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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 CH₃I−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 CH₂I−I isomer (iso-diiodomethane).⁶⁻⁹ The decay of CH₂I−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.¹⁻⁴ 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 CH₂I−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 CH₂I−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 amounts of iodo-photocyclopropanated products, in addition to I₂.¹⁷ Both CH₂I−I and the CHI⁺ 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-dimethylcyclohexene (diMe-c₆). A similar study was conducted of the photocyclopropanation reaction between the CH₂I−I isomer of CHI₃ and c₆.

| TABLE 1: Rate Constants (kᵢ) of the First-Order Process CH₂I−I → Products and CHI⁺−I → Products in the Alkene-Free Solvents |
|---|---|---|
| solvent | CH₂I−I | CHI⁺−I |
| n-C₆H₁₄ | (1.8 ± 0.4) × 10⁵ | |
| c-C₅H₁₂ | (4.1 ± 0.5) × 10⁵ | (5.5 ± 0.5) × 10⁵ |
| CH₂Cl₂ | (2.2 ± 1.1) × 10⁵ | (5.7 ± 0.7) × 10⁵ |
| CH₃CN | (4.3 ± 0.3) × 10⁶ | (4.4 ± 0.7) × 10⁶ |
| diMe-c₆ | (4.2 ± 0.2) × 10⁶ | |

* 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. ¹⁷ The kobs rates and their standard deviations based on repeated measurements at very low photolysis energies (µJ pulse⁻¹): 15 (CH₂Cl₂), 35 (CH₃CN) for CH₂I₂, and 3.5 (CH₂Cl₂), 35 (c-C₅H₁₂) for CHI⁺−I, this work.
Experimental Section

In our setup, 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 J/nm pulse−1 samples of CH2I2 (1 mM) in the deoxygenated solvents cyclohexane (□), dichloromethane (O), and acetonitrile (▼). The slope of the linear fit (lines) gives the second-order kq rate constants summarized in Table 2. As seen in the inset, the 390 nm absorption band of the CH2I−I isomer in CH3Cl solution decays as a single exponential with the corresponding decay rate constant kobs−olefin in the presence of excess c7. The cycloalkene concentration (M) in the photolyzed solution is shown beside each decay curve.

Scheme 2

Table 2: Photocyclopropanation Rate Constants (kobs−olefin) for the CH2I−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>n-C6H14</td>
<td>(2.3 ± 0.5) × 107 s−1</td>
<td>(4.4 ± 0.3) × 106 s−1</td>
<td>(4.6 ± 0.3) × 105 s−1</td>
<td>(4.5 ± 0.3) × 106 s−1</td>
<td>(3.6 ± 0.3) × 107 s−1</td>
</tr>
<tr>
<td>c-C6H12</td>
<td>(2.2 ± 0.1) × 107 s−1</td>
<td>(4.1 ± 0.5) × 106 s−1</td>
<td>(3.4 ± 0.2) × 105 s−1</td>
<td>(3.7 ± 0.3) × 106 s−1</td>
<td>(6.0 ± 0.1) × 107 s−1</td>
</tr>
<tr>
<td>CH2Cl2</td>
<td>(2.1 ± 0.1) × 107 s−1</td>
<td>(3.4 ± 0.2) × 106 s−1</td>
<td>(3.2 ± 0.2) × 105 s−1</td>
<td>(4.8 ± 0.3) × 106 s−1</td>
<td>(4.8 ± 0.2) × 107 s−1</td>
</tr>
<tr>
<td>CH3CN</td>
<td>(2.0 ± 0.1) × 107 s−1</td>
<td>(6.2 ± 0.3) × 106 s−1</td>
<td>(4.2 ± 0.9) × 105 s−1</td>
<td>(4.2 ± 0.9) × 106 s−1</td>
<td>(5.8 ± 0.5) × 107 s−1</td>
</tr>
<tr>
<td>1,2-C2H2Cl2</td>
<td>1.7a</td>
<td>1b</td>
<td>1.4c</td>
<td>3.6f</td>
<td>8.7f</td>
</tr>
</tbody>
</table>

* In M−1 s−1. a Reference 7. b The investigated concentration range of cycloalkenes is 0.03−1 M. c As above, but 0.03−0.5 M. d As above, but 0.03−0.3 M. e As above, but 0.003−0.1 M. f Relative rates, refs 3, 4.
faster than does c6. Table 3 contains 10 7 rate constants measured here. The slope of the linear fit gives the second-order rate constant in Table 3. The 460 and 600 nm absorption bands of CH 2 I 2 are most appropriate under a wide range of photocyclopropanation conditions because the reaction dye and therefore CHI 2 I isomer is much bulkier and more sterically demanding than the CH 2 I 2 isomer of CH 2 I 2 and the CHI 2 I isomers, both produced by 310 nm laser photolysis, exhibit similar behavior in the presence of a variety of cycloalkenes; the decay of the CH 2 I 2 and CHI 2 I isomers becomes progressively faster and the I 2 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 in 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, CH 2 Cl 2 will be most appropriate under a wide range of photocyclopropanation conditions because the reaction is slow in the nonpolar solvent c-C 6 H 12 and the isomer stability decreases in the strongly polar solvent CH 3 CN.

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References and Notes

(24) We noticed a typographical error in ref 7, p 243. We bring to the attention of the reader that the observed decay rate ($k_{obs}$) 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 $k_0 = (1.8 \pm 0.4) \times 10^5$ s$^{-1}$ and $k_1 = (3.68 \pm 0.79) \times 10^6$ M$^{-1/2}$ s$^{-1}$ (instead of $k_1 = (3.68 \pm 0.79) \times 10^6$ M$^{-1/2}$ s$^{-1}$).