

Time-Resolved Resonance Raman and Density Functional Theory Investigation of Iodocyclopropanation and Addition Reactions with Alkenes after Ultraviolet Photolysis of Iodoform

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A time-resolved resonance Raman spectroscopic investigation is reported for the ultraviolet photolysis of CHI₃ in pure cyclohexane and mixed cyclohexane/cyclohexene solvents. The ICHI–I species is observed in pure cyclohexane solvent. Upon addition of cyclohexene, the ICHI–I species lifetime is reduced and new bands from an I₂:cyclohexene complex are observed. Density functional theory computations show that ICHI–I and CHI₂ species have similar barriers of reaction toward addition to the C=C of ethylene. The addition reaction of ICHI–I with ethylene results in formation of an iodocyclopropane and I₂ molecule while addition of ·CHI₂ results in initial formation of a diiodopropyl radical intermediate. Ultraviolet photolysis of CHI₃ in the presence of cyclohexene is known to produce a reasonable yield of iodonorcarane product and some addition reaction products. We present a mechanism for the iodocyclopropanation reaction that is consistent with both experimental and theoretical characterization of reaction intermediates formed after ultraviolet photolysis of CHI₃. We briefly discuss the concentration dependence of the time-resolved resonance Raman spectra and photochemistry in relation to the competition between the reaction of the ICHI–I and CHI₂ species with the C=C bond of olefins.

Introduction

Polyhalomethanes have long been used as reagents for addition reactions^{1,2} (such as “Kharasch addition”) and for cyclopropanation reactions^{3–19} with olefins. Polyhalomethanes are also of interest in atmospheric chemistry

because they are important sources of reactive halogens released into both the troposphere and stratosphere.^{20–27} Ultraviolet photolysis of diiodomethane in the presence of olefins leads to production of cyclopropanated products with high stereospecificity.^{5,12,14,15} The lack of C–H insertion reaction and the high stereospecificity of the diiodomethane photocyclopropanation reaction indicate the carbenoid species is not a free carbene. Ultraviolet photolysis of iodoform (CHI₃) in the presence of cyclohexene has been reported to produce noticeable amounts of the iodonorcarane product as well as addition reaction products.^{6,7} Ultraviolet photolysis of several other polyhalomethanes (such as CHBr₂, CHClBr₂, CHBr₃, and CHBr₂) in the presence of cyclohexene was also observed to produce some halonorcarane products.^{6,7}

We have recently used time-resolved resonance Raman spectroscopy to probe the identity and structures of intermediates produced following ultraviolet photolysis of polyhalomethanes in room temperature solutions and observed in a number of cases that isopolyhalomethane photoproducts were produced.^{28–36} Density functional

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theory calculations were used to examine the chemical reactivity of isodiiodomethane ($\text{CH}_2\text{I}-\text{I}$), $\cdot\text{CH}_2\text{I}$, and the CH_2I^+ cation species toward olefins.³⁷ This work showed that $\text{CH}_2\text{I}-\text{I}$ easily reacts with ethylene to form a cyclopropane product and iodine molecule leaving group via a one-step reaction with a barrier height of only ~ 2.9 kcal/mol while the $\cdot\text{CH}_2\text{I}$ radical and CH_2I^+ cation species were found to react with ethylene via a two-step reaction mechanism with a significantly larger barrier to form a cyclopropane product.³⁷ A time-resolved resonance Raman study of CH_2I_2 photolysis in cyclohexene solution found that $\text{CH}_2\text{I}-\text{I}$ is formed and subsequently reacts with cyclohexene on the 5–10 ns time scale and then almost immediately forms an I_2 :cyclohexene complex from the I_2 leaving group of the reaction.³⁸ These experimental results in conjunction with the density functional theory computational results indicate that the $\text{CH}_2\text{I}-\text{I}$ is the methylene-transfer agent mainly responsible for the photocyclopropanation of olefins following ultraviolet photolysis of CH_2I_2 .^{37,38} We presented a reaction mechanism for photocyclopropanation that is consistent with both experimental and theoretical characterization of reaction intermediates and products produced after ultraviolet photolysis of CH_2I_2 in condensed-phase environments. Comparison of the structures and properties of the $\text{CH}_2\text{I}-\text{I}$ species with the ICH_2ZnI Simmons–Smith carbenoid species suggested that their different structures and modes of activation of the methylene carbon could account for their different chemical reactivities toward olefins.^{39,40}

In this paper we present a time-resolved resonance Raman spectroscopic study of ultraviolet photolysis of CHI_3 in the presence and absence of cyclohexene. A density functional theory investigation of the reactions of CHI_2 radicals and $\text{ICH}_2\text{I}-\text{I}$ with ethylene is also given. We find a noticeable amount of $\text{ICH}_2\text{I}-\text{I}$ (with a half-life on the order of 500 ns) is formed in pure cyclohexane. When a small amount of cyclohexene is added to cyclohexane solvent, the $\text{ICH}_2\text{I}-\text{I}$ Raman bands become smaller and have a much shorter lifetime and new bands due to an I_2 :cyclohexene complex appear. This indicates that $\text{ICH}_2\text{I}-\text{I}$ reacts with cyclohexene to form an I_2 leaving group that readily forms the observed I_2 :cyclohexene complex. However, photolysis of CHI_3 in pure cyclohexene results in no observable $\text{ICH}_2\text{I}-\text{I}$ bands and mainly bands due to the I_2 :cyclohexene complex. Density functional theory calculations indicate that additions of $\text{ICH}_2\text{I}-\text{I}$ isomer and CHI_2 radicals to ethylene have very similar barriers to

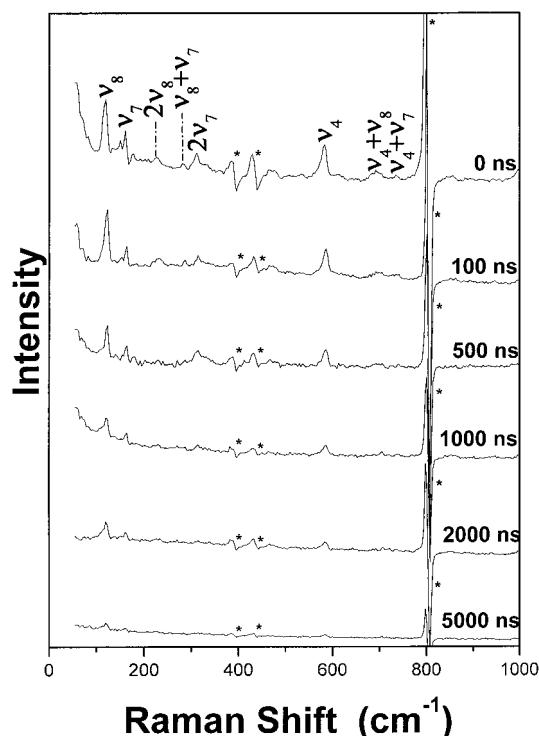


Figure 1. Time-resolved resonance Raman (TR^3) spectra of $\text{ICH}_2\text{I}-\text{I}$ obtained in cyclohexane solution using 266 nm pump and 341.5 nm probe wavelengths. The time delay between the pump and probe beams is indicated to the right of each spectrum. Some of the larger Raman bands are labeled with their assignments (ν_8 , ν_7 , $2\nu_8$, $\nu_8 + \nu_7$, $2\nu_7$, ν_4 , $\nu_4 + \nu_8$, and $\nu_4 + \nu_7$). The text and ref 28 provide more details of the vibrational assignments for $\text{ICH}_2\text{I}-\text{I}$. Asterisks label places where solvent or parent Raman band subtraction artifacts are present. Crosses label stray light or ambient light artifacts.

reactions (about 8–10 kcal/mol), and this suggests they compete effectively with one another for reaction with the carbon double bond of olefins. This is consistent with our present time-resolved spectroscopy experiments and previously reported photochemistry results for iodoform.^{6,7} We discuss the reaction mechanisms for addition reactions to olefins following ultraviolet photolysis of CHI_3 and present a mechanism for iodocyclopropanation consistent with both experimental and computational examination of reaction intermediates produced after ultraviolet photolysis of CHI_3 .

Results and Discussion

Figure 1 shows time-resolved resonance Raman spectra of the $\text{ICH}_2\text{I}-\text{I}$ species in cyclohexane solvent (using 266 nm pump and 341.5 nm probe excitation wavelengths). The spectra in Figure 1 are similar to those reported previously for transient resonance Raman spectra of $\text{ICH}_2\text{I}-\text{I}$.²⁸ The larger $\text{ICH}_2\text{I}-\text{I}$ bands include the nominal I–I stretch mode (ν_8) at ~ 117 cm^{-1} , the nominal C–I–I bend mode (ν_7) at ~ 144 cm^{-1} , and the nominal CH wag (ν_4) at ~ 579 cm^{-1} . The reader is referred to ref 28 for details of the assignment of the Raman vibrational bands to the $\text{ICH}_2\text{I}-\text{I}$ species. B3LYP/6311G** calculations found the HOMO of $\text{ICH}_2\text{I}-\text{I}$ to be $0.42[2p_x(\text{C})] - 0.32[5p_y(\text{I}_2)] - 0.16[5s(\text{I}_3)] - 0.13[5p_x(\text{I}_3)] - 0.44[5p_x(\text{I}_4)] + 0.21[5p_y(\text{I}_4)] + 0.50[5p_z(\text{I}_4)]$ (where I2 and I3 are the I atoms attached to the C atom and I4 is attached

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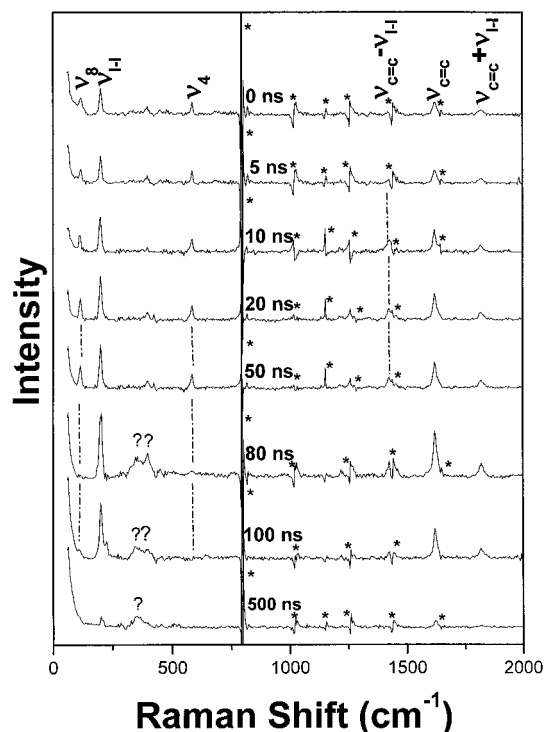


Figure 2. TR³ spectra of ICHI-I and I₂:cyclohexene complexes obtained in cyclohexane/cyclohexene solution (5% cyclohexene by volume) using 266 nm pump and 319.9 nm probe wavelengths. The time delay between the pump and probe beams is indicated to the right of each spectrum. Some of the larger Raman bands are labeled with their assignments (ν_8 and ν_4 for ICHI-I; ν_{I-I} , $\nu_{C=C} - \nu_{I-I}$, $\nu_{C=C}$, and $\nu_{C=C} + \nu_{I-I}$ for the I₂:cyclohexene complex). Asterisks label places where solvent or parent Raman band subtraction artifacts are present. Crosses label stray light or ambient light artifacts. Question marks label Raman bands that appear in the 80, 100, and 500 ns spectra and that are due to a long-lived unidentified photoproduct species.

to I3). The carbon atom has hybridization with the three I atoms, where the C atom appears similar to sp² and the weak I-I bond is similar to a 3-electron-2-center bond. Examination of Figure 1 reveals that the ICHI-I species has a half-life of about 500 ns to 1 μ s. The lifetime of ICHI-I is significantly longer than that found for the closely related CH₂I-I molecule, which had a half-life of \sim 20 ns and a small signal in its 80 ns spectrum.³⁸ This indicates that the ICHI-I species is noticeably more stable than the CH₂I-I species in room temperature cyclohexane solutions. This could possibly be due to a larger barrier for isomerization back to the parent CHI₃ molecule and/or greater stabilization of ICHI-I by the solvent compared to CH₂I-I.

Time-resolved 319.9 nm resonance Raman spectra were obtained after 266 nm photolysis of CHI₃ in cyclohexane solvent with various concentrations of cyclohexene reactant (1.3%, 5%, 25%, and 100 % by volume, respectively) added to the solvent. Figures 2 and 3 show the spectra obtained using 5% and 25% cyclohexene in cyclohexane solvent, respectively. Figures S-1 and S-2 in the Supporting Information show spectra obtained using 1.3% and 100% cyclohexene. In the presence of cyclohexene reactant, a new species is formed on the nanosecond time scale, with its larger bands at \sim 200, \sim 395, \sim 1625, \sim 1425, and \sim 1825 cm⁻¹ attributed to formation of an I₂:cyclohexene complex. Resonance Raman spectra of sev-

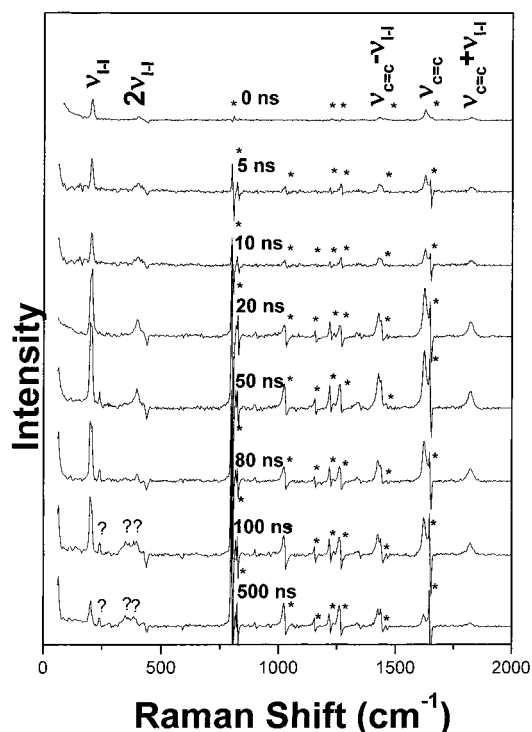


Figure 3. TR³ spectra of I₂:cyclohexene complexes obtained in cyclohexane/cyclohexene solution (25% cyclohexene by volume) using 266 nm pump and 319.9 nm probe wavelengths. The time delay between the pump and probe beams is indicated to the right of each spectrum. The larger Raman bands are labeled with their assignments as in Figure 2. Asterisks label places where solvent or parent Raman band subtraction artifacts are present. Crosses label stray light or ambient light artifacts. Question marks label Raman bands that appear in the 100 and 500 ns spectra and that are due to a long-lived unidentified photoproduct.

eral I₂:alkene complexes showed these spectra characteristically have most of their Raman intensity in the overtones and combination bands of the nominal I-I stretch mode (fundamental \sim 200 cm⁻¹) and the nominal C=C stretch mode (fundamental \sim 1625 cm⁻¹).⁴¹ The I-I stretch mode forms distinct difference and combination bands with the nominal C=C stretch mode, and this indicates the resonance Raman spectra are due to the I₂:alkene complex and not their separated species.⁴¹ Thus, the new resonance Raman bands observed when cyclohexene reactant is present are assigned to the I₂:cyclohexene complex as follows: the fundamental of the nominal I-I stretch to the band at \sim 200 cm⁻¹, the first overtone of the I-I stretch to the band at \sim 395 cm⁻¹, the nominal C=C stretch fundamental to the band at \sim 1625 cm⁻¹, the difference band and combination band of the C=C stretch and I-I stretch to the bands at \sim 1425 and \sim 1825 cm⁻¹, respectively.

Inspection of Figure 2 shows that Raman bands for both the ICHI-I and I₂:cyclohexene complex species appear with the ICHI-I bands noticeably decreasing in intensity between 50 and 100 ns and the I₂:cyclohexene bands increasing in intensity between 0 and 100 ns and then decreasing to very little intensity in the 500 ns spectrum. The Raman bands in the 500 ns spectrum appear to be due mainly to a longer lived photoproduct

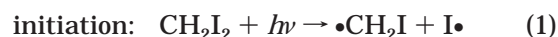
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species and not the ICHI–I or I₂:cyclohexene intermediates. There is some correlation between the decrease of the ICHI–I bands and the increase in the I₂:cyclohexene bands. This and the much shorter lifetime of ICHI–I in the presence of cyclohexene suggest that ICHI–I reacts with cyclohexene to produce an I₂ leaving group that can readily complex with other cyclohexene molecules. Similar spectra were found in the 1.3% cyclohexene in cyclohexane solvent (see Figure S-1). When the cyclohexene reactant concentration is increased to 25% (see Figure 3), no Raman bands of ICHI–I are observed and the I₂:cyclohexene complex Raman bands appear at early times and grow in intensity up to about 50 ns time delay and then decrease somewhat between 50 and 500 ns, with some new product bands appearing in the 100 and 500 ns spectra. When the CHI₃ photolysis is done in pure cyclohexene solvent (see Figure S-2), the I₂:cyclohexene complex resonance Raman bands appear very fast (within 5 ns) and noticeably start to decay from 80 to 500 ns. We note the temporal behavior of the $\sim 1425\text{ cm}^{-1}$ difference Raman band relative to the $\sim 1825\text{ cm}^{-1}$ combination band could potentially reveal something about the temperature or vibrational excitation of the I₂:cyclohexene complex formed from reaction of ICHI–I with cyclohexene, but the solvent subtraction in this region makes it difficult to unambiguously comment on this from the present spectra.

It is interesting to compare the time-resolved resonance Raman spectra for CH₂I₂ in cyclohexene solvent³⁸ with those presented here for CHI₃ in cyclohexene solvent. Raman bands for the CH₂I–I species were easily observed in time-resolved resonance Raman spectra after photolysis of CH₂I₂ in pure cyclohexene solvent, and these bands decreased in intensity as the I₂:cyclohexene complex Raman bands increased in intensity.³⁸ However, photolysis of CHI₃ in pure cyclohexene solvent only leads to fast formation of I₂:cyclohexene complex Raman bands and no noticeable intensity in ICHI–I Raman bands (see Figure S-2). However, ICHI–I Raman bands do become apparent at low concentrations of cyclohexene (1.3% and 5% by volume) in cyclohexane solvent (see Figures 2 and S-1). These results suggest that ICHI–I is not easily formed in high concentrations of cyclohexene but can be formed fairly well at low concentrations of cyclohexene in cyclohexane solvent while CH₂I–I can be easily formed at high concentrations of cyclohexene. To better understand this difference in behavior for the photolysis of CHI₃ and CH₂I₂ in the presence of cyclohexene reactant, it is useful to examine the initial photochemistry of CHI₃ and CH₂I₂.

Ultraviolet photolysis of CHI₃ in both gas⁴² and solution^{43,44} phases appears to mainly lead to direct C–I bond cleavage to produce $\cdot\text{CHI}_2$ and I atom fragments. Similarly, ultraviolet photolysis of CH₂I₂ in both gas^{42,45–53} and

solution^{54–56} phases results in direct C–I bond cleavage to form $\cdot\text{CH}_2\text{I}$ and I atom fragments. Time-of-flight photofragment spectroscopy experiments^{46,51} and IR emission experiments^{52,53} indicate the $\cdot\text{CH}_2\text{I}$ fragment is formed with a good deal of internal excitation of its vibrational and rotational degrees of freedom. Solution-phase femtosecond time-resolved absorption spectroscopy studies demonstrated that the C–I bond cleavage occurs within several hundred femtoseconds and some geminate recombination of the photofragments occurs on the 500 fs to 1 ps time scale.^{54–56} Picosecond time-resolved resonance Raman spectroscopy demonstrated that this solvent-induced recombination of the $\cdot\text{CH}_2\text{I}$ and I atom fragments leads to appreciable formation of vibrationally hot CH₂I–I isomer photoproduct molecules within several picoseconds after photolysis.³³ Thus, the mechanism of formation of the CH₂I–I isomer photoproduct molecules is the following two steps:



recombination to produce isomer:



We expect that the ICHI–I molecules observed in our nanosecond time-resolved resonance Raman experiments in cyclohexane and mixed cyclohexane/cyclohexene solvents are also formed mostly via geminate recombination of the $\cdot\text{CHI}_2$ and I atom fragments within the solvent cage similar to the analogous isomer of diiodomethane (CH₂I–I).

We explored the chemical reactivity of the CH₂I–I isomer molecule using density functional theory calculations and found that it readily reacts with ethylene to form a cyclopropane and iodine molecule products via a one-step reaction with a computed barrier height of only $\sim 2.9\text{ kcal/mol}$.³⁷ However, the $\cdot\text{CH}_2\text{I}$ with ethylene reaction occurred via a two-step mechanism that first formed a relatively stable iodopropyl radical intermediate in the first step (barrier computed to be $\sim 5.2\text{ kcal/mol}$) that then had a larger barrier ($\sim 13.5\text{ kcal/mol}$) to react and produce cyclopropane and iodine atom products.³⁷ Recent nanosecond time-resolved resonance Raman experiments showed that the CH₂I–I species reacts with cyclohexene to give an iodine molecule leaving group on the 5–10 ns time scale that almost immediately forms an I₂:cyclohexene complex.³⁸ This combined with the density functional theory results^{37,38} (and the fact that norcaradiene, the cyclopropanated product of cyclohexene, is the principle product^{5,12,15} produced after photolysis of diiodomethane in cyclohexene solution) indicates the CH₂I–I species is the methylene-transfer agent mainly responsible for cyclopropanation of olefins involving ultraviolet photolysis of diiodomethane. The key reaction

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step for the $\text{CH}_2\text{I}-\text{I}$ cyclopropanation process is given below:

reaction of $\text{CH}_2\text{I}-\text{I}$ with olefin:



In the presence of olefins, the I_2 leaving group may then easily form an I_2 :olefin complex as shown below in reaction 4 that can be readily observed in time-resolved resonance Raman experiments as shown in previous work on CH_2I_2 ³⁸ and our present work on CHI_3 .

formation of I_2 :olefin complex:



Density functional theory calculations were done to explore the chemical reactivity of $\text{ICHI}-\text{I}$ and $\cdot\text{CHI}_2$ with ethylene to form iodocyclopropane product and an I_2 or I leaving group, respectively. Previous investigations on similar isomers of polyhalomethanes and halomethyl radicals with ethylene showed that the optimized geometries and barriers to reaction did not change very much between using the 6-311G** and Sadlej-pVTZ basis sets.³⁷ The calculations involving three I atoms are more computationally demanding than those for two I atoms so we have only performed the calculations with the 6-311G** basis set for the reactions of $\text{ICHI}-\text{I}$ with ethylene reported here. Figure 4 shows the optimized geometry for selected reactants, transition state(s), intermediates, and products for the reactions of $\text{ICHI}-\text{I}$ and CHI_2 radical with ethylene to form an iodocyclopropane product. Figure 5 depicts a schematic diagram showing the calculated relative energies (kcal/mol) for the reactants, transition state(s), intermediates, and products for the reactions of $\text{ICHI}-\text{I}$ (top) and $\cdot\text{CHI}_2$ (bottom) with ethylene to form an iodocyclopropane product. The $\text{ICHI}-\text{I}$ molecule approaches the $\text{CH}_2=\text{CH}_2$ molecule asymmetrically and preferentially attacking one of the CH_2 groups from above the molecular plane in a manner similar to that of the isomer $\text{CH}_2\text{X}-\text{X}$ (where $\text{X} = \text{I}, \text{Br},$ or Cl) reactions with ethylene.^{37,39} A transition state (TS1) was found on the way to the products iodocyclopropane and I_2 . The barrier to reaction was found to be 10.3 kcal/mol at the B3LYP/6-311G** level of theory. $\cdot\text{CHI}_2$ also reacts with ethylene via an asymmetric attack on one of the CH_2 groups similar to the $\text{ICHI}-\text{I}$ species. But its reaction to iodocyclopropane product proceeds by a two-step reaction mechanism where the first step leads to formation of a diiodopropyl radical intermediate followed by a second step to produce an iodocyclopropane product and an I atom leaving group. The barriers to reaction for the first and second steps were found to be ~ 8.5 and ~ 16.4 kcal/mol, respectively, at the B3LYP/6-311G** level of theory.

It is interesting that the barrier for reaction of the $\text{ICHI}-\text{I}$ species with ethylene (~ 10.3 kcal/mol) is only moderately different from that found for the addition reaction of the CHI_2 radical with ethylene (~ 8.5 kcal/mol) to make a diiodopropyl radical intermediate. This suggests that the $\text{ICHI}-\text{I}$ and CHI_2 species compete effectively with one another to react with the $\text{C}=\text{C}$ bond in olefins. At low olefin concentrations one could expect the initially formed CHI_2 radical and I atom fragments would mostly collide with solvent molecules and produce noticeable amounts of $\text{ICHI}-\text{I}$ or parent CHI_3 via gemi-

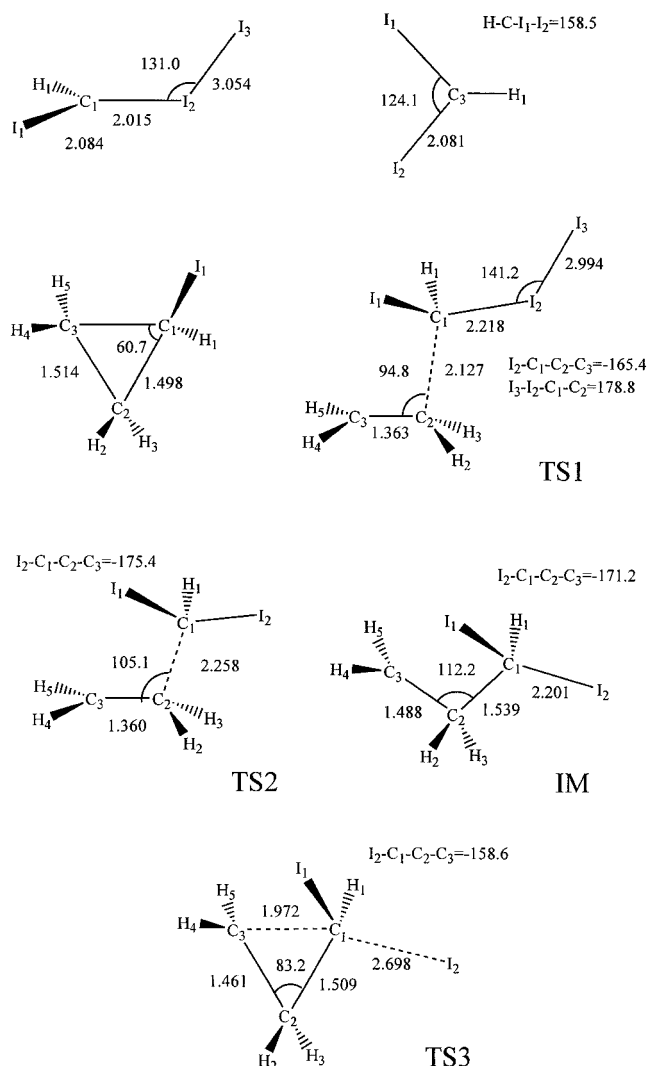


Figure 4. Schematic diagrams of the optimized geometry for selected reactants, transition state(s), and reaction products for the reactions of the $\text{ICHI}-\text{I}$ and CHI_2 radical with ethylene. The numbers present selected key structural parameters from the B3LYP/6-311G** density functional theory calculations (bond lengths in angstroms and bond angles in degrees) for the species shown ($\text{ICHI}-\text{I}$, TS1, iodocyclopropane, CHI_2 radical, TS2, IM (intermediate), and TS3).

nate recombination. This is consistent with the experimental observation of $\text{ICHI}-\text{I}$ in our nanosecond time-resolved resonance Raman spectra obtained in pure cyclohexane solvent (see Figure 1) and in the presence of low concentrations of cyclohexene (see Figure 2 where cyclohexene is present at 5% by volume). The density functional theory calculations indicate that $\cdot\text{CHI}_2$ reacts somewhat more easily than $\text{ICHI}-\text{I}$ with olefins. At high concentrations of cyclohexene, the initially formed $\cdot\text{CHI}_2$ fragment from CHI_3 photolysis would have a greater chance to directly react with cyclohexene before being able to form some $\text{ICHI}-\text{I}$ via geminate recombination. This would likely increase the relative amount of CHI_2 radical addition products compared to the cyclopropanated product formed from reaction of the $\text{ICHI}-\text{I}$ with the olefin. When more CHI_2 radicals directly add to the $\text{C}=\text{C}$ bond of cyclohexene, there will be more free I atoms that will be able to diffuse and form I_2 that then quickly forms an equilibrium with I_2 :cyclohexene complexes. This

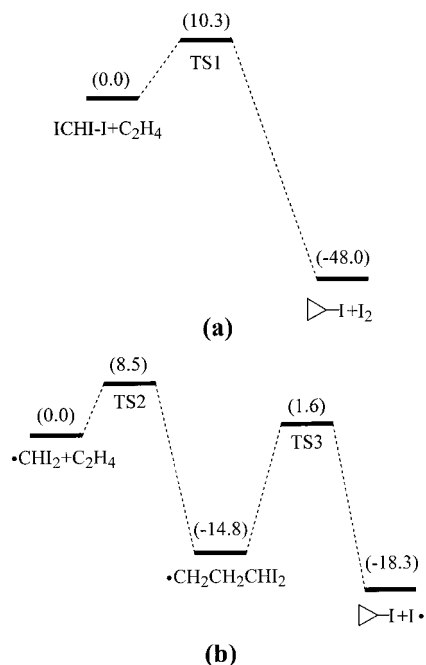
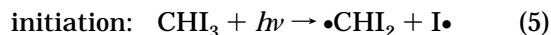


Figure 5. Schematic diagram showing the computed relative energies (kcal/mol) for the reactants, transition state(s), intermediates, and reaction products for the reactions of ICHI-I with ethylene (a) and CHI₂ with ethylene (b). All energies are from the B3LYP/6-311G** computations.

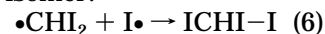
is consistent with our time-resolved resonance Raman experiments at higher concentrations of cyclohexene (25% and 100% by volume) shown in Figures 3 and S-2 that show almost no ICHI-I bands and mostly I₂:cyclohexene complex Raman bands. The hypothesis that there is more •CHI₂ addition product formation at high olefin concentrations and more iodocyclopropanation products at low olefin concentrations is also consistent with some synthetic literature results. For example, Yang and Marolewski⁷ found that higher concentrations of CHI₃ and 1,3-butadiene (8 and 17 g, respectively, in 300 mL of CH₂Cl₂ solvent) gave a lower yield of ~33% of the iodocyclopropanated product compared to the higher yield of ~61% for lower concentrations of CHI₃ and 1,3-butadiene (1 and 11 g, respectively, in 200 mL of CH₂Cl₂ solvent). Similarly, higher concentrations of CHI₃ and cyclohexene (8 and 4.1 g, respectively, in 100 mL of CH₂Cl₂ solvent) gave a lower yield of ~70% of the iodocyclopropanated product compared to the higher yield of ~86% for lower concentrations of CHI₃ and cyclohexene (2 and 0.82 g, respectively, in 50 mL of CH₂Cl₂ solvent). The competition between the ICHI-I and CHI₂ species to react with the C=C bond can account for both the concentration dependence of the time-resolved resonance Raman spectra for the intermediates of ICHI-I and/or I₂:cyclohexene complex and the yield of iodonorcarane product produced from CHI₃ photolysis.⁷ We note that the iodonorcarane product was characterized by Marolewski and Yang with elemental analysis and ultraviolet, infrared, NMR, and mass spectra.⁶ This characterization was consistent with the structure of iodonorcarane,⁶ and the analogous preparation and characterization of 7-chloronorcarane produced from photolysis of CHClBr₂ in the presence of cyclohexene were compared to those of an authentic sample of 7-chloronorcarane produced from another synthetic method.⁶ Our photolysis of CHI₃ in the presence of cyclohexene was done under conditions very similar

to those employed in previously reported photochemical synthesis experiments.

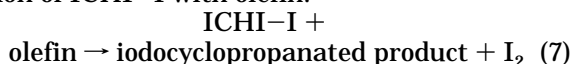
The mechanism and species responsible for the iodocyclopropanation reaction using ultraviolet photolysis of CHI₃ in the presence of olefins are not clear in the literature. Yang and Marolewski⁷ observed that iodocyclopropanation of *trans*- and *cis*-butenes using ultraviolet photolysis of CHI₃ resulted in stereospecific iodocyclopropanation and no isomerization of the *cis*-butene. They noted that formation of cyclopropane from radical intermediates would be expected to be nonstereospecific addition and also lead to fast isomerization of *cis*-butene. This indicates •CHI₂ is not mainly responsible for the cyclopropanation reaction, and they proposed that an iodomethylene species was the intermediate responsible for the iodocyclopropanation.⁷ They noted that, in contrast to methylene, fluoromethylene and chloromethylene have a singlet ground state,⁵⁷ and iodomethylene is likely to have a singlet ground state and a chemical reactivity similar to that of singlet methylene. This iodomethylene species was proposed to be formed via cleavage of two C-I bonds following ultraviolet photolysis.⁷ Subsequent gas-phase molecular beam experiments⁴² demonstrated that ultraviolet photolysis of CHI₃ resulted in no observable I₂ from direct photodissociation and the primary dissociation reaction only gave cleavage of one C-I bond to produce •CHI₂ and I atom fragments. Laser flash photolysis experiments for CHI₃ in solution also found that only •CH₂I and I atom fragments are the primary photoproducts formed immediately after ultraviolet excitation of CHI₃ in the condensed phase.^{43,44} These experiments strongly suggest that the iodomethylene species is not responsible for the iodocyclopropanation reaction observed after photolysis of CHI₃ in the presence of olefins. Time-resolved resonance Raman experiments show that noticeable amounts of ICHI-I can be formed in cyclohexane/cyclohexene solutions and ICHI-I reacts with the cyclohexene to give an I₂ leaving group. This in conjunction with the density functional theory calculation results and the fact that ultraviolet photolysis of CHI₃ in the presence of cyclohexene results in appreciable formation of iodonorcarane product^{6,7} indicates that ICHI-I reacts with olefins to produce iodocyclopropanated product and an I₂ leaving group. We propose the following reaction mechanism for the iodocyclopropanation of olefins using ultraviolet photolysis of CHI₃:



recombination to produce isomer:



reaction of ICHI-I with olefin:



formation of I₂:olefin complex:



This reaction mechanism is similar to the one found for the cyclopropanation of olefins using ultraviolet photolysis of CH₂I₂.^{37,38} The rate-determining step (7) was predicted from B3LYP/6-311G** calculations to have a

barrier of about 10.3 kcal/mol for reaction with ethylene. The iodocyclopropanated product could also conceivably be produced from the two-step $\cdot\text{CHI}_2$ reaction shown at the bottom of Figure 5. However, the rate-determining step for the two-step $\cdot\text{CHI}_2$ iodocyclopropanation reaction was estimated from B3LYP/6-311G** calculations to have a barrier of about 16.4 kcal/mol for reaction with ethylene. The $\cdot\text{CHI}_2$ pathway is probably a minor channel compared to the $\text{ICHI}-\text{I}$ iodocyclopropanation reaction (which has an estimated barrier of about 10.3 kcal/mol).

We have observed polyhalomethane isomer photoproducts produced after ultraviolet photolysis of a number of polyhalomethanes (including CH_2I_2 , CH_2Br_2 , CHI_3 , CH_2BrI , CHBr_3 , CF_3Br , CBr_4 , CH_2ClI , CHBr_2Cl , and CCl_3Br) in room temperature solutions using time-resolved resonance Raman spectroscopy experiments.^{28–36} Our previous work on CH_2I_2 and the present study on CHI_3 suggest that isomers of polyhalomethanes can be effective carbenoids and are likely the major methylene-transfer agent in many of these types of photocyclopropanation reactions. We note that ultraviolet photolysis of a number of polyhalomethanes such as CH_2FBr_2 , CHClBr_2 , CHBr_3 , and CHIBr_2 in the presence of cyclohexene were also observed to produce some halonorcarane products.^{6,7} The yield of the halonorcarane products was noticeably increased when the photocyclopropanation reactions were done in an inert solvent such as benzene or dichloromethane accompanied by stirring of the reaction mixture with aqueous sulfuric acid.⁷ This is consistent with our hypothesis that the $\text{ICHI}-\text{I}$ species is mainly responsible for the iodocyclopropanation reaction via the mechanism shown in reactions 5–8. By using an inert solvent, one could minimize competing radical side reactions such as the Kharasch addition of polyhalomethanes. This would help increase the chances of formation of $\text{ICHI}-\text{I}$ via solvent-induced geminate recombination of the CHI_2 and I fragments as indicated in reaction 6. The aqueous sulfuric acid helps remove molecular iodine that can trap reactive intermediates and is the leaving group of halocyclopropanation reactions involving the isomer photoproducts of CHI_3 or CHXI_2 .

It is intriguing that ultraviolet photolysis of CHBr_2Cl gave formation of a noticeable amount of the chloronorcarane product in the presence of cyclohexene but peroxide-catalyzed addition of CHBr_2Cl resulted in only appreciable amounts of the Kharasch-type adduct (50%) as the volatile product.⁶ We recently observed that ultraviolet photolysis of CHBr_2Cl leads to appreciable formation of $\text{CHClBr}-\text{Br}$ product.³⁴ We expect that $\text{CHClBr}-\text{Br}$ will act as a carbenoid to react with cyclohexene to give a chloronorcarane product and Br_2 leaving group similar to other isopolyhalomethanes such as $\text{CH}_2\text{I}-\text{I}$ and $\text{ICHI}-\text{I}$, which produced norcarane and iodonorcarane, respectively. Thus, ultraviolet photolysis of CHBr_2Cl can produce $\text{CHClBr}-\text{Br}$ product (from solvent-induced recombination of the initially produced CHClBr and Br fragments) that may react with cyclohexene to form the observed chloronorcarane product.⁶ However, peroxide-catalyzed addition of CHBr_2Cl does not form the $\text{CHClBr}-\text{Br}$ product and therefore gave only appreciable amounts of the Kharasch-type adduct (50%) as the volatile product.⁶ This and related work for CH_2I_2 ^{29,33,37,38} and CHI_3 (ref 28 and this work) suggest that isopolyhalomethane species such as $\text{CHClBr}-\text{Br}$ (and $\text{CH}_2\text{I}-\text{I}$ and $\text{ICHI}-\text{I}$) can compete with radical

addition reactions (such as the Kharasch polyhalomethane addition reaction) and produce appreciable amounts of (halo)cyclopropanation products. The yield of the (halo)cyclopropanated product varies considerably with the number and types of halogens in the polyhalomethane molecule,^{5–7,15} and this is likely due in part to the varying chemical reactivity of the isomer species and the relevant radical fragments and competition between their reactions with olefins. This is consistent with our density functional theory calculations for $\text{CH}_2\text{X}-\text{X}$ isomer and CH_2X radical (where $\text{X} = \text{Cl}, \text{Br}, \text{I}$) reactions with olefins that show the barriers to reaction vary noticeably with the identity of the halogen atom.³⁹ Further experimental and theoretical work is ongoing to better elucidate how the carbenoid behavior and properties of isopolyhalomethane species change with the type and number of halogen substituents.

Experiment and Computational Methods

Samples of CHI_3 (99%) were made with concentrations of about 0.02 M in cyclohexane (spectroscopic grade) and cyclohexene (99+%) solvents. The time-resolved resonance Raman spectroscopy experiments employed an experimental apparatus and methods similar to those previously published,³⁸ and only a short account will be given here. The excitation wavelengths for the pump and probe laser beams were obtained from the harmonics and/or H_2 Raman-shifted laser lines of two Nd:YAG nanosecond pulsed lasers. The time delay between the pump and probe beams was set using a pulse delay generator to synchronize and control the timing of both the firing of the flashlamps and Q-switches for the two lasers. The relative timing of the pump and probe laser beams was measured using two fast photodiodes whose output was displayed on a 500 MHz oscilloscope, and a jitter of less than 5 ns was observed between the two laser pulses.

A near collinear geometry was used to loosely focus the pump and probe laser beams onto a flowing liquid jet of sample. The Raman-scattered light was collected using reflective optics and imaged through a depolarizer and the entrance slit of a 0.5 m spectrograph. The spectrograph grating dispersed the Raman light onto a liquid nitrogen cooled CCD detector, and a signal was acquired for about 300 s before being read out to an interfaced PC computer. Five to ten of these readouts were summed to find the Raman spectrum at each time delay. Pump-only, probe-only, and pump–probe spectra were obtained for each time delay. A background scan was also obtained before and after each experimental trial, and the known cyclohexane and cyclohexene solvent Raman bands were used to calibrate the wavenumber shifts of the resonance Raman spectra. The solvent and parent CHI_3 Raman bands were deleted from the pump–probe spectra by subtracting the probe-only and pump-only Raman spectra so as to find the time-resolved resonance Raman spectra.

Density functional theory calculations were used to examine the potential energy surfaces of addition reactions of ethylene with the $\text{ICHI}-\text{I}$ and $\cdot\text{CHI}_2$ species. The stationary structures on the surfaces were fully optimized at the B3LYP or UBP3LYP level of theory^{58,59} using C_1 symmetry. Analytical frequency calculations were done to confirm the optimized structure to be a minimum or a first-order saddle point and to also find the zero-point energy correction. IRC computations were done to confirm the transition states connecting the related reactants and products as well as to characterize the reaction coordinate. The 6-311G** basis set and the Gaussian 98 program suite⁶⁰ were used for the calculations.

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research. We thank Professor Wei-Hai Fang for useful discussions.

Supporting Information Available: Selected output from the calculations showing the Cartesian coordinates, total energies, and vibrational zero-point energies for the reactants, transition state(s), intermediates, and products for the reactions of ICHI-I and $\cdot\text{CHI}_2$ with ethylene to form an iodocyclopropane product and two figures (S-1 and S-2) showing the time-resolved 319.9 nm resonance Raman spectra of reaction products obtained after 266 nm photolysis of CHI_3 in 1.3% cyclohexene in cyclohexane and 100% cyclohexene solvents, respectively. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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