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Reactivity of Iso-diiodomethane and Iso-iodoform, Isomers of CH$_2$I$_2$ and CHI$_3$, toward the Double Bond of a Variety of Cycloalkenes

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The metastable CH$_2$I−I and CH$_2$I$_2$−I isomers formed by UV photolysis of CH$_2$I$_2$ and CHI$_3$ 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 CH$_3$CN. However, CH$_2$Cl$_2$ will be the more appropriate reaction medium because the isomer thermal stability is greater in CH$_2$Cl$_2$ than in the more polar CH$_3$CN.

Introduction

Photocyclopropanation via ultraviolet irradiation of diiodomethane (CH$_2$I$_2$) and iodoform (CHI$_3$) in the presence of olefins at room temperature in solution is a reaction of synthetic value, and it has recently received renewed attention. The reaction mechanism and criteria for selection of an optimal set of conditions remain little understood. UV photolysis of CH$_2$I$_2$ 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 CH$_2$I and I to form the CH$_2$I−I isomer (iso-diiodomethane). The decay of CH$_2$I−I follows a mixture of first-order (dissociation back to the radicals, and, in very polar solvent, to ions) and second-order (trapping by CH$_2$I and I) processes, Scheme 1.

Upon UV photolysis of CH$_2$I$_2$ in the presence of cyclohexene (c6) in solution, CH$_2$I−I was found to react with c6 with expulsion of I$_2$, This behavior is consistent with the isomer serving as the methylene transfer agent. According to IR absorption spectra of the CH$_2$I−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 (H$_2$C−I⋯I)$. Density functional theory (DFT) calculations on isolated molecules indicate that the CH$_2$I part of the CH$_2$I−I isomer has cationic character and that CH$_2$I−I can react with an olefin (ethylene) in one step to yield cyclopropane and I$_2$. UV photolysis of iodoform (CHI$_3$) in solution leads to similar steps: cleavage of the C−I bond, recombination into the CH$_2$I−I isomer (iso-iodoform), and cage escape of the geminate radical pair. Also, there is evidence for considerable radical trapping of the CH$_2$I−I intermediate. Previous photochemical synthetic studies reported that UV irradiation of CHI$_3$ in the presence of c6 and several linear alkenes produces synthetically useful products and CH$_2$I−I → Products in the Alkene-Free Solvents

<table>
<thead>
<tr>
<th>solvent</th>
<th>CH$_2$I−I</th>
<th>CHI$_3$−I</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C$<em>6$H$</em>{14}$</td>
<td>(1.8 ± 0.4) × 10$^5$</td>
<td>(4.1 ± 0.5) × 10$^5$</td>
</tr>
<tr>
<td>c-C$<em>4$H$</em>{10}$</td>
<td>(2.2 ± 1.1) × 10$^5$</td>
<td>(4.3 ± 0.3) × 10$^5$</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>(4.3 ± 0.3) × 10$^5$</td>
<td>(4.4 ± 0.7) × 10$^5$</td>
</tr>
</tbody>
</table>

* Obtained in ref 7 by extrapolating the measured photolysis energy dependence of the k$_{obs}$ rate from low to infinitely low energies. See also ref 24. Obtained as above, ref 16. The k$_{obs}$ rates and their standard deviations based on repeated measurements at very low photolysis energies (μJ pulse$^{-1}$): 15 (CH$_3$Cl), 35 (CH$_3$CN) for CHI$_3$, and 3.5 (CH$_2$Cl$_2$), 35 (c-C$_4$H$_{10}$) for CH$_2$I$_2$. Both CH$_2$I−I and the CHI$_3$ radical were proposed to be iodomethylene transfer agents.

In the present work, we wish to report transient spectroscopic studies of the photocyclopropanation reaction between the CH$_2$I−I isomer of CH$_2$I$_2$ 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 CH$_2$I−I isomer of CH$_3$I and c6.
The CH₂I₂ (1 mM) and CHI₃ (1 mM) samples (20°C) were deoxygenated and sealed in a 1 cm cuvette equipped with a magnetic stirrer. CH₂I₂ and CHI₃ (both from Fluka, >98%), solvents (Merck, p.a.), c₅H₁₂ (Aldrich, 99%+), c₅H₁₂ (Fluka, ≥98.5%), c₇H₁₄ (Aldrich, 97%), Me-c₆H₁₂ (Fluka, ≥99%), and diMe-c₆H₁₄ (Sigma) were used as received.

After excitation of CH₃I and CHI₃, the decay of the CH₂I⁻1 and CHI⁻1 isomer products was monitored via their absorption bands centered at ~390 and 560 nm (CH₂I⁻1, ref 7) and at ~450 and 600 nm (CHI⁻1, ref 16). The observed decay rate of the CH₂I⁻1 and CHI⁻1 isomers in the presence of excess olefin (kobs-olefin) is described by kobs-olefin = kobs + kq × [olefin], where kobs is the observed isomer decay rate constant under the same conditions with no olefin present, and kq is the second-order photocyclopropanation rate constant. The kobs rates are approximated as kobs = kq + kq × [radicals, isomer], where kq is the total trapping rate constant.

Results and Discussion

The CH₂I⁻1 isomer intermediate is produced by means of 310 nm nanosecond photolysis of CH₂I₂ in deoxygenated cyclohexane, dichloromethane, and acetonitrile. The CHI⁻1 isomer is formed from CHI₃ in the same way. Under low excitation conditions, the decay rate constant (kobs,0) of both the CH₂I⁻1 and CHI⁻1 isomers is observed to be in the 10⁻⁶–10⁻⁷ s⁻¹ range, with little I₂ formed directly. The true first-order rate constants (kq) of the decay of CH₂I⁻1 and CHI⁻1 in neat solvents can be obtained by extrapolating the isomer decay rates measured under low excitation conditions to infinitely low power that corresponds to the rate in the absence of trapping, Table 1. The kq rates are 10 times faster in CH₂CN than in the less polar c-C₅H₁₂ and CH₂Cl₂, because of the opening of the ionic decay channel.

The decay of the CH₂I⁻1 isomer is accelerated by the addition of increasing concentrations of cycloalkenes in all three solvents, Figure 1. The absorption rise of I₂ at low alkene concentrations and alkene/I₂ charge-transfer complexes²⁰ (probe wavelength, 320 nm) at high alkene concentrations occurs with rate constants similar to those of the CH₂I⁻1 isomer decay. This behavior is consistent with cyclopropanation of the alkene C=C bond by CH₂I⁻1, Scheme 1. Generally, as the polarity of the solvent increases on going from c-C₅H₁₂ to CH₂Cl₂, the cyclopropanation rate (kq) increases by a factor of 100, and going from CH₂Cl₂ to CH₂CN increases the kq 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 carbencic carbon and one alkene carbon or as the closed carbocation with partial bonding between the carbencic carbon and both alkene carbon atoms. The latter probably occurs based on the observed stereospecificity for the photocyclopropanation reactions involving simple alkenes.³,⁷

The effect of the ring size is modest, Table 2. The reaction 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 CH₂I⁻1 is a highly energetic species lying approximately 170 kJ mol⁻¹ above the ground state of CH₂I₁₃,¹⁴ and that the transition state for an exothermic reaction closely resembles reactants according to Hammond’s Postulate.²² The less strained c₆ and c₇ will have a smaller transition state energy and react faster than the more strained c₅.

Methyl substitution at the cyclohexene double bond has a more profound effect, Table 2. Me-c₆ reacts about 10 times
faster than does c6 in all solvents. This is because the resulting partial tertiary carbenium ion is more stabilized through hyperconjugation as compared to a secondary carbenium ion. The partial tertiary carbenium ion is more stabilized through hyperconjugation as compared to a secondary carbenium ion.

The CH2—I isomer reacts with c6 in a manner analogous to CH3—I, but a factor of 4 slower. Figure 2 and Table 3. The CH2—I isomer is much bulkier and more sterically demanding than the CH3—I isomer, which has a much more open structure, and therefore CH2—I cannot react with olefins as easily as CH3—I does. The cyclopropanation efficiency of the CH2—I and CH3—I isomers is determined by the speed of the iodo-methylene (methylene) 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 CH3—I is only slightly smaller than that of CH2—I in c6—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 CH2—I than of CH3—I,1,6 suggests that significantly larger alkene concentrations (about 4 times) should be employed to obtain similar photocyclopropanation yields when using the CH3 reagent than when using the CH2I2 reagent, contrary to what has been conjectured in refs 5 and 18.

Conclusions

In summary, the CH2—I isomer of CH3I2 and the CH3—I isomer of CH3I, both produced by 310 nm laser photolysis, exhibit similar behavior in the presence of a variety of cyclalkenes; the decay of the CH2—I and CH3—I isomers becomes progressively faster and the I2 develops with similar rate constants with increasing concentration of the cyclalkene, 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 c6—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


TABLE 3: Rate Constants (k*) for the CH3—I and CH2—I Isomers in Photocyclopropanation of Cyclohexene

<table>
<thead>
<tr>
<th>solvent</th>
<th>CH3—I</th>
<th>CH2—I</th>
</tr>
</thead>
<tbody>
<tr>
<td>c6—C6H12</td>
<td>(4.1 ± 0.5) × 10^10</td>
<td>(0.7 ± 0.3) × 10^10</td>
</tr>
<tr>
<td>CH2Cl2</td>
<td>(3.4 ± 0.2) × 10^10</td>
<td>(0.7 ± 0.1) × 10^10</td>
</tr>
<tr>
<td>CH3CN</td>
<td>(6.2 ± 0.3) × 10^10</td>
<td>(2.0 ± 0.3) × 10^10</td>
</tr>
<tr>
<td>CH2I2</td>
<td>(4.2 ± 0.9) × 10^10</td>
<td>(2.0 ± 0.9) × 10^10</td>
</tr>
</tbody>
</table>

* In M⁻¹ s⁻¹, ‡ For the investigated concentration range of cyclohexene, see Table 2. * For the investigated concentration range of cyclohexene, see Table 2. ** The investigated concentration range of cyclohexene is 0.03–2 and 0.05–1 M, respectively. Reference 7.

Figure 2. Dependence of the pseudo first-order kobs—Δt₀ decay rate of the CH2—I isomer (symbols) on cyclohexene (c6) content of the photolyzed (0.035 mJ pulse⁻¹) sample of CH2I (1 mM) in the deoxygenated solvents c6—C6H12 (●), CH2Cl2 (○), and CH3CN (▲). The slope of the linear fit gives the second-order k* rate constants shown in Table 3. The 460 and 600 nm absorption bands of CH2—I immediately after the photolysis pulse remain constant as the c6 concentration increases up to 2 M in c6—C6H12 (as shown for the 460 nm band in the inset), and up to 1 M in CH2Cl2 and CH3CN after deconvolution of the measured kinetic traces with the apparatus response function, suggesting that under these conditions there is no appreciable cyclohexene trapping of the nascent CH2I radical prior to its germinate recombination into the CH2—I isomer, contrary to what has been suggested in refs 5 and 18.
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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 $k_1 = (3.68 \pm 0.79) \times 10^6$ M$^{-1/2}$ s$^{-1}$).