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Picosecond Time-Resolved Resonance Raman Study of $CH_2I{-}I$ Produced after Ultraviolet Photolysis of CH_2I_2 in CH_3OH, CH_3CN/H_2O and CH_3OH/H_2O Solutions

Wai Ming Kwok,[†] Chensheng Ma,[†] Anthony W. Parker,*[,‡] David Phillips,*[,†] Michael Towrie,[‡] Pavel Matousek,[‡] and David Lee Phillips*[,§]

Department of Chemistry, Imperial College of Science, Technology and Medicine, Exhibition Road, London SW7 2AY, U.K., Central Laser Facility, CLRC Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, U.K., and Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong S. A. R., P. R. China

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We present picosecond time-resolved resonance Raman spectroscopy experiments investigating the photoproducts produced after ultraviolet photolysis of CH_2I_2 in CH_3OH solution and in 50% CH_3OH/50% H_2O and 50% CH_3CN/50% H_2O by volume mixed solvents. We observe that isodiiodomethane ($CH_2I{-}I$) is formed within several picoseconds and has a lifetime that significantly depends on the solvent system (time constant of 3.8 ns in CH_3OH, 1.8 ns in 50% CH_3CN/50% H_2O, and 0.8 ns in 50% CH_3OH/50% H_2O). Our results indicate that $CH_2I{-}I$ can be formed via geminate recombination in aqueous environments but will have a shorter lifetime than in previous experiments done in several organic solvents. The variations in the lifetime of $CH_2I{-}I$ in the presence of H_2O and CH_3OH could be due to its chemical reaction with the O−H bond and/or possibly faster cleavage of the weak I−I bond in aqueous solutions. We briefly discuss the potential role of $CH_2I{-}I$ in the release of reactive halogens in aqueous environments.

Introduction

Polyhalomethanes such as CH_2I_2, CH_2BrI, and CH_2Br_2 have been observed in the troposphere and are believed to be significant sources of reactive halogens released into the atmosphere.[1−6] Atmospheric photolysis rates have been estimated as a function of solar zenith angle and altitude for CH_2I_2, CH_2BrI, and CH_2Br_2 on the basis of their gas phase ultraviolet absorption spectra.[5] Recent measurements in the marine boundary layer of the troposphere linked the photolysis of CH_2I_2 and CH_2BrI to an increase in the concentrations of iodine oxide (IO).[7] These observations have led to an increased interest in the photochemistry of polyhalomethanes. Polyhalomethanes are also of interest in synthetic chemistry reactions for the cyclopropanation of olefins and diiodomethylation of carbonyl compounds.[8−15]

Ultraviolet photolysis of gas phase CH_2I_2 leads to direct C−I bond cleavage and formation of a highly excited CH_2I radical and an iodine atom (I and/or I*).[16−21] Gas phase resonance Raman studies indicated the short-time photodissociation dynamics were multidimensional and consistent with significant internal excitation of the CH_2I fragment.[22−25] Although it is energetically possible at wavelengths below 333 nm to produce CH_2 and I_2 products, this process is symmetry-forbidden[26,27] and does not become significant until photolysis energies are >6.4 eV.[28,29] The basic features of the ultraviolet gas phase photolysis of CH_2I_2 are fairly well understood,[16−29] but the same photodissociation reaction in condensed phase or solvated environments leads to more complex and intriguing dynamics and photochemistry. Excitation of CH_2I_2 by ultraviolet light, direct photoionization and pulse radiolysis all lead to formation of characteristic transient absorption bands ∼385 and ∼570 nm.[30−39] These transient absorption bands were variously assigned to be due to a number of species including trapped electrons,[30] the cation of CH_2I_2,[34,36,38] and the isomer of CH_2I_2.[32,33,39] Another proposed assignment suggested the 385 nm band was due to the $CH_2I_2^+$ cation and the 570 nm band was due to the CH_2I radical.[31,35] A recent transient resonance Raman study indicated that the isodiiodomethane ($CH_2I{-}I$) species is mainly responsible for the 385 nm band on the nanosecond time scale.[40] Further work showed that both the $CH_2I{-}I$ and $CH_2I_2^+$ species can make contributions to the 570 nm transient absorption band on the nanosecond time-scale depending on the excitation conditions.[41] Picosecond time-resolved resonance Raman (ps-TR^3) experiments[42] demonstrated that the $CH_2I{-}I$ species is formed vibrationally hot within several picoseconds after photolysis of the parent CH_2I_2 in cyclohexane and acetonitrile solvents. The time-resolved vibrational spectroscopy experiments[40,42] in conjunction with previous results from gas phase experiments[16−21] and solution phase femtosecond transient absorption experiments[37−39] indicates that solvation leads to formation of some $CH_2I{-}I$ product via geminate or near-geminate recombination of the initially produced CH_2I and I photofragments within the solvent cage. Photolysis of a number of other polyhalomethanes in room temperature organic solvents has been observed to produce noticeable amounts of isopolyhalomethane species.[43−49]

Most of the condensed phase photochemistry and spectroscopy studies involving polyhalomethanes have been done in organic solvents and not aqueous or mixed aqueous solvents. Thus, it is not clear if isopolyhalomethanes are produced in noticeable amounts following ultraviolet photolysis in aqueous solutions. This would have some bearing on whether isopolyhalomethanes have any relevance in atmospheric chemistry. In

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* To whom correspondence should be addressed. E-mail: phillips@hkucc.hku.hk. Fax: 852-2857-1586.

[†] Imperial College of Science.

[‡] CLRC Rutherford Appleton Laboratory.

[§] University of Hong Kong.

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this paper we report ps-TR^3 spectra observed following ultraviolet excitation of CH_2I_2 in CH_3OH solution and in 50% CH_3OH/50% H_2O (CH_3OH/H_2O) and 50% CH_3CN/50% H_2O (CH_3CN/H_2O) by volume mixed solvents. Isodiiodomethane (CH_2I-I) photoproduct was observed to form within several picoseconds and its lifetime varied noticeably with the solvent system. To our knowledge, this is the first observation of an isopolyhalomethane being produced as a photoproduct in a largely aqueous environment. These results suggest that CH_2I-I can be produced in noticeable amounts in aqueous environments. We briefly discuss the possible role of CH_2I-I in the release of reactive halogens in aqueous environments.

Experiment

CH_2I_2 (99%) and spectroscopic grade CH_3OH, CH_3CN, and deionized H_2O were used to prepare sample solutions. All solutions were prepared with concentration of 2.5×10^{-2} mol dm^{-3} of CH_2I_2. The ps-TR^3 experiments were done using a system based on optical parametric amplifiers that has been described in detail elsewhere[42,48−50] so only a brief description will be given here. A 800 nm pulse from a femtosecond titanium sapphire oscillator was amplified to 2−3 mJ at 1 kHz in a regenerative amplifier (Spectra-Physics) and then frequency doubled in a 2 mm type I BBO (Beta-barium borate) crystal to produce the 400 nm probe pulses for the ps-TR^3 experiments. The 267 nm third harmonic of the regenerative amplifier was used for the pump excitation wavelength. Typical pump and probe pulse energies were in the 5−15 μJ range with ~1 ps pulse widths (fwhm). The pump and probe pulses had parallel polarization and were loosely focused to about a 100 μm diameter spot size on a 500 μm flowing liquid stream of sample. The Raman scattered light was collected at 90° using a parabolic aluminum mirror ($f^{\#} = 0.8$, $f = 4$ cm) and then dispersed in a triple stage spectrograph onto a liquid nitrogen cooled CCD detector.

Each spectrum shown here had a scaled probe before pump and scaled net solvent measurements subtracted to delete solvent and diidomethane ground-state Raman bands. Copper wires were placed in the samples to absorb the iodine product. The samples showed less than a few percent degradation as measured by UV absorption obtained before and after the ps-TR^3 experiment. Solvent Raman bands were used to calibrate the spectra with an estimated accuracy of about ±10 cm^{-1} in absolute frequency and the total collection time was about 400 s for the spectrum at each delay time. The divergence of the pump−probe laser beams and uncertainty of the collimation over the relatively long delay line travel length may give a moderate systematic error in the absolute time-constant values (on the order of 10%), but the relative values are more accurate because this systematic error would cancel.

Results and Discussion

Because CH_2I_2 is not very soluble in H_2O, we used largely aqueous mixed solvent systems composed of CH_3OH/H_2O and CH_3CN/H_2O solvents with mole fractions of about 0.69 and 0.74, respectively, for H_2O to dissolve enough CH_2I_2 to make the time-resolved resonance Raman experiments feasible. Figure 1 presents ps-TR^3 spectra obtained for photoproducts formed after 267 nm photolysis of CH_2I_2 in CH_3OH/H_2O solvent and using a 400 nm probe wavelength. Similar spectra were obtained in CH_3OH and CH_3CN/H_2O solvents and are shown in the Supporting Information. Inspection of Figure 1 shows that the photoproduct Raman bands appear within several picoseconds, similar to experiments reported earlier in pure cyclohexane and CH_3CN solvents.[42] Comparison of the spectra in Figure 1 and the figures in the Supporting Information with corresponding spectra obtained previously in pure cyclohexane and CH_3CN solvents shows that the same photoproduct bands are observed in all the spectra.[42] This indicates that the CH_2I-I photoproduct species is produced in noticeable amounts in the CH_3OH, CH_3OH/H_2O, and CH_3CN/H_2O solvents. The reader is referred to previous TR^3 studies of refs 40 and 42 for details of the Raman band assignments to the CH_2I-I photoproduct.

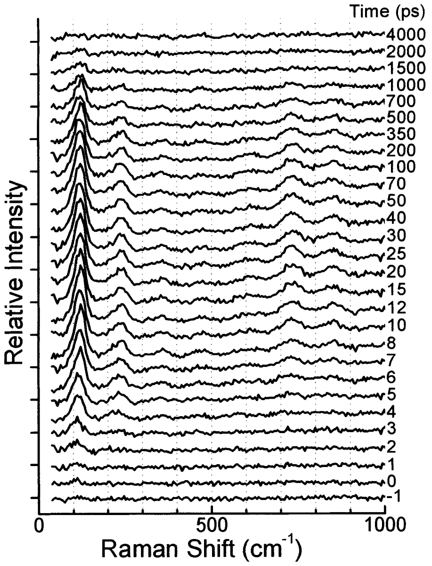

Figure 1. Stokes picosecond time-resolved resonance Raman spectra of the CH_2I-I isomer product formed after 267 nm photolysis of CH_2I_2 in a 50% CH_3OH/50% H_2O by volume mixed solvent. Spectra were acquired at varying pump and probe (400 nm) time delays.

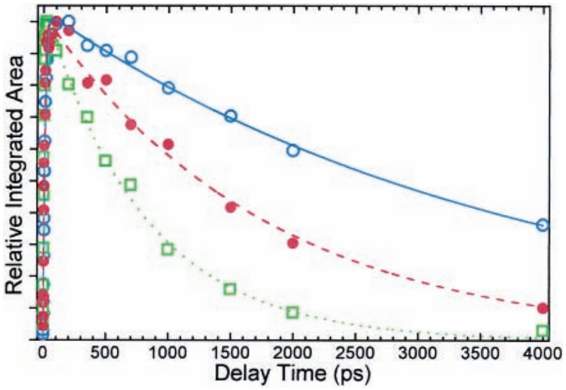

Figure 2. Plots of the relative integrated area of the ν_{I-I} Raman band at different delay times (from 0 to 4000 ps) obtained in CH_3OH (blue open circles), 50% CH_3CN/50% H_2O (red solid circles), and 50% CH_3OH/50% H_2O (green open squares) solvents, respectively. The blue solid line (CH_3OH), red dashed line (50% CH_3CN/50% H_2O), and green dotted line (50% CH_3OH/50% H_2O) represent least-squares fits to the data (see text and Table 1 for more details).

The Raman band at about 120 cm^{-1} due to the fundamental I−I stretch mode (ν_{I-I}) of the CH_2I-I photoproduct was integrated at the different delay times to examine the kinetics of the growth and decay of the CH_2I-I photoproduct. Figures 2 and 3 depict plots of the relative integrated area of the ν_{I-I} Raman band at different delay times in the CH_3OH, CH_3OH/H_2O and CH_3CN/H_2O solvents. Figure 2 shows the intensity of the ν_{I-I} Raman band from 0 to 4000 ps and Figure 3 from 0

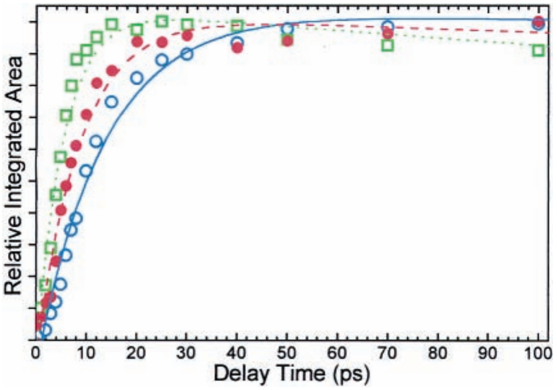

Figure 3. Plots of the relative integrated area of the ν_{I-I} Raman band at different delay times (from 0 to 100 ps) obtained in CH_3OH (blue open circles), 50% CH_3CN/50% H_2O (red solid circles), and 50% CH_3OH/50% H_2O (green open squares) solvents, respectively. The blue solid line (CH_3OH), red dashed line (50% CH_3CN/50% H_2O), and green dotted line (50% CH_3OH/50% H_2O) representleast-squares fits to the data (see text and Table 1 for more details).

TABLE 1: Best Fit Parameters Used To Fit the Relative Integrated Area of the ν_{I-I} Raman Band at Different Delay Times Shown in Figures 2 and 3 (See Text and Eq 1 for More Details)

solvent system	t_1, ns	t_2, ps	A	B
CH_3OH	3.8	13.4	103.3	100.0
50% CH_3CN/50% H_2O	1.8	8.7	102.2	100.0
50% CH_3OH/50% H_2O	0.8	5.5	104.6	100.0

to 100 ps. The relative integrated areas of the ν_{I-I} Raman band were fit to a simple function (the lines represent this best fit in Figures 2 and 3):

$$I(t) = Ae^{-(t-t_0)/t_1} - Be^{-(t-t_0)/t_2} \quad (1)$$

where $I(t)$ is the relative integrated area of the ν_{I-I} Raman band, t_0 is the relative to time zero delay (this is a fitting parameter), t_1 is the decay time-constant of the ν_{I-I} Raman band, t_2 is the growth time-constant of the ν_{I-I} Raman band, and A and B are constants.

Table 1 gives the best fit parameters used to fit the relative integrated area of the ν_{I-I} Raman band at different delay times shown in Figures 2 and 3.

Examination of Figure 2 and Table 1 shows that the decay of the CH_2I-I photoproduct varies significantly with the type of solvent (time constant of ~3.8 ns in CH_3OH, 1.8 ns in CH_3CN/H_2O, and 0.8 ns in CH_3OH/H_2O). Similarly, inspection of Figure 3 and Table 1 shows that the growth of the CH_2I-I photoproduct varies noticeably with solvent (time-constant of ~13.4 ps in CH_3OH, 8.7 ps in $CH_3CN/H_2O$and 5.5 ps in CH_3OH/H_2O). The changes in the growth of the ν_{I-I} Raman band is similar to the picosecond growth of the 400 nm transient absorption spectrum measured by recent time-resolved absorption spectroscopy following ultraviolet photolysis of CH_2I_2 in acetonitrile solvent, which showed one component with $\tau = 6.7$ ps and a second component with $\tau = 69$ ps.[39] These two components were attributed to vibrational relaxation of the initially produced "hot" CH_2I-I photoproduct. It is interesting that similar changes have been observed in the time-resolved absorption of CH_2I_2 at 400 nm after it was photoexcited to two quanta of the C−H stretch mode in CCl_4 and $CDCl_3$ solvents.[51] This study observed vibrational relaxation times of $\tau_1 = 10.8$ ps, $\tau_2 = 68$ ps and $\tau_1 = 11.2$ ps, $\tau_2 = 51$ ps, respectively.[51] The first relaxation component was attributed to intramolecular vibrational relaxation of the CH_2I_2 molecule and the second component to energy transfer of the CH_2I_2 molecule to the solvent.[51] We note that several other femtosecond time-resolved absorption spectroscopy studies observed similar two component vibrational relaxation times after infrared photoexcitation of CH_2I_2 under varying conditions.[52−54] The vibrational relaxation of CH_2I-I and CH_2I_2 are similar to one another with two distinct components (one on the order of 7−12 ps and a second on the order of 20−70 ps). This suggests the first vibrational relaxation component observed in the femtosceond time-resolved absorption experiments in acetonitrile solvent[39] is due to intramolecular vibrational relaxation, and this correlates with the growth of the ν_{I-I} Raman band in the ps-TR^3 spectra shown in Figure 1 observed on a similar time scale. The second longer vibrational relaxation component observed in the femtosecond study on the tens of picoseconds time scale correlates with the vibrational intensity changes observed in the ps-TR^3 anti-Stokes bands of the CH_2I-I product on the tens of picosecond time scale (see Figures 3 and 5 in ref 42).

Our results in conjunction with femtosecond time-resolved absorption experiments by other groups on the CH_2I-I[39] and CH_2I_2 molecules[51−54] suggest that the appearance time or growth of the Stokes bands in the picosecond time-resolved Raman spectra of the CH_2I-I can be attributed to the initial intramolecular vibrational relaxation. Similarly, the changes in the intensities of the anti-Stokes Raman bands can be attributed to intermolecular vibrational relaxation of the highly excited CH_2I-I molecule. For the highly excited CH_2I-I molecule it appears the initial dynamics of the Stokes and anti-Stokes bands in the picosecond Raman spectra could be useful to distinguish intramolecular and intermolecular vibrational relaxation.

The CH_2I-I photoproduct observed in the ps-TR^3 spectra obtained in CH_3OH, CH_3CN/H_2O, and CH_3OH/H_2O solvents appears to be produced to a similar but not identical degree, as previously found in cyclohexane and CH_3CN solvents.[42] However, the lifetime of the CH_2I-I product becomes noticeably shorter in the mixed aqueous solutions and shows a correlation with the amount of OH bonds present in the solvent system. We note that CH_2I-I has been shown both theoretically and experimentally to act as a good methylene transfer agent (or carbenoid species) toward carbon double bonds and can produce cyclopropanated products with high stereospecificity[55−58] similar to reaction of singlet methylene with carbon double bonds.[59,60] Density functional theory calculations indicate CH_2I-I reacts with ethylene via a one-step reaction with a barrier of about 2.9 kcal/mol to form a cyclopropane product and iodine molecule leaving group.[55] Similar calculations for singlet methylene reaction with ethylene show no barrier to reaction with the potential energy surface going downhill from reactants to a cyclopropane product,[55] and this is in good agreement with previous ab initio studies.[59,60] These results indicate that CH_2I-I and singlet methylene exhibit very similar chemical reactivity toward carbon double bonds with the CH_2I-I being moderately less reactive. Singlet methylene is a very reactive species and may undergo reaction with H_2O to produce a CH_3OH molecule product.[61−65] This type of reaction is analogous to the known reactions of carbenes to insert into O−H bonds of alcohols.[66] Insofar as CH_2I-I exhibits a similar reactivity toward water as the singlet methylene species, then it would not be unreasonable to expect that CH_2I-I may react in an analogous fashion. Such a reaction could possibly account for the noticeably shorter lifetimes of CH_2I-I in the presence of H_2O.

It is intriguing that there is a noticeably shorter lifetime for CH_2I_2 in the CH_3OH/H_2O solvent than the CH_3CN/H_2O solvent even though they have the same H_2O concentration. This could possibly indicate that $CH_2I{-}I$ may also react with OH bonds of alcohols to some extent. There is some evidence in the literature that $CH_2I{-}I$ may react with alcohols.[67] For example, ultraviolet photolysis of CH_2I_2 in low temperature 3-methylpentane glass with 1.7 mM ethanol at 77 K produces a strong ∼385 nm transient absorption band (shown to be due to the $CH_2I{-}I$ in ref 40) that decays to form bands due to an I_3^- product when the 77 K glass is allowed to warm and melt (see Figure 8 of ref 67). This indicates the $CH_2I{-}I$ species reacts with ethanol to eventually produce an I_3^- product. We note that similar experiments demonstrated ultraviolet photolysis of CH_2I_2 in a 3-methylpentane 77 K glass with 0.27 M 2-methylbutene showed a similar formation of $CH_2I{-}I$ product transient absorption band at ∼385 nm that decayed to produce an I_2:2-methylbutene complex and I_2 product absorption bands with clear isobestic points (see Figure 5 of ref 67). This indicates that $CH_2I{-}I$ reacts with olefins such as 2-methylbutene to produce an I_2 leaving group. These results for reaction with 2-methylbutene are consistent with later time-resolved Raman[40−42] and density functional theory studies that elucidated the reaction mechanism for photocyclopropanation using ultraviolet photolysis of CH_2I_2 in the presence of olefins. At this point it is unclear how the reaction of $CH_2I{-}I$ occurs but the formation of I_3^- in the low temperature studies of Brown and Simon[67] suggest that I^- or I_2^- is a leaving group of the reaction. In addition, the known reactions of other carbene species to insert into the O−H bond of alcohols suggest the reaction for $CH_2I{-}I$ with alcohols may take place via some variation of an O−H insertion insofar as the $CH_2I{-}I$ species behaves like a typical carbene.

We note that the $CH_2I{-}I$ has some radical ion pair character[40] and dissociation into CH_2I^+ and I^- could possibly take place in highly polar solvents such as the mixed aqueous solvents investigated here. Thus, the shorter lifetime of the $CH_2I{-}I$ species in the mixed aqueous solvents could possibly be explained by this dissociation reaction rather than the O−H bond insertion type reactions of a carbenoid species. However, the strong correlation of the shorter $CH_2I{-}I$ lifetimes with the amount of O−H bonds present suggests that simple dissociation of the I−I bond is likely not the main reaction pathway, although this may occur concurrently and compete with potential reactions with O−H bonds.

Our studies indicate that $CH_2I{-}I$ can be produced in largely aqueous environments and this has potential implications for atmospheric chemistry reactions occurring in solvated environments (near surfaces, aerosols, water, ice, etc). The formation of the $CH_2I{-}I$ occurs via a geminate recombination process within a solvent cage in both organic solvents and largely aqueous solvents and is unlikely to occur in the gas phase. This suggests that $CH_2I{-}I$ formation and its subsequent reactions would be phase dependent. Similar geminate recombination processes have been observed in the photodissociation of OClO in both organic and aqueous solutions.[68−73] These studies found that ground state OClO is generally re-formed vibrationally hot and some ClOO isomer is produced tens of picoseconds later via some photoisomerization process and not by geminate recombination of the fragments.[68−73] We note that in the case of polyhalomethanes such as CH_2I_2 this solvent-induced geminate recombination produces not only the parent CH_2I_2 but also a highly reactive isomer species with carbenoid character that easily reacts with carbon double bonds in a manner similar to singlet methylene.

The possibility that isopolyhalomethanes such as $CH_2I{-}I$ may be able to react with alkenes in the troposphere was previously raised when its carbene-like behavior toward carbon double bonds started to be noted.[46,47] Our observation that $CH_2I{-}I$ can be readily produced in a largely aqueous solvent suggests that this may be worthwhile to pursue further. Isoprene (2-methyl-1,3-butadiene) emissions by vegetation into the atmosphere make up about 40% of the total mass of nonmethane organic compounds released into the atmosphere, are the largest source of summertime ozone in North America, and act as a important source of HOOH to the troposphere.[74−76] In light of the $CH_2I{-}I$ species being highly reactive toward carbon double bonds found in alkenes such as isoprene and other volatile organic compounds observed in the atmosphere, it may be prudent to try to estimate the relative importance of these types of reactions for the degradation of alkenes as well as release of reactive halogens to the atmosphere. Such reactions between $CH_2I{-}I$ and other isopolyhalomethanes with alkenes would form cyclopropanated products and halogen molecule leaving groups. Relatively little is known about the chemical reactions of isopolyhalomethanes and there remains a great deal of further work to be done to measure the quantum yields for production, lifetimes, and kinetics of their reactions toward atmospherically relevant alkenes such as isoprene. This and other information are needed to help estimate the level of their influence on atmospheric chemistry. However, the relatively short lifetimes of $CH_2I{-}I$ in largely aqueous solutions and the low concentrations of polyhalomethanes and alkenes in the natural environment suggest isopolyhalomethane reactions will probably only play a minor role in atmospheric chemistry.

The probable reactions of $CH_2I{-}I$ and other isopolyhalomethanes toward O−H bonds in water similar to O−H insertion reactions for singlet methylene and other carbenes with alcohols (or water) would potentially be of greater importance to atmospheric chemistry because these are reactions with the solvent molecule prevalent in the natural environment. Further work is in progress to investigate the chemical reactivity of isopolyhalomethanes such as $CH_2I{-}I$ toward O−H bonds in alcohols and H_2O.

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Supporting Information Available: Two figures of ps-TR^3 obtained in CH_3OH and H_2O/CH_3CN solvents. This material is available free of charge via the Internet at http://pubs.acs.org.

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