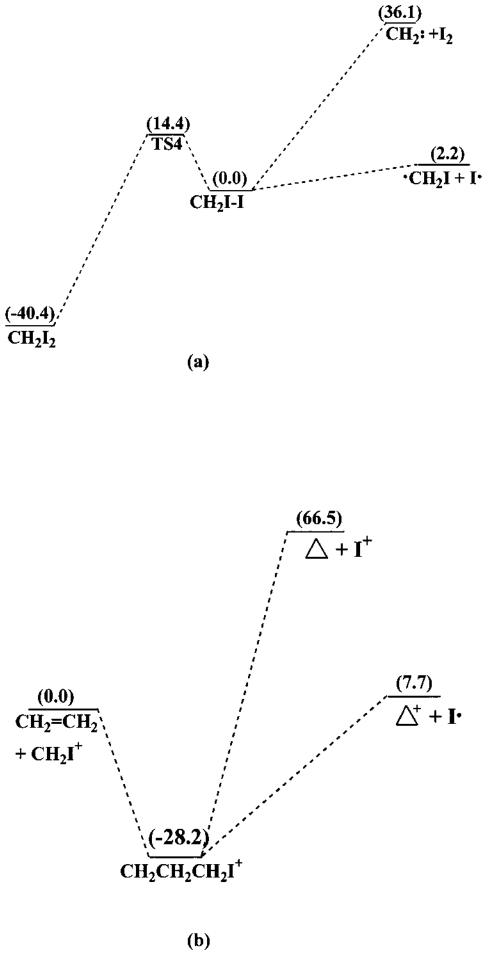

Figure 3. Schematic diagram showing the computed relative energies (in kcal/mol) for the reactants, transition state(s), intermediates, and reaction products for the dissociation reactions of $CH_2I{-}I$ (a) and CH_2I^+ with ethylene (b). All energies are from B3LYP computations except for the relative energies of the $CH_2{:} + I_2$ and $\cdot CH_2I + I\cdot$ products which were obtained from CASSCF (CAS(10,8)) calculations. See text for more details.

C. The Isomerization and Dissociation Reactions of $CH_2I{-}I$. Since $CH_2I{-}I$ is an energetic molecule, the isomerization or dissociation reactions of $CH_2I{-}I$ molecules may be in competition with the reaction of $CH_2I{-}I$ and $CH_2{=}CH_2$. The isomerization to the parent CH_2I_2 molecules has been theoretically investigated before.[36,37] The barrier was estimated to be 32.2 kcal/mol (134.6 kJ/mol) from the MP2/6-31G(d) calculations.[36] A transition state was found on the isomerization pathway to CH_2I_2, and the barrier height was calculated to be 14.4 kcal/mol at the B3LYP/Sadlej-PVTZ level of theory. This difference in the computed value for the barrier height for isomerization of $CH_2I{-}I$ for the MP2/6-31G(d) and B3LYP/Sadlej-PVTZ calculations is mainly a method effect since MP2 computations tend to overestimate barrier heights by about 5−10 kcal/mol, while the DFT calculations at the B3LYP level of theory tend to underestimate the barrier height by a few kcal/mol.[38,39] The potential energy profile for this reaction is shown in Figure 3a.

The dissociation pathways to $\cdot CH_2I + \cdot I$ and $CH_2{:} + I_2$ were optimized with the CAS(10,8) method. No potential barrier was found above endothermicity for the two dissociation reactions. The dissociation energies to $\cdot CH_2I + I\cdot$ and $CH_2{:} + I_2$ were estimated to be 2.2 and 36.1 kcal/mol, respectively, at the CAS(10,8) level. These values become 3.5 and 32.0 kcal/mol, respectively, using the CAS(14,10) calculations at the CAS(10,8) computed structures. The differences between the CAS(10,8) and CAS(14,10) results are moderate and suggest that the CAS(10,8) computations provide a reasonable estimate for the dissociation reactions.

D. Reaction of CH_2I^+ and Ethylene. We have previously noted that the charge distribution of the CH_2I part of the $CH_2I{-}I$ molecule is similar to that of CH_2I^+ which has been proposed to be the species that reacts with olefins in cyclopropanation reactions using ultraviolet photoexcitation of diiodomethane.[5,16] The B3LYP calculations show that the reaction of CH_2I^+ and $CH_2{=}CH_2$ takes place very easily, but does not generate cyclopropane. When the CH_2I^+ approaches $CH_2{=}CH_2$, a stable cation of $CH_2CH_2CH_2I^+$ is formed (shown in Figure 1). With respect to the system of $CH_2I^+ + CH_2{=}CH_2$, the $CH_2CH_2CH_2I^+$ cation has a stabilization energy of 28.2 kcal/mol. The $CH_2CH_2CH_2I^+$ cation can dissociate into cyclopropane and I^+ or into the cyclopropane cation and I·. Inspection of these reaction pathways in Figure 3b shows that there is very little possibility for either of these reactions to occur.

Discussion

We note that the B3LYP method tends to modestly underestimate reaction barrier heights. The intramolecular proton transfer in the ground state and in the lowest two triplet states of malonaldehyde was investigated using both B3LYP and CSSD(T) methods with a 6-311G** basis set.[38] This study found barrier heights of 3.0 kcal/mol in S_0, 4.3 kcal/mol in T_1, and 8.1 kcal/mol in T_2 at the B3LYP level of theory and barrier heights of 4.3 kcal/mol in S_0, 6.6 kcal/mol in T_1, and 12.2 kcal/mol in T_2 at the CSSD(T) level of theory. The dissociation reaction of CH_3CHO (T_1) to $CH_3(S_0) + HCO(S_0)$ was recently investigated by Schaefer and co-workers[39] using B3LYP and RCCSD methods and a TZ2PF basis set. They found values of 5468 and 6701 cm^{-1}, respectively, from the B3LYP/TZ2PF and RCCSD/TZ2PF computations for the vibrationless barrier height to dissociation (without the zero-point energy correction). Generally, the B3LYP calculations underestimate the barrier height by a few kcal/mol with respect to the CSSD(T) values.[38,39] We expect that our B3LYP computed barrier heights are likely accurate to within a few kcal/mol.

The reaction of the CH_2I^+ and $CH_2{=}CH_2$ is expected to proceed easily. However, our present calculations indicate that this reaction does not lead to formation of cyclopropane but to the $CH_2CH_2CH_2I^+$ cation. Ultraviolet photodissociation of diiodomethane in the presence of olefins in the solution was found to give cyclopropanated products with high stereospecificity.[2−5] Thus, the CH_2I^+ cation cannot be the photoproduct of the diiodomethane photodissociation that reacts with olefins to give cyclopropanated product, although CH_2I^+ has been proposed to be the species that reacts with olefins to give cyclopropanated products.[5]

Excitation of gas-phase diiodomethane with ultraviolet light (<5 eV) leads to a direct photodissociation reaction that gives a CH_2I radical and an iodine atom.[40−44] The $\cdot CH_2I$ photofragment receives substantial excitation of its internal degrees of

---

(36) Glukhovtsev, M. N.; Bach, R. D. *Chem. Phys. Lett.* **1997**, *269*, 145−150.

(37) Orel, A. E.; Kuhn, O. *Chem. Phys. Lett.* **1999**, *304*, 285−292.

(38) Barone, V.; Adamo, C. *J. Chem. Phys.* **1996**, *105*, 11007−11019.

(39) King, R. A.; Allen, W. D.; Schaefer, H. F., III. *J. Chem. Phys.* **2000**, *112*, 5585−5592.

(40) Kawasaki, M.; Lee, S. J.; Bersohn, R. *J. Chem. Phys.* **1975**, *63*, 809−814.

(41) Schmitt, G.; Comes, F. J. *J. Photochem.* **1980**, *14*, 107−123.

(42) Kroger, P. M.; Demou, P. C.; Riley, S. J. *J. Chem. Phys.* **1976**, *65*, 1823−1834.

freedom.[40−44] The $\cdot CH_2I$ radical may react with $CH_2{=}CH_2$ with high efficiency. As shown in Figure 2b, the reaction from $CH_2I + CH_2{=}CH_2$ to $C_3H_6 + I\cdot$ is a two-step process with a barrier of 13.5 kcal/mol for the second step that is the rate-determining step. This reaction pathway is not very likely to take place since the internal energy of the initially formed $\cdot CH_2I$ radical would be expected to be lost to the surrounding solvent molecules very quickly (probably on the order of tens of picoseconds). We note that collisional deactivation studies of $\cdot CH_2I$ by Baughcum and Leone[44] indicated that deactivation occurs in the range of 5−10 hardsphere collisions in CH_2I_2 to about 70−140 hardsphere collisions in Ar gas.[44] Similarly, recent ultrafast transient absorption[15] and time-resolved resonance Raman[45] studies showed that the initial vibrationally hot $CH_2I{-}I$ species formed from $\cdot CH_2I$ and $I\cdot$ recombination vibrationally cools in about 10−20 ps. In addition, very recent ultrafast transient absorption experiments done for CH_2I_2 following excitation of two quanta of the C−H stretch vibration by a 100 fs laser pulse found intramolecular vibrational relaxation of ∼10 ps and energy transfer to the solvent in the range of ∼20 to ∼70 ps.[46] These studies for the initially formed $\cdot CH_2I$ fragment and the related vibrationally excited $CH_2I{-}I$ and CH_2I_2 molecules suggest that $\cdot CH_2I$ is thermalized before undergoing reaction with olefins (like ethylene) and face the relatively large reaction barriers for each step of the reaction (see Figure 2b). Therefore, the $\cdot CH_2I$ produced from the ultraviolet photodissociation of diiodomethane is not likely the carbenoid species that reacts with olefins to give cyclopropanated products.

There appears to be no barrier for recombination of the initially formed $\cdot CH_2I$ and $I\cdot$ fragments in condensed phase environments and the $CH_2I{-}I$ molecule can be formed in noticeable quantities.[8,9,15,16,45] Both nanosecond[16] and picosecond[45] transient resonance Raman experiments demonstrated that the $CH_2I{-}I$ species was readily generated following ultraviolet photoexcitation of diiodomethane in room-temperature solutions using both nonpolar (cyclohexane) and polar (acetonitrile) solvents. Once the $CH_2I{-}I$ molecule is formed, it can readily undergo cyclopropanation reaction in the presence of $CH_2{=}CH_2$ in solution phase to give C_3H_6 and I_2 products via a single step with a low barrier to reaction (∼2.9 kcal/mol) (see Figure 2a). There is also additional evidence in the literature that indicates that isodiiodomethane does indeed react with olefins to give cyclopropanated products and an iodine molecule leaving group.[47] Brown and Simons[47] found that ultraviolet excitation of diiodomethane and other polyhalomethanes produced "color centers" that exhibited characteristic intense transient absorption bands in the 350−470 nm region (∼385 nm for the diiodomethane photoproduct) in 77 K frozen hydrocarbons. When trace amounts of olefins were added and the 77 K matrix sample was allowed to warm, new transient absorption bands ∼310−320 nm appeared with clean isobestic points between the "color center" transient absorption bands and the new ∼310−320 nm absorption bands (see Figures 4 and 5 in ref 46). These new ∼310−320 nm transient absorption bands were convincingly assigned to halogen molecule−olefin species (like I_2−olefin and Br_2−olefin species), and the new transient absorption bands do not appear in the absence of the olefins.[47] Ultraviolet photoexcitation of polybromomethanes in the absence of olefins gave no discernible Br_2 product.[47] We have recently shown that these intense "color center" transient absorption bands produced following ultraviolet excitation of polyhalomethanes in the condensed phase are really associated with the isopolyhalomethane species[16,32,48−50] including isodiiodomethane,[16,45] isodibromomethane,[50] and isobromoform.[33] These experimental results[47] combined with our recent transient resonance Raman studies[16,45] and our present density functional theory investigation lead us to conclude that the isodiiodomethane species is the methylene transfer agent in cyclopropanation of olefins via ultraviolet excitation of diiodomethane in room-temperature solutions. The following reaction scheme is consistent with the experimental and theoretical observation of intermediates observed following photolysis of diiodomethane in the condensed phase.

initiation step

$$CH_2I_2 + h\nu \rightarrow \cdot CH_2I + I\cdot \tag{1}$$

recombination to produce isomer

$$\cdot CH_2I + I\cdot \rightarrow CH_2I{-}I \tag{2}$$

reaction of $CH_2I{-}I$ with olefin

$$CH_2I{-}I + \text{olefin} \rightarrow \text{cyclopropanated product} + I_2 \tag{3}$$

formation of X_2−olefin complex

$$X_2 + \text{olefin} \Leftrightarrow X_2{-}\text{olefin complex} \tag{4}$$

Several types of experiments[15,16,45] clearly show the initially formed $\cdot CH_2I$ and $I\cdot$ fragments in step 1 can recombine within a few picoseconds to give the $CH_2I{-}I$ photoproduct that has the characteristic intense ∼385 nm transient absorption band in step 2. Both our present density functional theory computations and the experimental results of Brown and Simons[47] indicate that the $CH_2I{-}I$ species readily reacts with olefins to give cyclopropanated product and iodine molecule as in step (3). Halogen molecules are known to readily react with olefins to form halogen molecule−olefin complexes as in step 4 for the I_2−olefin complex.[51−54]

There are several reports that both ultraviolet excitation of either diiodomethane or dibromomethane in the presence of olefins give cyclopropanated products.[2,55,56] This and observation of a number of isomers of polyhalomethanes formed after ultraviolet photoexcitation in room-temperature solutions[15,16,33,45,48−50] (including $CH_2I{-}I$ and $CH_2Br{-}Br$) and our present DFT computational results suggest that a number of isopolyhalomethane species may exhibit carbenoid behavior with varying chemical reactivity toward olefins. Further experimental and theoretical work is needed to better elucidate the chemical reactivity of these interesting isopolyhalomethane species.

---

(43) Baughcum, S. L.; Hafmann, H.; Leone, S. R.; Nesbitt, D. *J. Faraday Discuss. Chem. Soc.* **1979**, *67*, 306−315.

(44) Baughcum, S. L.; Leone, S. R. *J. Chem. Phys.* **1980**, *72*, 6531−6545.

(45) Kwok, W. M.; Ma, C.; Parker, A. W.; Phillips, D.; Towrie, M.; Matousek, P.; Phillips, D. L. *J. Chem. Phys.* **2000**, *113*, 7471−7478.

(46) Bingemann, D.; King, A. M.; Crim, F. F. *J. Chem. Phys.* **2000**, *113*, 5018−5025.

(47) Brown, G. P.; Simons, J. P. *Trans. Faraday Soc.* **1969**, *65*, 3245−3257.

(48) Zheng, X.; Phillips, D. L. *Chem. Phys. Lett.* **2000**, *324*, 175−182.

(49) Zheng, X.; Phillips, D. L. *J. Chem. Phys.* **2000**, *113*, 3194−3203.

(50) Zheng, X.; Kwok, W. M.; Phillips, D. L. *J. Phys. Chem. A* **2000**, *104*, 10464−10470.

(51) Ayres, R. L.; Michejda, C. J.; Pack, E. P. *J. Am. Chem. Soc.* **1971**, *93*, 1389−1394.

(52) Prissette, J.; Seger, G.; Kochanski, E. *J. Am. Chem. Soc.* **1978**, *100*, 6941−6947.

(53) Bellucci, G.; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1985**, *107*, 2464−2471.

(54) Bellucci, G.; Chiappe, C.; Bianchini, R.; Lenoir, D.; Herges, R. *J. Am. Chem. Soc.* **1995**, *117*, 12001−12002.

(55) Neuman, R. C., Jr.; Wolcott, R. G. *Tetrahedron Lett.* **1966**, 6267−6272.

(56) Marolewski, T.; Yang, C. N. *J. Chem. Soc., Chem. Commun.* **1967**, 1225−1226.

If singlet CH_2: radicals exist in solution containing $CH_2{=}CH_2$, the reaction between the CH_2: radical and $CH_2{=}CH_2$ could be the dominant channel for formation of C_3H_6. As pointed out before, the dissociation of $CH_2I{-}I$ to CH_2: + I_2 is endothermic by 36.1 kcal/mol. This clearly shows that the singlet CH_2: radical cannot be formed through the $CH_2I{-}I$ dissociation. Although it is energetically feasible to produce CH_2: and I_2 by diiodomethane photodissociation at wavelengths below 330 nm, this process is symmetry-forbidden for the ultraviolet transition.[57,58] If photons with high energies (>6.4 eV) are used for excitation of diiodomethane, CH_2I_2 can undergo unimolecular detachment to CH_2: and I_2, but still a minor channel compared with the $\cdot CH_2I + I$ channel.[59,60] Therefore, there is little possibility that the singlet CH_2: radical will be formed using ultraviolet CH_2I_2 photodissociation, and the singlet CH_2: radical is not the species that acts as a reagent of cyclopropanation of olefins via ultraviolet excitation of diiodomethane. This conclusion is in good agreement with previous experimental evidence that showed a lack of C−H insertion products and a high degree of selectivity for addition to more highly substituted alkenes.[2−5]

It is interesting that $CH_2I{-}I$ reacts with both a lower barrier to reaction and via a single reaction step in a direct manner (like an elementary reaction step) with ethylene to give cyclopropane and an iodine molecule. This is substantially different from the reaction of either $\cdot CH_2I$ or CH_2I^+ with ethylene which require two reaction steps with both steps having much larger barriers to overcome. The $\cdot CH_2I$ and CH_2I^+ species both form relatively stable iodopropyl radical and iodopropyl cation intermediates, respectively, while $CH_2I{-}I$ does not. This appears to be an important reason for the effectiveness of the $CH_2I{-}I$ species as a methylene transfer agent. The $CH_2I{-}I$ reaction with ethylene also gives a stable iodine molecule product while the $\cdot CH_2I$ and CH_2I^+ reactions with ethylene give either an iodine atom or iodine cation product. This suggests that the leaving group from the cyclopropanation reaction may also be important to having an effective species for cyclopropanation reaction with olefins.

The Simmons−Smith reaction[1] uses a Zn(Cu) couple to activate diiodomethane to react with olefins to give cyclopropanation products. The Simmons−Smith chemical reaction has been noted to have a different reactivity toward olefins than the photochemical reaction of diiodomethane in the presence of olefins.[2−5] For example, the photochemical reaction of diiodomethane (via the $CH_2I{-}I$ species) reacts with limonene more rapidly at the more highly substituted cyclohexenyl double bond, while the Simmons−Smith chemical reaction using the Zn−Cu couple reacts more rapidly at the less highly substituted isopropenyl double bond.[4,5] This suggests that the methylene transfer agent in the Simmons−Smith chemical reaction is distinctly different from the isodiiodomethane species that reacts with olefins in the photocyclopropanation reaction using ultraviolet excitation of diiodomethane. Thus, the Simmons−Smith chemical reaction probably occurs via a carbenoid that is similar yet distinct from the $CH_2I{-}I$ carbenoid found for the photochemical cyclopropanation reaction. It is interesting to note that the Simmons−Smith reaction has a molecular leaving group (ZnI_2) similar to the I_2 leaving group found for the photocyclopropanation reaction (via the $CH_2I{-}I$ carbenoid).

Acknowledgment. This work was supported by grants from the Committee on Research and Conference Grants (CRCG), the Research Grants Council (RGC) of Hong Kong, the Hung Hing Ying Physical Sciences Research Fund, and the Large Items of Equipment Allocation 1993−94 from the University of Hong Kong.

Supporting Information Available: Selected output from the density functional theory computations for the reactions of $CH_2I{-}I$, $\cdot CH_2I$, and CH_2I^+ species with ethylene (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA003090G

---

(57) Koffend, J. B.; Leone, S. R. *Chem. Phys. Lett.* **1981**, *81*, 136−141.

(58) Cain, S. R.; Hoffman, R.; Grant, R. *J. Phys. Chem.* **1981**, *85*, 4046−4051.

(59) Marvet, U.; Dantus, M. *Chem. Phys. Lett.* **1996**, *256*, 57−62.

(60) Zhang, Q.; Marvet, U.; Dantus, M. *J. Chem. Phys.* **1998**, *109*, 4428−4442.