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Reactivity of Iso-diiodomethane and Iso-iodoform, Isomers of CH_2I_2 and CHI_3, toward the Double Bond of a Variety of Cycloalkenes

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The metastable $CH_2I{-}I$ and $CHI_2{-}I$ isomers formed by UV photolysis of CH_2I_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_3CN. However, CH_2Cl_2 will be the more appropriate reaction medium because the isomer thermal stability is greater in CH_2Cl_2 than in the more polar CH_3CN.

Introduction

Photocyclopropanation via ultraviolet irradiation of diiodomethane (CH_2I_2) and iodoform (CHI_3) 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 CH_2I_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 $CH_2I^{\cdot}$ and $I^{\cdot}$ to form the $CH_2I{-}I$ isomer (iso-diiodomethane).[6−9] The decay of $CH_2I{-}I$ follows a mixture of first-order (dissociation back to the radicals, and, in very polar solvent, to ions) and second-order (trapping by $CH_2I^{\cdot}$ and $I^{\cdot}$) processes, Scheme 1.[7]

Upon UV photolysis of CH_2I_2 in the presence of cyclohexene (**c6**) in solution, $CH_2I{-}I$ was found to react with **c6** with expulsion of I_2.[7,10] This behavior is consistent with the isomer serving as the methylene transfer agent.[1−4] According to IR absorption spectra of the $CH_2I{-}I$ 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 ($H_2C^+{-}I{\cdots}I^-$).[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 CH_2I part of the $CH_2I{-}I$ isomer has cationic character and that $CH_2I{-}I$ can react with an olefin (ethylene) in one step to yield cyclopropane and I_2.[14] UV photolysis of iodoform (CHI_3) in solution leads to similar steps: cleavage of the C−I bond, recombination into the $CHI_2{-}I$ isomer (iso-iodoform), and cage escape of the geminate radical pair.[15,16] Also, there is evidence for considerable radical trapping of the $CHI_2{-}I$ intermediate.[16] Previous photochemical synthetic studies reported that UV irradiation of CHI_3 in the presence of **c6** and several linear alkenes produces synthetically useful amounts of iodocyclopropanated products, in addition to I_2.[17] Both $CHI_2{-}I$ and the $CHI_2^{\cdot}$ radical were proposed to be iodomethylene transfer agents.[5,18]

In the present work, we wish to report transient spectroscopic studies of the photocyclopropanation reaction between the $CH_2I{-}I$ isomer of CH_2I_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 $CHI_2{-}I$ isomer of CHI_3 and **c6**.

SCHEME 1

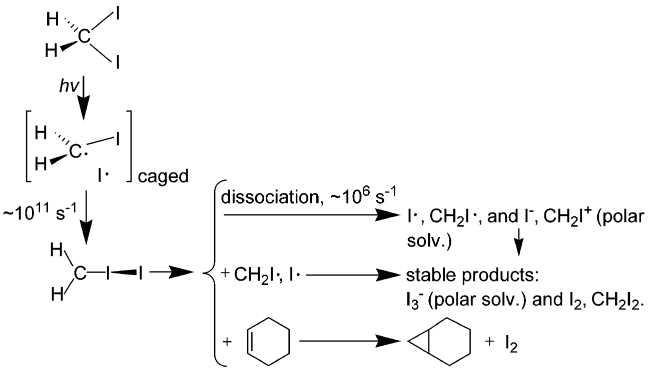

TABLE 1: Rate Constants (k_0) of the First-Order Process $CH_2I{-}I \rightarrow$ Products and $CHI_2{-}I \rightarrow$ Products in the Alkene-Free Solvents

	k_0 (s^{-1})	
solvent	$CH_2I{-}I$	$CHI_2{-}I$
n-C_6H_{14}	$(1.8 \pm 0.4) \times 10^{5}$ [a]	
c-C_6H_{12}	$(4.1 \pm 0.5) \times 10^{5}$ [c]	$(5.5 \pm 0.5) \times 10^{5}$ [b]
CH_2Cl_2	$(2.2 \pm 1.1) \times 10^{5}$ [c]	$(5.7 \pm 0.7) \times 10^{5}$ [c]
CH_3CN	$(4.3 \pm 0.3) \times 10^{6}$ [a]	$(4.4 \pm 0.7) \times 10^{6}$ [b] $(4.2 \pm 0.2) \times 10^{6}$ [c]

[a] 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. [b] Obtained as above, ref 16. [c] The k_{obs} rates and their standard deviations based on repeated measurements at very low photolysis energies (μJ pulse^{-1}): 15 (CH_2Cl_2), 35 (CH_3CN) for CHI_3, and 3.5 (CH_2Cl_2), 35 (c-C_6H_{12}) for CH_2I_2, this work.

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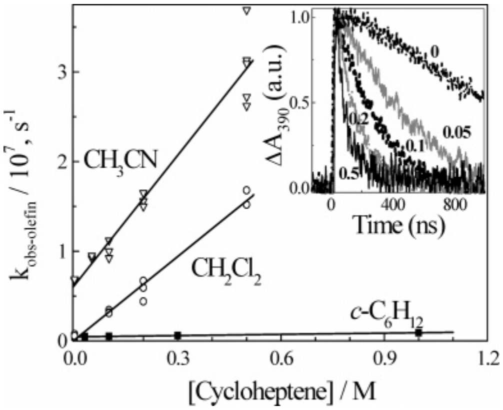
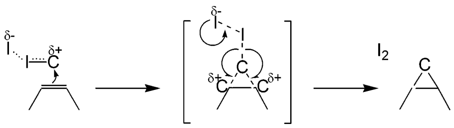


Figure 1. The pseudo first-order $k_{obs-olefin}$ decay rates (symbols) of the CH_2I-I isomer plotted against cycloheptene (**c7**) content for the photolyzed (0.04 mJ pulse^{-1}) samples of CH_2I_2 (1 mM) in the deoxygenated solvents cyclohexane (■), dichloromethane (○), and acetonitrile (▽). The slope 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 CH_2I-I isomer in CH_2Cl_2 solution decays as a single exponential with the corresponding decay rate constant $k_{obs-olefin}$ 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 3.5−70 μJ into a 2 mm diameter spot at the sample. The CH_2I_2 (1 mM) and CHI_3 (1 mM) samples (20 ± 1 °C) were deoxygenated and sealed in a 1 cm cuvette equipped with a magnetic stirrer. CH_2I_2 and CHI_3 (both from Fluka, >98%), solvents (Merck, p.a.), **c6** (Aldrich, 99+%), **c5** (Fluka, ≥98.5%), **c7** (Aldrich, 97%), **Me-c6** (Fluka, ≥99%), and **diMe-c6** (Sigma) were used as received.

After excitation of CH_2I_2 and CHI_3, the decay of the CH_2I-I and CHI_2-I isomer products was monitored via their absorption bands centered at ~390 and 560 nm (CH_2I-I, ref 7) and at ~450 and 600 nm (CHI_2-I, ref 16). The observed decay rate of the CH_2I-I and CHI_2-I isomers in the presence of excess olefin ($k_{obs-olefin}$) is described by $k_{obs-olefin} = k_{obs} + k_q \times$ [olefin], where k_{obs} is the observed isomer decay rate constant under the same conditions with no olefin present, and k_q is the second-order photocyclopropanation rate constant. The k_{obs} rates are approximated as $k_{obs} = k_0 + k_t \times$ [radicals, isomer], where k_t is the total trapping rate constant.

Results and Discussion

The CH_2I-I isomer intermediate is produced by means of 310 nm nanosecond photolysis of CH_2I_2 in deoxygenated cyclohexane, dichloromethane, and acetonitrile. The CHI_2-I isomer is formed from CHI_3 in the same way. Under low excitation conditions, the decay rate constant (k_{obs}) of both the CH_2I-I and the CHI_2-I isomers is observed to be in the 10^6−10^7 s^{-1} range, with little I_2 formed directly. The true first-order rate constants (k_0) of the decay of CH_2I-I and CHI_2-I 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 k_0 rates are 10 times faster in CH_3CN than in the less polar c-C_6H_{12} and CH_2Cl_2, because of the opening of the ionic decay channel.[7]

The decay of the CH_2I-I isomer is accelerated by the addition of increasing concentrations of cycloalkenes in all three solvents, Figure 1. The absorption rise of I_2 at low alkene concentrations and alkene:I_2 charge-transfer complexes[20] (probe wavelength, 320 nm) at high alkene concentrations occurs with rate constants similar to those of the CH_2I-I isomer decay. This behavior is consistent with cyclopropanation of the alkene C═C bond by CH_2I-I, Scheme 1. Generally, as the polarity of the solvent increases on going from c-C_6H_{12} to CH_2Cl_2, the cyclopropanation rate (k_q) increases by a factor of 100, and going from CH_2Cl_2 to CH_3CN increases the k_q 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 carbenic carbon and one alkene carbon or as the closed carbocation with partial bonding between the carbenic carbon and both alkene carbon atoms. The latter probably occurs based on the observed stereospecificity for the photocyclopropanation reactions involving simple alkenes.[3,17]

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 CH_2I-I is a highly energetic species lying approximately 170 kJ mol^{-1} above the ground state of CH_2I_2[13,14] 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

TABLE 2: Photocyclopropanation Rate Constants (k_q^{a}) for the CH_2I-I Reagent

	alkene				
solvent	**c5**	**c6**	**c7**	**Me-c6**	**diMe-c6**
n-C_6H_{14}		$(4.4 \pm 0.3) \times 10^{5\,b}$			
c-C_6H_{12}	$(2.3 \pm 0.5) \times 10^{5\,c}$	$(4.1 \pm 0.5) \times 10^{5\,c}$	$(4.6 \pm 0.3) \times 10^{5\,c}$	$(4.5 \pm 0.3) \times 10^{6\,c}$	$(3.6 \pm 0.3) \times 10^{6\,f}$
CH_2Cl_2	$(2.2 \pm 0.1) \times 10^{7\,d}$	$(3.4 \pm 0.2) \times 10^{7\,d}$ $(3.4 \pm 0.2) \times 10^{7\,b}$	$(3.2 \pm 0.2) \times 10^{7\,c}$	$(3.7 \pm 0.3) \times 10^{8\,e}$	$(6.0 \pm 0.1) \times 10^{7\,f}$
CH_3CN	$(2.1 \pm 0.1) \times 10^{7\,d}$	$(6.2 \pm 0.3) \times 10^{7\,d}$ $(4.2 \pm 0.9) \times 10^{7\,b}$	$(4.8 \pm 0.3) \times 10^{7\,c}$	$(4.8 \pm 0.2) \times 10^{8\,e}$	$(5.8 \pm 0.5) \times 10^{7\,f}$
1,2-$C_2H_4Cl_2$	1.7^g	1^g	1.4^g	3.6^g	8.7^g

[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.

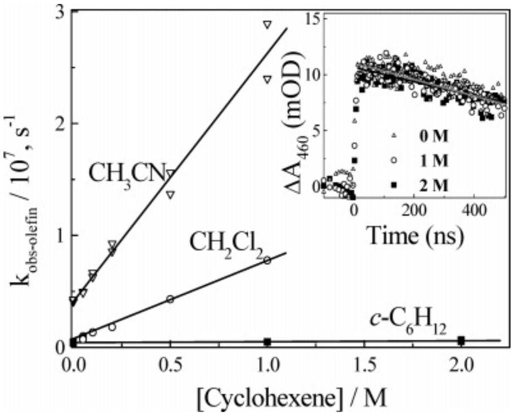


Figure 2. Dependence of the pseudo first-order $k_{\mathrm{obs-olefin}}$ decay rate of the CHI_2—I isomer (symbols) on cyclohexene (**c6**) content of the photolyzed (0.035 mJ pulse^{-1}) sample of CHI_3 (1 mM) in the deoxygenated solvents c-C_6H_{12} (■), CH_2Cl_2 (○), and CH_3CN (▽). The slope of the linear fit gives the second-order k_q rate constants shown in Table 3. The 460 and 600 nm absorption bands of CHI_2—I immediately after the photolysis pulse remain constant as the **c6** concentration increases up to 2 M in c-C_6H_{12} (as shown for the 460 nm band in the inset), and up to 1 M in CH_2Cl_2 and CH_3CN 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 $CHI_2^{\cdot}$ radical prior to its geminate recombination into the CHI_2—I isomer, contrary to what has been suggested in refs 5 and 18.

TABLE 3: Rate Constants (k_q[a]) for the CH_2I—I and CHI_2—I Isomers in Photocyclopropanation of Cyclohexene

	reactant	
solvent	CH_2I—I	CHI_2—I
c-C_6H_{12}	$(4.1 \pm 0.5) \times 10^{5}$ [b]	$(0.7 \pm 0.3) \times 10^{5}$ [c]
CH_2Cl_2	$(3.4 \pm 0.2) \times 10^{7}$ [b]	$(0.7 \pm 0.1) \times 10^{7}$ [d]
CH_3CN	$(6.2 \pm 0.3) \times 10^{7}$ [b] $(4.2 \pm 0.9) \times 10^{7}$ [e]	$(2.0 \pm 0.3) \times 10^{7}$ [d]

[a] In M^{-1} s^{-1}. [b] For the investigated concentration range of cyclohexene, see Table 2. [c,d] The investigated concentration ranges of cyclohexene are 0.03—2 and 0.05—1 M, respectively. [e] Reference 7.

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. 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 CH_2I_2-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 CH_2Cl_2 and 1,2-$C_2H_4Cl_2$ are of similar polarity. On the other hand, during the prolonged broadband UV irradiation used in the previous synthetic work, $CH_2I^{\bullet}$, the $CH_2I_2{}^{\bullet}I$ complex, and CH_2I^+ cation, involved in the liquid-phase photochemistry of CH_2I_2,[7] all might react with olefins via slow routes to produce cyclopropanated products,[14,23] thus affecting the relative cyclopropanation yields.

The CHI_2—I isomer reacts with **c6** in a manner analogous to CH_2I—I, but a factor of 4 slower, Figure 2 and Table 3. The CHI_2—I isomer is much bulkier and more sterically demanding than the CH_2I—I isomer, which has a much more open structure, and therefore CHI_2—I cannot react with olefins as easily as CH_2I—I does. The cyclopropanation efficiency of the CHI_2—I and CH_2I—I isomers is determined by the speed of the iodomethylene (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 CHI_2—I is only slightly smaller than that of CH_2I—I in c-C_6H_{12} and CH_2Cl_2, whereas both isomers are stable to the same extent in CH_3CN. This, and the somewhat lower quantum yield for the formation of CHI_2—I than of CH_2I—I,[7,16] suggests that significantly larger alkene concentrations (about 4 times) should be employed to obtain similar photocyclopropanation yields when using the CHI_3 reagent than when using the CH_2I_2 reagent, contrary to what has been conjectured in ref 5.

Conclusions

In summary, the CH_2I—I isomer of CH_2I_2 and the CHI_2—I isomer of CHI_3, both produced by 310 nm laser photolysis, exhibit similar behavior in the presence of a variety of cycloalkenes; the decay of the CH_2I—I 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 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, CH_2Cl_2 will be most appropriate under a wide range of photocyclopropanation conditions because the reaction is slow in the nonpolar solvent c-C_6H_{12} and the isomer stability decreases in the strongly polar solvent CH_3CN.

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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_{obs}) of the $CH_2I{-}I$ 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 $k_1 = (3.68 \pm 0.79) \times 10^8$ $M^{-1/2}$ s^{-1} (instead of $k_1 = (3.68 \pm 0.79) \times 10^6$ $M^{-1/2}$ s^{-1}).