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Reactivity of Iso-diiodomethane and Iso-iodoform, Isomers of CH₂I₂ and CHI₃, toward the Double Bond of a Variety of Cycloalkenes

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The metastable CH₂I−I and CH₂−I isomers formed by UV photolysis of CH₂I₂ and CHI₃ transfer methylene and iodomethylene groups, respectively, to a variety of cycloalkenes, leading to their cyclopropanation. More than a 100-fold increase of the reaction rate with increasing solvent polarity suggests a dipolar transition state. The fastest second-order rates observed were in CH₃CN. However, CH₂Cl₂ will be the more appropriate reaction medium because the isomer thermal stability is greater in CH₂Cl₂ than in the more polar CH₃CN.

Introduction

Photocyclopropanation via ultraviolet irradiation of diiodomethane (CH₂I₂) and iodoform (CHI₃) in the presence of olefins at room temperature in solution is a reaction of synthetic value,1−4 and it has recently received renewed attention.5 The reaction mechanism and criteria for selection of an optimal set of conditions remain little understood. UV photolysis of CH₂I₂ in solution has been recently shown to lead to the cleavage of one of the two C−I bonds followed by the efficient primary geminate combination of CH₂I⁺ and I− to form the CH₂−I isomer (iso-diiodomethane).6−9 The decay of CH₂−I follows a mixture of first-order (dissociation back to the radicals, and, in very polar solvent, to ions) and second-order (trapping by CH₂I⁺ and I−) processes, Scheme 1.7

Upon UV photolysis of CH₂I₂ in the presence of cyclohexene (c6) in solution, CH₂I−I was found to react with c6 with expulsion of I₂.7,10 This behavior is consistent with the isomer serving as the methylene transfer agent.10−13 According to IR absorption spectra of the CH₂I−I molecules trapped in frozen matrices, one of the possible resonance forms for this isomer species is the contact ion pair structure with an electrophilic C-atom (H₂C⁺−I−⋯I−).11,12 Ab initio MP2 calculations suggest a noticeable bonding interaction between the two iodine atoms.13 Density functional theory (DFT) calculations on isolated molecules indicate that the CH₂I part of the CH₂−I isomer has cationic character and that CH₂I−I can react with an olefin (ethylene) in one step to yield cyclopropane and I₂.14 UV photolysis of iodoform (CHI₃) in solution leads to similar steps: cleavage of the C−I bond, recombination into the CH₂I−I isomer (iso-iodoform), and cage escape of the geminate radical pair.15,16 Also, there is evidence for considerable radical trapping of the CH₂−I intermediate.16 Previous photochemical synthetic studies reported that UV irradiation of CHI₃ in the presence of c6 and several linear alkenes produces synthetically useful products and CH₂I−I → Products in the Alkene-Free Solvents

<table>
<thead>
<tr>
<th>solvent</th>
<th>CH₂I−I</th>
<th>CHI−I</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C₆H₁₄</td>
<td>(1.8 ± 0.4) × 10⁵⁶</td>
<td>(5.5 ± 0.5) × 10⁵⁶</td>
</tr>
<tr>
<td>c-C₆H₁₂</td>
<td>(4.1 ± 0.5) × 10⁵⁵</td>
<td>(5.7 ± 0.7) × 10⁵⁴</td>
</tr>
<tr>
<td>CH₃Cl</td>
<td>(2.2 ± 1.1) × 10⁵⁵</td>
<td>(4.4 ± 0.7) × 10⁵⁴</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>(4.3 ± 0.3) × 10⁵⁶</td>
<td>(4.2 ± 0.2) × 10⁵⁶</td>
</tr>
</tbody>
</table>

* Obtained in ref 7 by extrapolating the measured photolysis energy dependence of the kobs rate from low to infinitely low energies. See also ref 24. ⁶ Obtained as above, ref 16. ⁷ The kobs rates and their standard deviations based on repeated measurements at very low photolysis energies (μJ pulse−¹): 15 (CH₂Cl₂), 35 (CH₃CN) for CH₂I, and 3.5 (CH₂Cl₂), 35 (c-C₆H₁₂) for CH₂I₂, this work.

amounts of iodocyclopropanated products, in addition to I₂.¹⁷ Both CH₂I−I and the CH₂⁺⁺ radical were proposed to be iodomethylene transfer agents.³,¹⁸

In the present work, we wish to report transient spectroscopic studies of the photocyclopropanation reaction between the CH₂I−I isomer of CH₂I₂ and several cycloalkenes, specifically cyclopentene (c5), cycloheptene (c7), 1-methylcyclohexene (Me-c6), and 1,2-dimethylocyclohexene (dMe-c6). A similar study was conducted of the photocyclopropanation reaction between the CH₂I−I isomer of CHI₃ and c6.
Figure 1. The pseudo first-order $k_{obs\rightarrow olefin}$ decay rates (symbols) of the CH2-I isomer plotted against cycloheptene (c7) content for the photolyzed (0.04 mJ pulse−1) samples of CH2I2 (1 mM) in the deoxygenated solvents cyclohexane (C), dichloromethane (O), and acetonitrile (X). The slope of the linear fit (lines) gives the second-order $k_q$ rate constants summarized in Table 2. As seen in the inset, the 390 nm absorption band of the CH2-I isomer in CH2Cl2 solution decays as a single exponential with the corresponding rate decay constant $k_{obs\rightarrow olefin}$ in the presence of excess c7. The cycloalkene concentration (M) in the photolyzed solution is shown beside each decay curve.

SCHEME 2

Experimental Section

In our setup,19 the 310 nm photolysis pulse (~8 ns FWHM) was produced by frequency doubling the 620 nm output from an OPO pumped by the 355 nm output from the Nd:YAG laser. The photolysis pulse typically delivered 3.5×10−16 J per pulse, with 100 pulses of 200 ns duration per pulse. The cycloalkene+I2 charge-transfer complexes20 (probe wavelength, 320 nm) at high alkene concentrations occurs with rate constants similar to those of the CH2-I isomer decay. This behavior is consistent with cyclopropanation of the alkene C=C bond by CH2-I, Scheme 1. Generally, as the polarity of the solvent increases on going from c-C6H12 to CH2Cl2, the cyclopropanation rate ($k_q$) increases by a factor of 100, and going from CH2Cl2 to CH3CN the rate increases the $k_b$ by a factor of ~1.5, Table 2. This is consistent with a photocyclopropanation mechanism involving a highly dipolar activated complex, as shown schematically in Scheme 2. This transition complex can be drawn either as the open carbocationic structure with a single bond between the carbene carbon and one alkene carbon or as the closed carbocation with partial bonding between the carbene carbon and both alkene carbon atoms. The latter probably occurs based on the observed stereospecificity for the photocyclopropanation reactions involving simple alkenes.

The effect of the ring size is modest, Table 2. The reaction rate for c5 is about one-half of the rate for c6 and c7, with the corresponding relative rates averaged over the solvents being 0.51, 1.0, and 0.94. This reactivity trend follows the ring strain energy.21 This can be understood by noting that CH2-I is a highly energetic species lying approximately 170 kJ mol−1 above the ground state of CH3I13,14 and that the transition state for an exothermic reaction closely resembles reactants according to Hammond’s Postulate. Thus the less strained c6 and c7 will have a smaller transition state energy and react faster than the more strained c5.

CH3 CN

Methyl substitution at the cyclohexene double bond has a more profound effect, Table 2. Me-c6 reacts about 10 times more slowly than the analogous Me-c7.

TABLE 2: Photocyclopropanation Rate Constants ($k_q^{o}$) for the CH2-I Reagent

<table>
<thead>
<tr>
<th>solvent</th>
<th>c5</th>
<th>c6</th>
<th>c7</th>
<th>Me-c6</th>
<th>diMe-c6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-C6H14</td>
<td>(2.3 ± 0.5 × 10^4)</td>
<td>(4.4 ± 0.3 × 10^4)</td>
<td>(4.6 ± 0.3 × 10^4)</td>
<td>(4.5 ± 0.3 × 10^4)</td>
<td>(3.6 ± 0.3 × 10^4)</td>
</tr>
<tr>
<td>c-C6H12</td>
<td>(2.2 ± 0.1 × 10^4)</td>
<td>(3.4 ± 0.2 × 10^4)</td>
<td>(3.2 ± 0.2 × 10^4)</td>
<td>(3.7 ± 0.3 × 10^4)</td>
<td>(6.0 ± 0.1 × 10^4)</td>
</tr>
<tr>
<td>CH2Cl2</td>
<td>(2.1 ± 0.1 × 10^4)</td>
<td>(6.2 ± 0.3 × 10^4)</td>
<td>(4.8 ± 0.3 × 10^4)</td>
<td>(4.8 ± 0.2 × 10^4)</td>
<td>(5.8 ± 0.5 × 10^4)</td>
</tr>
<tr>
<td>CH3CN</td>
<td>1.7e</td>
<td>1.7e</td>
<td>1.4e</td>
<td>3.6e</td>
<td>8.7e</td>
</tr>
</tbody>
</table>

a In M−1 s−1. b Reference 7. c The investigated concentration range of cycloalkenes is 0.03−1 M. d As above, but 0.03−0.5 M. e As above, but 0.03−0.3 M. f As above, but 0.003−0.1 M. g Relative rates, refs 3.4.
faster than does e6 in all solvents. This is because the resulting partial tertiary carbenium ion is more stabilized through hyperconjugation as compared to a secondary carbenium ion. Going from Me-c6 to diMe-c6 results in a significant decrease in rate, probably because increasing substitution increases the steric hindrance, which offsets the increasing nucleophilicity of the more substituted cycloalkene; this behavior parallels that of the Simmons-Smith cyclopropanation reaction, cf., with refs 3 and 4.

Previously, the relative cyclopropanation rates for the same alkenes were obtained from relative product yields after continuous UV irradiation (450 W Hg arc lamp) of CH2I2-containing 1,2-dichloroethane solutions in the presence of equal amounts of two reactive alkenes,3 Table 2. These rates do not correlate with the second-order rate constants measured here. It seems to be unreasonable to attribute the difference solely to the solvent, because CH2Cl2 and 1,2-C6H4Cl2 are of similar polarity. On the other hand, during the prolonged broadband UV irradiation used in the previous synthetic work, CH2I2, the CH3I3-I complex, and CH3I+ cation, involved in the liquid-phase photochemistry of CH2I2,7 all might react with olefins via slow routes to produce cyclopropanated products,14,23 thus affecting the relative cyclopropanation yields.

The CH2I−I isomer reacts with e6 in a manner analogous to CH3-I−, but a factor of 4 slower, Figure 2 and Table 3. The CH2I−I isomer is much bulkier and more sterically demanding than the CH3-I− isomer, which has a much more open structure, and therefore CH2I−I cannot react with olefins as easily as CH3-I− does. The cyclopropanation efficiency of the CH2I−I and CH2I−I isomers is determined by the speed of the iodo-methylene (methylenec) group transfer and isomer intramolecular decay, in conjunction with competing trapping of isomers by radicals. The relative importance of the latter process can be reduced by using low photolysis flux. As seen in Table 1, the intrinsic thermal stability of CH2I−I is only slightly smaller than that of CH3-I− in c-C6H12 and CH2Cl2, whereas both isomers are stable to the same extent in CH3CN. This, and the somewhat lower quantum yield for the formation of CH2I−I than of CH3-I−,7,16 suggests that significantly larger alkene concentrations (about 4 times) should be employed to obtain similar photocyclopropanation yields when using the CH3I reagent than when using the CH2I2 reagent, contrary to what has been conjectured in refs 5 and 18.

**Conclusions**

In summary, the CH2I−I isomer of CH2I2 and the CH2I−I isomer of CH3I, both produced by 310 nm laser photolysis, exhibit similar behavior in the presence of a variety of cycloalkenes; the decay of the CH2I−I and CH2I−I isomers becomes progressively faster and the I2 develops with similar rate constants with increasing concentration of the cycloalkene, consistent with the fact that these isomers serve as the methylene transfer agents in the photocyclopropanation of olefins. The dramatic (more than 100-fold) increase of the cyclopropanation rate with increasing solvent polarity is strong evidence of a dipolar transition state. The cycloalkene ring size is found to have a modest (less than a factor of 2) effect on the reaction rate, whereas methyl substitution of the cyclohexene C≡C bond has a more pronounced effect. Among the three solvents investigated, CH2Cl2 will be most appropriate under a wide range of photocyclopropanation conditions because the reaction is slow in the nonpolar solvent c-C6H12 and the isomer stability decreases in the strongly polar solvent CH3CN.

**Acknowledgment.** We are very grateful to Prof. Torbjörn Frejd and Patrick El-Khoury for many useful discussions. A.N.T. acknowledges support from BGSU (RCE Grant 038/0582).

**References and Notes**


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**TABLE 3**: Rate Constants ($k_\text{PHOTO}$) for the CH3-I and CH2I−I Isomers in Photocyclopropanation of Cyclohexene

<table>
<thead>
<tr>
<th>solvent</th>
<th>CH3-I</th>
<th>CH2I−I</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-C6H12</td>
<td>4.1 ± 0.5</td>
<td>0.7 ± 0.3 × 10^5</td>
</tr>
<tr>
<td>CH2Cl2</td>
<td>3.4 ± 0.2</td>
<td>0.7 ± 0.1 × 10^4</td>
</tr>
<tr>
<td>CH3CN</td>
<td>6.2 ± 0.3</td>
<td>2.0 ± 0.3 × 10^4</td>
</tr>
<tr>
<td></td>
<td>4.2 ± 0.9</td>
<td>1.5 ± 10^3</td>
</tr>
</tbody>
</table>

*a* In M$^{-1}$ s$^{-1}$. *b* For the investigated concentration range of cyclohexene, see Table 2. *c* The investigated concentration range of cyclohexene are 0.03–2 and 0.05–1 M, respectively. *d* Reference 7.
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(24) We noticed a typographical error in ref 7, p 243. We bring to the attention of the reader that the observed decay rate ($k_{\text{obs}}$) of the CH$_2$I$^-$I isomer plotted against its starting concentration in n-hexane obeys the power law equation with the resultant fitting parameters $k = (1.8 \pm 0.4) \times 10^5$ s$^{-1}$ and $k_1 = (3.68 \pm 0.79) \times 10^6$ M$^{-1/2}$ s$^{-1}$ (instead of $k_1 = (3.68 \pm 0.79) \times 10^5$ M$^{-1/2}$ s$^{-1}$).