| Title       | Comparison of the dehalogenation of polyhalomethanes and production of strong acids in aqueous and salt (NaCl) water environments: Ultraviolet photolysis of CH₂I₂ |
|-------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------
| Author(s)   | Guan, X; Du, Y; Li, YL; Kwok, WM; Phillips, DL                                                                                                                                                    |
| Citation    | Journal Of Chemical Physics, 2004, v. 121 n. 17, p. 8399-8409                                                                                                                                   |
| Issued Date | 2004                                                                                                                                                                                            |
| URL         | http://hdl.handle.net/10722/42366                                                                                                                                                              |
| Rights      | This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License.                                                                           |
Comparison of the dehalogenation of polyhalomethanes and production of strong acids in aqueous and salt (NaCl) water environments: Ultraviolet photolysis of CH$_2$I$_2$

Xiangguo Guan, Yong Du, Yun-Liang Li, Wai Ming Kwok, and David Lee Phillips

Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong, People's Republic of China

(Received 29 March 2004; accepted 13 August 2004)

The ultraviolet photolysis of CH$_2$I$_2$ was studied in water and salt water solutions using photochemistry and picosecond time-resolved resonance Raman spectroscopy. Photolysis in both types of environments produces mainly CH$_2$(OH)$_2$ and HI products. However, photolysis of CH$_2$I$_2$ in salt water leads to the formation of different products/intermediates (CH$_3$Cl and Cl$_2$) not observed in the absence of salt in aqueous solutions. The amount of CH$_2$(OH)$_2$ and HI products appears to decrease after photolysis of CH$_2$I$_2$ in salt water compared to pure water. We briefly discuss possible implications of these results for photolysis of CH$_2$I$_2$ and other polyhalomethanes in sea water and other salt aqueous environments compared to nonsalt water solvated environments.


I. INTRODUCTION

The photochemistry and chemistry of a range of polyhalomethanes such as CH$_2$I$_2$, CH$_3$BrI, CHBr$_3$, CCl$_4$, CFCl$_3$, and others have been observed in the atmosphere and are important sources of reactive halogens in the natural environments.$^{1-8}$ The photochemistry of CH$_2$I$_2$ and CH$_3$BrI have been linked to the production of IO during localized ozone-depletion events in the marine boundary layer of the troposphere.$^{7,8}$ The photochemistry of CH$_2$I$_2$ was also recently linked to the formation of iodine aerosols although the mechanism for formation remains unclear.$^9$ Both gas and condensed phase photochemistry and chemistry are important for describing chemical reaction processes in the natural environment.$^{7,8,9}$

Reactions relevant to the activation of halogens in aqueous sea-salt particles have received much interest.$^9$–$^{21}$ Recent experiments have found that the water dimer is present at 294 K and it was suggested that larger water clusters (with $n = 3$–$6$) may also exist in amounts comparable to ambient aerosol in the background troposphere.$^{22}$ A theoretical investigation employing complete basis set-atomic pair natural orbit basis set atomic (CBS-APNO) free energies to estimate the number of higher order water clusters found excellent agreement between a predicted calculated concentration of $4 \times 10^{14}$ water dimers/cm$^3$ compared to the experimental value of $6 \times 10^{14}$ water dimers/cm$^3$ at a temperature of 292.4 K.$^{22,23}$

Ultraviolet photolysis of polyhalomethanes in the gas phase typically results in one direct carbon-halogen bond scission reaction to produce halomethyl radical and halogen atom fragments.$^{24-40}$ In condensed phase environments, these initially produced photofragments can undergo solvent induced geminate recombination to form appreciable amounts of isopolyhalomethanes.$^{41-59}$ We have recently investigated the chemical reactivity of isopolyhalomethanes both theoretically and experimentally and found they are carbonoid species that can react with C=C bonds in olefins to produce cyclopropanated products and a halogen molecule leaving group.$^{54,55,60-67}$ The experimental and theoretical results for the isodiiodomethane species indicated that it is probably the predominant carbonoid responsible for the cyclopropanation of olefins when employing the method of ultraviolet photolysis of CH$_2$I$_2$ and a reaction mechanism was proposed.$^{60-62,65,67}$ Other isopolyhalomethanes were also found to be able to undergo similar reactions with C=C bonds of olefins.$^{54,55,63-64,67}$

Carbenoids and carbenes such as singlet methylene and dichlorocarbenene can also react via O-H insertion reactions with the O-H bonds of water and alcohols.$^{68-77}$ For example, the reactions of singlet methylene and dichlorocarbenene with water give CH$_3$OH and CHCl$_2$OH products, respectively.$^{68-77}$ We have recently used picosecond time-resolved resonance Raman (ps-TR$_3$) experiments to directly observe the reaction of isobromoform with water to produce a CHBr$_2$OH product species.$^{78,79}$ This indicates isopolyhalomethanes are also able to react with water to make halogenated methanol products.$^{78,79}$ A recent study of the ultraviolet photolysis of low concentrations of CH$_2$I$_2$ in water found that this resulted in almost complete conversion into CH$_2$(OH)$_2$ and 2HI products.$^{80}$ Ps-TR$_3$ spectra in mixed aqueous solvents (25% to 75% water) found appreciable amounts of isodiiodomethane (CH$_2$I–I) were produced within several picoseconds and its decay became significantly faster with increasing water concentration suggesting the CH$_2$I–I species could be reacting with water. Ab initio calculations indicate the CH$_2$I–I species reacts readily with water via a water catalyzed O-H insertion/HI elimination reaction followed by its CH$_2$IOH product decaying via a water catalyzed HI elimination reaction to produce a formaldehyde product that further reacts with water to produce the
methanediol \([\text{CH}_2(\text{OH})_2]\) final product observed in the photochemistry experiments.\(^\text{80}\)

In this paper, we investigate the photochemistry of \(\text{CH}_2\text{I}_2\) in salt water environments and compare these results to those previously found in pure water and/or water/acetonitrile mixed solvents. These results should help better understand the photochemistry of \(\text{CH}_2\text{I}_2\) and other polyhalomethanes found in sea water in the marine boundary layer. Photochemistry and time-resolved resonance Raman experiments indicate that the \(\text{Cl}^-\) ions from salt (\(\text{NaCl}\)) can scavenge some of the initial \(\text{CH}_2\text{I}\) and \(\text{I}\) photofragments produced after ultraviolet photolysis of the parent \(\text{CH}_2\text{I}_2\) molecule to make \(\text{Cl}_2\) and \(\text{CH}_2\text{Cl}\) products/intermediates. However, there is still substantial solvent induced geminate recombination of the initial photofragments to make isodiodomethane that then reacts with water to eventually produce \(\text{CH}_2(\text{OH})_2\) and \(\text{HI}\) products. We briefly discuss the likely implications for the phase dependent photochemistry of \(\text{CH}_2\text{I}_2\) and other polyhalomethanes in different natural environments that contain substantial quantities of saltlike sea water and aqueous sea-salt particles and those that contain little or no saltlike fresh water droplets and/or ice particles.

II. EXPERIMENTAL DETAILS

A. Photochemistry experiments

Sample solutions were prepared using commercially available \(\text{CH}_2\text{I}_2\) (99%), \(^{13}\text{CH}_2\text{I}_2\), formaldehyde in water (reagent grade), \(\text{D}_2\text{O} 99.9\%\) D, de-ionized water, and \(\text{NaCl}\). Samples of about \((1 \times 10^{-4}) M\) \(\text{CH}_2\text{I}_2\) in water and \(0.5 M\) \(\text{NaCl}\) solution were prepared for use in the photochemistry experiments. These sample solutions were put in a 10 cm path length glass holder with quartz windows and excited by an about 3 mJ 266 nm unfocused laser beam from the fourth harmonic of a Nd:Y AG—yttrium aluminum garnet laser in the photolysis experiments. The absorption spectra for the photolyzed samples were acquired with a 1 cm UV grade cell and a Perkin Elmer Lambda 19 UV/VIS spectrometer. The \(pH\) of the photolyzed samples was obtained using a THERMO Orion 420A \(pH\) meter using a 8102BN combination electrode that was calibrated with 7.00 \(pH\) and 4.01 \(pH\) buffer solutions. Both the \(^{13}\text{C}\) and \(^1\text{H}\) NMR spectra were acquired using a Bruker Advance 400 DPX spectrometer and \(\phi=5 \text{ mm}\) sample tubes at room temperature.

B. Picosecond time-resolved resonance Raman (ps-TR\(^3\)) spectroscopy experiments

A commercial femtosecond mode-locked Ti: sapphire regenerative amplifier laser was used for the experiments. The output from the laser (800 nm, 1 ps, 1 kHz) was doubled and tripled to by potassium dihydrogen phosphate (KDP) crystals to produce the 400 nm probe and 267 nm pump excitation wavelengths used in the experiments. Fluorescence depletion of \(\text{trans}\)-stilbene was used to determine the time-zero delay between the pump and probe laser beams by varying the optical delay between the pump and probe beams to a position were the depletion of the stilbene fluorescence was halfway to the maximum fluorescence depletion by the probe laser. The time-zero determination was estimated to be accurate to \(\pm 0.5 \text{ ps}\) and a typical cross correlation time was found to be about 1.5 ps full width at half maximum. The pump and probe laser beams with magic angle polarization were loosely focused onto a flowing liquid stream of sample (about 500 \(\mu\text{m}\) thick) with typical pulse energies and spot sizes at the sample of 15 \(\mu\text{J}\) and 250 \(\mu\text{m}\) for the pump beam and 8 \(\mu\text{J}\) and 150 \(\mu\text{m}\) for the probe beam. A backscattering geometry was used to excite the sample and to collect the Raman scattered light that was then imaged through the entrance slit of a 0.5 m spectrometer. The grating (1200 groove/mm blazed at 250 nm) of the spectrometer dispersed the Raman light onto a liquid nitrogen cooled CCD detector mounted on the exit port of the spectrometer.

Each spectrum shown for our present study was obtained from subtraction of scaled probe-before-pump and scaled net solvent measurements from a pump-probe spectrum in order to remove the ground state \(\text{CH}_2\text{I}_2\) Raman bands and residual solvent Raman bands, respectively. The known Raman shifts of the solvent Raman bands were employed to calibrate the spectra with an estimated uncertainty of \(\pm 5 \text{ cm}^{-1}\) in absolute frequency. Commercially available \(99\%\) \(\text{CH}_2\text{I}_2\), spectrscopic grade acetonitrile, and \(\text{NaCl}\) were used to prepare half liter volume \(\text{CH}_2\text{I}_2\) \((7 \times 10^{-3} M)\) sample solutions with varying salt concentrations (0, 0.2M, and 0.5M \(\text{NaCl}\)) and water concentrations (0%, 25%, 50% and 75% by volume). The samples showed less than a few percent decomposition during the experiments as determined from UV/VIS spectra taken before and after the ps-TR\(^3\) measurements.

C. Nanosecond time-resolved resonance Raman (ns-TR\(^3\)) spectroscopy experiments

The ns-TR\(^3\) experimental apparatus and methods have been detailed previously\(^{62,64,65}\) so only a short description will be given here. The ns-TR\(^3\) experiments employed two Nd:YAG lasers that were electronically synchronized via a pulse delay generator to control the relative timing of their flashlamps and \(Q\) switches. The relative timing of the 266 nm pump and 255 nm probe laser pulses was monitored using a fast photodiode whose output was displayed on a 500 MHz oscilloscope. The jitter was found to be \(<5 \text{ ns}\). The laser beams were lightly focused onto a flowing liquid stream of sample using a near collinear geometry and the Raman scattered light was acquired using a backscattering geometry. The Raman light was then imaged through a depolarizer and entrance slit of a 0.5 m spectrometer and dispersed by a grating onto a liquid nitrogen cooled CCD detector mounted on the exit of the spectrometer. The Raman signal was accumulated for about 300 to 600 s by the CCD detector before being read out to an interfaced PC computer. About 10–20 of these readouts were summed to obtain a resonance Raman spectrum. Pump-only, probe-only, and pump-probe resonance Raman spectra were acquired as well as a background scan. The probe-only spectrum was subtracted from the pump-probe spectrum to remove precursor and solvent Raman bands, and then the pump-only spectrum and background scan were also subtracted in order to obtain the time-resolved resonance Raman spectrum.

The known Raman shifts of the solvent Raman bands were used to calibrate the spectra with an estimated uncer-
tainty of ±5 cm⁻¹ in absolute frequency. Commercially available K₂S₂O₈ and NaCl 99% were used to prepare a sample solution. This sample with 0.05 M K₂S₂O₈ and 0.5 M NaCl in a 75% water/25% acetonitrile solution was photolyzed to produce an authentic Cl₂NaCl in a 75% water/25% acetonitrile solution was photo-indicating the I⁻ ion in the 225 nm region increase in intensity as a new absorption band due to I₂ appears at about 252 nm with a clear isobestic point at 253 nm. The I₂ absorption band is essentially identical to that found for KI salt dissolved in water and NaCl solutions.

Fig. 1 reveals that in both cases the absorption bands due to CH₂I₂ in pure water and NaCl aqueous solution are identical to that found for CH₂I₂, I₂ and spectroscopic grade acetonitrile and NaCl were used to prepare half liter volume CH₂I₂[(1×10⁻²)M] and I₂[(2×10⁻³)M] sample solutions with 0.5 M NaCl in a 75% water/25% acetonitrile by volume solvent. UV/VIS spectra taken before and after the ns-TR³ measurements indicated the samples showed less than a few percent decomposition over the experiments.

III. RESULTS AND DISCUSSION

A. Product analysis of CH₂I₂ ultraviolet photolysis in water and salt water

Figure 1 shows ultraviolet/visible spectra acquired following photolysis for varying times using 266 nm laser excitation of a (1×10⁻³)M CH₂I₂ sample in pure water (A) and in salt water solution (0.5M NaCl) (B). Examination of Fig. 1 reveals that in both cases the absorption bands due to CH₂I₂ in the 280–320 nm region decrease in intensity while those due to the I⁻ ion in the 225 nm region increase in intensity as the time for photolysis increases. Inspection of Fig. 1 shows there is a clear isobestic point at around 253 nm indicating the I⁻ is directly produced from the CH₂I₂ parent molecule. The pH of the sample solutions was also measured at the same time the absorption spectra were acquired. The molar extinction coefficients for CH₂I₂ and I⁻ were used to find the concentrations of these species for each of the photolysis times from the UV/VIS spectra presented in Fig. 1 and the change in the concentration of H⁺ was determined from the pH measurements. Plots of Δ[Γ⁻] versus Δ[CH₂I₂] during the photochemistry experiments were made and are presented in (a) and (c) of Fig. 2. The increase in [Γ⁻] versus the decrease in [CH₂I₂] during the photochemistry experiments reveal a linear relationship with a slope of about 2 for the experiments done in pure water solvent and a slope of about 1.4 in the salt water (0.5 M NaCl) solvent. These results indicate that ultraviolet photolysis of CH₂I₂ at low concentrations in water and salt water (0.5M NaCl) solvents releases about 2I⁻ and 1.4I⁻ final products, respectively. Plots of the changes in the [H⁺] concentrations found from the pH measurements were plotted versus the changes in the [Γ⁻] concentrations and these are given in (b) and (d) of Fig. 2. The plots of Δ[Γ⁻] versus Δ[CH₂I₂] have linear correlation and slopes of about 1 and 0.8, respectively for CH₂I₂ photolysis in pure water and in salt water (0.5 M NaCl), respectively. The preceding results from the UV/VIS and pH photochemistry experiments presented in Figs. 1 and 2 indicate that photolysis of low concentrations of CH₂I₂ produces 2H⁺ and 2I⁻ products in pure water and about 1.15H⁺ and 1.4I⁻ products in the 0.5 M NaCl salt water solvent. Most of the H⁺ and Γ⁻ products formed are probably from HI leaving group(s) that dissociate into H⁺ and I⁻ in the aqueous solvents.
To learn more about the fate of the carbon atom from the CH₂I₂ parent molecule after ultraviolet photolysis in the salt water (0.5 M NaCl) solvent, we employed a carbon-13 labeled sample of CH₂I₂. We then repeated the ultraviolet photolysis experiments given in Figs. 1 and 2 and obtained ¹H-NMR and ¹³C-NMR spectra before, during, and after complete photolysis of ¹³CH₂I₂ in D₂O salt water (0.5 M NaCl) solvent as shown in Fig. 3. Spectra obtained in the pure water solvent were essentially the same as that reported in Ref. 80 and the reader is referred to Figs. 1 and 3 for the ¹H-NMR and ¹³C-NMR spectra for the spectra found for photolysis of CH₂I₂ in pure water. The ¹H-NMR and ¹³C-NMR bands due to the parent ¹³CH₂I₂ (3.9 and −63.9 ppm, respectively) are labeled in Fig. 3 and upon photolysis these bands become noticeably smaller and new bands due to ¹³CH₂(OD)₂ (doublet at 4.7 ppm and 82.5 ppm, respectively) and ¹³CH₂ICl (doublet at 5 and 2.8 ppm, respectively) were produced (see middle spectra of Fig. 3). The assignment of spectral bands for the ¹³CH₂(OD)₂ and ¹³CH₂ICl products were confirmed by comparison to spectra of authentic samples of methandiol and CH₂ICl. Further ultraviolet photolysis appears to also convert the ¹³CH₂ICl product into ¹³CH₂(OD)₂ (see bottom spectra of Fig. 3). This prompted us to also do an analogous photochemistry experiment using CH₂ICl in pure D₂O solvent and taking ¹H-NMR spectra before, during, and after 266 nm photolysis as shown in Fig. 4. Inspection of Fig. 4 shows that ultraviolet photolysis of CH₂ICl in pure D₂O appears to produce methanediol [CH₂(OD)₂] product and these results are consistent with those we found in the photolysis of CH₂I₂ in salt water as shown in Fig. 3.

The preceding experimental photochemistry results suggest that the main reaction occurring after ultraviolet photolysis of low concentrations of CH₂I₂ in pure water and salt water leads to the following overall reaction:

\[
\text{CH}_2\text{I}_2 + h\nu + n\text{H}_2\text{O} \rightarrow \text{CH}_2\text{(OH)}_2 + 2\text{HI} + (n - 2)\text{H}_2\text{O.}
\] (1)
However, in the salt water solution this reaction is not the only significant one and the formation of the CH$_2$ICl product lowers the amount of formation of both the CH$_2$(OH)$_2$ and HI products which indicates another reaction is competing with the main overall reaction given in Eq. (1).

We note that photochemistry experiments done with an unfocused nanosecond laser beam and a Hg lamp source of light resulted in essentially the same results for the production of the products for low concentrations of CH$_2$I$_2$ in water and salt water. The reader is referred to Ref. 80 for a comparison of the laser photolysis and the Hg photolysis experiments in pure water. This indicates the photoproducts observed in Figs. 1–4 are produced mainly from one-photon excitation of CH$_2$I$_2$.

To help better understand how the ultraviolet photolysis of CH$_2$I$_2$ in salt water leads to mainly formation of methandiol [CH$_2$(OH)$_2$] and HI products accompanied by CH$_2$ICl product, we have done additional picosecond and nanosecond time-resolved resonance Raman (ps-TR$^3$ and ns-TR$^3$, respectively) experiments in salt water environments and compare them to results previously found in pure water. This is detailed in the following section.

B. Picosecond and nanosecond time-resolved resonance raman experiments

Figure 5 shows ps-TR$^3$ spectra obtained following 267 nm photolysis of CH$_2$I$_2$ in H$_2$O/CH$_3$CN mixed solvents with different concentrations of NaCl using a 400 nm probe excitation wavelength. Spectra in Figs. 5(a)–5(c) were obtained in 0.0M, 0.2M and 0.5M NaCl in 75% H$_2$O/25% CH$_3$CN solution, respectively. Spectra in Figs. 5(d) and 5(e) were obtained using the same NaCl concentration (0.2M) with different water concentrations of 50% H$_2$O/50% CH$_3$CN and 75% H$_2$O/25% CH$_3$CN solutions, respectively. The Raman bands observed for the first photoproduct species (from several picoseconds to several hundred picoseconds) are straight forward to assign to the isodiiodomethane (CH$_2$I–I) species and the reader is referred to Refs. 49, 52, and 59 for details of the assignment.

Inspection of Fig. 5 shows that the CH$_2$I–I photoproduct Raman bands appear within several picoseconds and then decay on the hundreds of picosecond to nanosecond time scale. As the salt concentration increases in Figs. 5(b) and 5(c) new photoproduct bands appear in the 500 ps to 5000 ps time scale that are not found in the spectra obtained in pure water (a). The new photoproduct Raman bands only appear in the presence of appreciable amounts of NaCl in the aqueous solution. Examination of the ps-TR$^3$ spectra in Figs. 5(d) and 5(e) obtained at the same salt concentration (0.2M NaCl) but with different water concentrations (with 50% H$_2$O and 75% H$_2$O, respectively) reveals that the new photoproduct Raman bands appear the same at 5000 ps. However, the decay of the CH$_2$I–I species becomes substantially faster at higher H$_2$O concentration and indicates that the CH$_2$I–I species reacts with H$_2$O. The results shown in Figs. 5(d) and 5(e) indicate the decay of the CH$_2$I–I species is not linked to the growth of the new photoproduct species Raman bands observed at 5000 ps and some other reaction is responsible for these bands.

The CH$_2$I–I Raman bands near 715 cm$^{-1}$ assigned to the fundamental C–I stretch mode ($v_3$) was integrated at different time delays so as to determine the kinetics of the growth and decay of the CH$_2$I–I species. Figure 6 (top) presents plots of the relative integrated area of the $v_3$ Raman band from 0 to 3000 ps in the 0.0M (solid square), 0.2M (solid star) and 0.5M (open triangle) NaCl in 75% H$_2$O/25% CH$_3$CN mixed solutions. Figure 6 (bottom) shows plots of the relative integrated area of the $v_3$ Raman band from 0 ps to 6000 ps in the 0.2M NaCl in 50% H$_2$O/50% CH$_3$CN (solid triangle) and 75% H$_2$O/25% CH$_3$CN (solid star) mixed solutions. The relative integrated areas of the $v_3$ Raman bands were fit to a simple function $I(t) = Ae^{-t/t_1} - Be^{-t/t_2}$ (dashed lines in Fig. 6 represent these fits), where $I(t)$ is the relative integrated area of the $v_3$ Raman band, $t$ is the time, $t_1$ is the decay time constant of the $v_3$ Raman band, $t_2$ is the growth time constant of the $v_3$ Raman band, and $A$ and $B$ are constants. The fits to the data in the top of Fig. 6 found the CH$_2$I–I species had growth time constants $t_2$ of about 6, 7, and 7 ps, and decay time constants $t_1$ of about 650, 480, and 430 ps for the 0.0M, 0.2M and 0.5M NaCl in 75% H$_2$O/25% CH$_3$CN so-
The fits to the data at the bottom of Fig. 6 found the CH$_2$I–I species had growth time constants $t_2$ of about 10 ps and 7 ps and decay time constants $t_1$ of about 1580 ps and 480 ps for the 0.2 M NaCl in 50% H$_2$O/50% CH$_3$CN and 75% H$_2$O/25% CH$_3$CN solutions, respectively.

The growth time constants for the CH$_2$I–I species are very similar in the different water and salt concentrations (all in the 6–10 ps range) and consistent with its formation by some solvent induced geminate recombination of the initially produced CH$_2$I radical and I atom photofragments as has been found previously in organic solvents and in mixed water solvents. The decay of the CH$_2$I–I species in salt water solutions with varying concentrations of salt becomes only moderately faster with increasing salt concentration (time constants of about 480 ps for 0.2 M NaCl and 430 ps for 0.5 M NaCl). The CH$_2$I–I species has appreciable radical ion pair character (e.g., such as CH$_2$I$^+I^-$) which would be expected to be perturbed by a changing solvent polarity or dielectric properties. Thus, the modest changes in the CH$_2$I–I decay time in different salt concentrations can probably be attributed to a moderate change in the stability of the CH$_2$I–I species in the salt solutions rather than some reaction with NaCl. This is consistent with previous observations that the lifetime of CH$_2$I–I does vary noticeably with the polarity of the solvent and the lack of any correlation of the CH$_2$I–I decay time with the appearance time of the second product species observed at longer delay times.

One possibility for the formation of the CH$_2$ICl product could be reaction of the initially formed CH$_2$I radical with H$_2$O. We observe almost identical behavior in the salt water solutions investigated here and similarly attribute this to the O–H insertion reaction of the CH$_2$I–I carbenoid species with H$_2$O as deduced in Ref. 80.

One of the photoproducts observed in the salt water photochemistry experiments is CH$_2$ICl and this species is not observed in the nonsalt water photochemistry experiments. One possibility for the formation of the CH$_2$ICl product could be reaction of the initially formed CH$_2$I radical photofragment with a nearby NaCl. If this occurs then one could expect the other I atom photofragment could be readily scavenged by Cl$^-$ ions from NaCl as well. Therefore, we performed 267 nm pump and 400 nm probe ps-TR$_3$ experiments with I$_2$ in a 0.5 M NaCl 75% H$_2$O/25% CH$_3$CN solution and compared this to the analogous experiment for CH$_2$I$_2$ and these spectra are shown in Fig. 7. Ultraviolet (267 nm) photolysis of I$_2$ would be expected to produce two I atom photofragments and it would be reasonable to expect that some of these may directly react with NaCl on the picosecond to nanosecond time scale. This is precisely what is observed in the ps-TR$_3$ spectra obtained after photolysis of I$_2$ in 0.5 M

![FIG. 7. Comparison of Stokes ps-TR$_3$ spectra obtained following 267 nm photolysis of I$_2$ (a) and CH$_2$I$_2$ (b) in solutions of 0.5 M NaCl in 75% H$_2$O/25% CH$_3$CN solvent. See text for more details.](Image)
NaCl 75% H₂O/25% CH₃CN solution. The fundamental vibrational frequency of 265 cm⁻¹ observed for the predominant progression of the photoproduct is in good agreement with the 271–273 cm⁻¹ observed previously for the Cl₂ time-resolved resonance Raman spectrum with 355 nm or 359 nm excitation. In the TR³ experiments of Tripathi, Schuler, and Fessenden, the Cl₂ and other dihalides such as Br₂ and I₂ were produced by OH oxidation of the halide,

\[ \text{OH} + X^- \rightarrow X + \text{OH}^- , \]

(2)

\[ X + X^- \rightarrow X_2^- , \quad \text{where} \quad X = \text{Cl, Br, I}. \]

(3)

The analogous reactions for I atoms with NaCl would be the following:

\[ \text{I} + \text{Na}^+ \text{Cl}^- \rightarrow \text{Cl}^- + \text{Na}^+ \text{I}^- , \]

(4)

\[ \text{Cl}^- + \text{Cl}^- \rightarrow \text{Cl}_2^- . \]

(5)

However, the I⁻/I⁻ one electron redox potential in water is \( \approx 1.3 \text{ eV} \) while the Cl⁻/Cl₂⁻ one electron redox potential in water is \( \approx 2.4 \text{ eV} \) and this makes the overall reaction \( \text{I} + \text{Cl}^- \rightarrow \text{Cl}^- + \text{I}^- \) endothermic by about 1.1 eV. This indicates the I⁺ + Cl⁻ → Cl⁺ + I⁻ reaction should not occur at an appreciable rate and thus is inconsistent with the fast formation observed in the ps-TR³ experiments. Therefore, some other mechanism than that given by Eqs. (4) and (5) must be responsible for the formation of Cl₂⁻.

We performed additional ns-TR³ experiments to produce an authentic Cl₂⁻ resonance Raman spectrum based on another known method of photolysis of persulphate in the presence of Cl⁻ ions similar to that done by Hynes and Wine in Ref. 81. At the same time we obtained spectra at about 5–10 ns after photolysis of samples of I₂ and CH₂I₂ in 0.5M NaCl in 75% water/25% acetonitrile solvent. These ns-TR³ spectra are shown in Fig. 8. Figure 8(a) displays the Cl₂⁻ ns-TR³ spectrum generated by photolysis of persulphate in the presence of Cl⁻ ions. This resonance Raman spectrum is in excellent agreement with that previously reported by Hynes and Wine using a similar method in Ref. 81. The Raman band shifts for the first three bands in Fig. 8(a) are about 275 cm⁻¹, 542 cm⁻¹, and 808 cm⁻¹ and these are in excellent agreement with those of 273±2 cm⁻¹, 543±2 cm⁻¹, 808±2 cm⁻¹ reported in Ref. 81. Thus, we are confident the spectrum shown in Fig. 8(a) is due to the Cl₂⁻ species. Comparison of this Cl₂⁻ resonance Raman spectra [Fig. 8(a)] to those obtained at about 5–10 ns after 266 nm photolysis of I₂ and CH₂I₂ in a 0.5M NaCl 75% water/25% acetonitrile solvent shows that essentially the same resonance Raman bands are found in both cases. This indicates Cl₂⁻ is also produced after photolysis of I₂ and CH₂I₂ in a 0.5M NaCl 75% water/25% acetonitrile solvent. In the spectrum shown in Fig. 8(c), some isodiiodomethane resonance Raman bands (labeled by iso) are also present similar to the 400 nm ps-TR³ spectra shown in Figs. 5 and 7.

The ps-TR³ spectra in Fig. 7 obtained after photolysis of I₂ in 0.5M NaCl 75% H₂O/25% CH₃CN solution is almost identical to that shown in the ns-TR³ experiments shown in Fig. 8 and those previously observed for Cl₂⁻. The ps-TR³ spectra for the Cl₂⁻ species produced from photolysis of I₂ in 0.5M NaCl 75% H₂O/25% CH₃CN solution are essentially identical to the ps-TR³ spectra of the second photoproduct species observed after 267 nm photolysis of CH₂I₂ in 0.5M NaCl 75% H₂O/25% CH₃CN solution. Therefore this second photoproduct species is also assigned to Cl₂⁻ produced from the reaction of I atoms with NaCl. This is consistent with its ps-TR³ spectral intensity becoming greater and having a faster appearance time as the concentration of the NaCl increases in the spectra shown in Figs. 7(b) and 7(c).

A possible mechanism that may account for fast formation of Cl₂⁻ after photolysis of I₂ and CH₂I₂ in NaCl water/acetonitrile mixed solvents could be the following:

\[ \text{I} + \text{Cl}^- \rightarrow \text{ICl}^- , \]

(6)

\[ \text{ICl}^- + \text{Cl}^- \rightarrow \text{Cl}_2^- + \text{I}^- . \]

(7)

Reaction step (6) would be expected to occur very fast since the I⁻ ion could be scavenged by the high concentration of Cl⁻ in the solution and is forming a new I⁻Cl⁻ bond. Reaction step (7) may also be very fast since the Cl⁻ concentration is very high and it is forming a moderately stronger bond (Cl₂⁻) than it is breaking (ICl⁻). Photolysis of I₂ in the salt water solutions did not produce any obvious Raman bands due to ICl⁻ at either the 400 nm or 355 nm probe wavelengths used in the ps-TR³ and ns-TR³ spectra shown in Figs. 7 and 8, respectively. This could suggest that ICl⁻ may be very short lived and not a stable species in the presence of Cl⁻ ions. It is conceivable that reaction steps (6) and (7) both occur very fast and thus there may not be enough buildup of the ICl⁻ concentration to see a large signal from this species.
in the TR$^3$ spectra examined thus far. The mechanism in reaction steps (6) and (7) is plausible for the fast formation of Cl$^{-}$ after ultraviolet photolysis of I$_2$ and CH$_2$I$_2$ in NaCl water/acetonitrile mixed solvents, but more experimental and theoretical work needs to be done to clearly establish the actual mechanism of Cl$^{-}$ formation. This should prove an interesting area of investigation for the photolysis of iodoalkanes in salt water environments.

C. Proposed reaction mechanism for the CH$_2$I$_2$ + hv + n(H$_2$O) → CH$_2$(OH)$_2$ + 2HI + (n - 2)H$_2$O overall reaction in water and salt water environments and formation of CH$_2$ICl and Cl$_2$ products in the presence of salt (NaCl)

Based on our present experimental results and other work already available in the literature, we propose the following reaction mechanism for the CH$_2$I$_2$ + hv + n(H$_2$O) → CH$_2$(OH)$_2$ + 2HI + (n - 2)H$_2$O overall reaction that we observe for photolysis of low concentrations of CH$_2$I$_2$ in aqueous solutions with and without NaCl present: Photolysis of CH$_2$I$_2$ to form CH$_2$I and I fragments

Step 1 CH$_2$I$_2$ + hv → CH$_2$I + I.

Solvent induced geminate recombination of the CH$_2$I and I fragments to form the CH$_2$I--I isomer

Step 2 CH$_2$I + I → CH$_2$I--I.

Water-catalyzed O–H insertion/HI elimination reaction of CH$_2$I--I with H$_2$O solvent

Step 3 CH$_2$I--I + n(H$_2$O) → CH$_2$I(OH) + HI + (n - 1)H$_2$O.

Water-catalyzed HI elimination reaction of CH$_2$I(OH) with H$_2$O solvent

Step 4 CH$_2$I(OH) + n(H$_2$O) → H$_2$CO + HI + n(H$_2$O).

Water (and/or acid) catalyzed addition of H$_2$O to H$_2$CO in H$_2$O solvent

Step 5 H$_2$CO + n(H$_2$O) → CH$_2$(OH)$_2$ + (n - 1)H$_2$O.

Add steps 1–5 to obtain this overall reaction

CH$_2$I$_2$ + hv + n(H$_2$O) → CH$_2$(OH)$_2$ + 2HI + (n - 2)H$_2$O.

Ultraviolet excitation of CH$_2$I$_2$ in both gas and solution phases is known to result in direct cleavage of the C–I bond to produce CH$_2$I radical and I atom fragments. This indicates step 1 in the above reaction mechanism is the primary photochemical start of the reaction. It has been clearly experimentally shown that some of the initially produced CH$_2$I radical and I atom fragments undergo solvent induced geminate recombination to form a CH$_2$I--I isomer species within a few picoseconds. This establishes that step 2 of the proposed reaction mechanism occurs to an appreciable degree in room temperature solutions and our present ps-TR$^3$ spectra in largely aqueous solvents shows this also occurs in water and salt water solutions.

Previous experimental and theoretical work indicate that isopolyhalomethanes such as CH$_2$I--I are effective carbenoid species that readily react with C=C bonds in olefins to make cyclopropanated products and also undergo O–H insertion reactions with water to produce halogenated methanols. We have also used ps-TR$^3$ experiments to directly observe this type of isopolyhalomethane O–H insertion reaction for the isobromofrom species reaction with water to form a dibromomethanol (CHBr$_2$OH) reaction product. Recent ab initio results indicate that CH$_2$I--I can undergo a water catalyzed O–H insertion/HI elimination reaction with water reasonably easily. These previous studies and our present observation of the much faster decay of the CH$_2$I--I species with increasing water concentration in both nonsalt and salt aqueous solutions indicate that CH$_2$I--I reacts mainly with water to produce an iodomethanol product and HI leaving group consistent with step 3 of the proposed reaction mechanism.

Chloromethanol is known to decompose in the dark to formaldehyde (H$_2$CO) and HCl products in both the gas phase and in the condensed phase (e.g., low temperature matrices). In so far as iodomethanol (CH$_2$IOH) behaves such as chloromethanol (CH$_2$ClOH) then one would expect iodomethanol (CH$_2$IOH) to decay into H$_2$CO and HI products consistent with step 4 of the proposed reaction mechanism. Recent ab initio calculations showed that iodomethanol (CH$_2$IOH) undergoes a water assisted HI elimination reaction to produce H$_2$CO and HI products and this provides further support for step 4 of the reaction mechanism. Formaldehyde (H$_2$CO) is known to react with water to produce methanediol [CH$_2$(OH)$_2$ bien. Thus one would expect the H$_2$CO product to be efficiently converted to methanediol (CH$_2$(OH)$_2$) in a water solvated environment consistent with step 5 of the proposed reaction mechanism.

The proposed reaction mechanism given here helps explain how photolysis of low concentrations of CH$_2$I$_2$ in aqueous solutions and salt (NaCl) aqueous solutions leads to formation of significant amounts of methanediol [CH$_2$(OH)$_2$] and HI products that are observed in our $^{13}$C-NMR, $^1$H-NMR, UV/VIS, and pH photochemistry results in both aqueous solutions and salt (NaCl) aqueous solutions (this work, see Figs. 1–3). The proposed reaction mechanism is also consistent with the known photolysis of CH$_2$I$_2$ in the gas and solution phases to make CH$_2$I radical and I photofragments. The reaction mechanism is also consistent with the direct ps-TR$^3$ observation of the CH$_2$I--I intermediate and its known chemical reactivity, the known chemistry of halomethanols and the known hydrolysis of H$_2$CO in aqueous environments.

In salt (NaCl) water solutions, two different products and/or intermediates (CH$_2$ICl and Cl$_2$) are observed that are not discernible in nonsalt aqueous solutions. This suggests these products is/are produced from some reaction(s) with NaCl. The formation of these products (CH$_2$ICl and Cl$_2$) in salt aqueous solutions also lower the relative amounts of I$^{-}$ and H$^+$ produced per CH$_2$I$_2$ molecule photolyzed (see Figs. 1 and 2). This suggests that the amount of the highly reactive CH$_2$I--I species produced that then further reacts with water to eventually form 2 HI leaving groups may be less in the presence NaCl than in nonsalt aqueous solutions.

It is conceivable that reactions of NaCl with the initially produced CH$_2$I radical and I atom from the ultraviolet photolysis of the CH$_2$I$_2$ molecule can account for both a lower yield of the very reactive isiodiodomethane (CH$_2$I--I) intermediate and the formation of the different CH$_2$ICl and Cl$_2$ products. For example, the reaction of I atoms with Cl$^{-}$ via...
reaction (6) to make an ICl\(^-\) product where the ICl\(^-\) subsequently reacts with a Cl\(^-\) ion via reaction (7) to make the Cl\(_2\) species can possibly explain the formation of the Cl\(_2\) species. The Cl\(_2\) species was observed in the TR\(^3\) experiments (see Figs. 7 and 8 as well as the discussion of the last part of Sec. III B). Similarly, the formation of the CH\(_2\)ICl product observed in the NMR photochemistry experiments (see Fig. 3) can conceivably be produced from one or more of the following reactions of CH\(_2\)I radicals with species known to be present in the system (Na\(_2\)Cl, Cl\(^-\), Cl\(_2\)):

\[
\begin{align*}
CH_2I^- + NaCl & \rightarrow CH_2ICl + Na, \\
CH_2I^- + Cl^- & \rightarrow CH_2ICl + e^-, \\
CH_2I^- + Cl_2 & \rightarrow CH_2ICl + Cl^-.
\end{align*}
\] (8)

(9)

(10)

Using our present 400 nm probe wavelength, we could not directly follow the decay of the CH\(_2\)I radical nor the formation of the CH\(_2\)ICI species in the ps-TR\(^3\) experiments since both species do not absorb appreciably at this wavelength. Thus, we cannot clearly establish the most likely reaction for the formation of the CH\(_2\)ICI species. However, it is very likely that one of the reactions of a CH\(_2\)I radical with species known to be present in the salt water reaction system produces the CH\(_2\)ICI products observed in the NMR photochemistry experiments of Fig. 3. We note that reaction (10) [CH\(_2\)I\(^-\)+Cl\(_2\)→CH\(_2\)ICl+Cl\(^-\)] is quite similar to the Cl\(^-\)+Cl\(_2\)→Cl\(_2\)+Cl\(^-\) reaction in aqueous solution recently studied by Barker and co-workers. In both reactions, a radical (either CH\(_2\)I or Cl\(^-\)) reacts with the Cl\(_2\) species to break its bond and produce a new bond in the neutral species (CH\(_2\)ICl or Cl\(_2\)) and a halogen ion leaving group (I\(^-\) or Cl\(^-\)). One may expect the CH\(_2\)I radical reaction may occur more easily since it is forming a stronger bond (C-Cl instead of C-Cl) than in the reaction to make a Cl\(_2\) product. Reaction (10) provides a decomposition pathway for the Cl\(_2\) intermediate that produces CH\(_2\)Cl and I\(^-\) products that have been observed in the NMR and UV/VIS photochemistry experiments.

D. Discussion of the water catalyzed O-H insertion/Hi elimination reactions and likely implications for decomposition of polyhalomethanes in water and salt water environments

The ultraviolet photolysis of CH\(_2\)I in the gas phase primarily undergoes direct C-I bond cleavage to produce CH\(_2\)I radical and I atom photofragments with a near unity quantum yield.\(^{54-56}\) However, we have observed that ultraviolet photolysis of low concentrations of CH\(_2\)I in aqueous environments without salt present leads to conversion of the parent molecule into HI and CH\(_2\)(OH)\(_2\) products with an appreciable photoquantum yield (Ref. 80). Corresponding ultraviolet photolysis of CH\(_2\)I in salt water solutions also leads to conversion of the parent molecule mostly into HI and CH\(_2\)(OH)\(_2\) products but also noticeable amounts of CH\(_2\)Cl and Cl\(_2\) species (this work). These results clearly indicate the ultraviolet photochemistry of CH\(_2\)I displays substantial phase dependence with greatly different reactions taking place in aqueous environments compared to the gas phase.

The reaction mechanism elucidated in Ref. 80 and briefly discussed here in Sec. III C can account for how ultraviolet photolysis of CH\(_2\)I in aqueous environments leads to appreciable production of HI and CH\(_2\)(OH)\(_2\) products. We note the water catalyzed reactions of isopolyhalomethanes and their reaction products may be noticeable sources of halogens and/or strong acids in the natural environment and this phase dependent water solvated photochemistry has not yet been considered in modeling the photochemistry of polyhalomethanes in the natural environment.

CH\(_2\)I\(_2\) and other polyhalomethanes such as CH\(_2\)IBr and CH\(_2\)ICI have been observed in sea water and in the marine boundary layer of the troposphere and their production attributed mostly to biogenic sources such as microalgae.\(^{7,93,94}\) The measured surface sea water levels of CH\(_2\)I\(_2\) and CH\(_2\)IBr were found to be lower than those computed from seaweed production and this is likely due to photodissociation in the water column.\(^{93,94}\) However, the levels of CH\(_2\)I and CH\(_2\)ICI calculated from measured emission rates and biomass estimates could not account for the high levels of these species in surface coastal waters and this may be due to additional marine sources for these compounds.\(^{93,94}\) Our present results for photolysis of CH\(_2\)I\(_2\) in salt (NaCl) water with comparable salt concentrations as sea water found that noticeable amounts of CH\(_2\)ICI are produced (see NMR photochemistry results of Fig. 3). This would be a different marine source of CH\(_2\)ICI and can potentially account for the higher than expected levels of CH\(_2\)ICI found in surface coastal waters. Further work is needed to better estimate the actual contribution of this different photochemical route to formation of CH\(_2\)ICI in surface sea water. We note that the relatively intense absorption of CH\(_2\)I at wavelengths longer than 300 nm in the sunlight region leads this molecule to have a very short lifetime in the natural environment since it is readily photodissociated. However, the CH\(_2\)ICI species has a substantially weaker absorption that is in the ultraviolet around 260 nm with very little absorption in the sunlight region. Thus, the CH\(_2\)ICI species would have a noticeably longer lifetime in the natural environment. This suggests that any CH\(_2\)ICI produced from photolysis of CH\(_2\)I\(_2\) in sea water may still be discernible long after the disappearance of the precursor CH\(_2\)I\(_2\) species. It would be interesting to examine the photolysis of CH\(_2\)I\(_2\) in the natural environment and see if this correlates with noticeable formation of CH\(_2\)ICI in surface coastal waters. The formation of CH\(_2\)ICI could potentially serve as a marker for salt water photolysis of CH\(_2\)I\(_2\) versus photolysis of CH\(_2\)I\(_2\) in nonsalt water environments such as pure water or ice particles, or in the gas phase where CH\(_2\)ICI is likely not directly produced from photolysis of CH\(_2\)I\(_2\).

Our present results and comparison of the ultraviolet photolysis of CH\(_2\)I\(_2\) in nonsalt and salt aqueous environments also has some interesting implications for photolysis of polyhalomethanes in aqueous sea salt particles. At relatively low concentrations to moderate concentrations of salt comparable to sea water, there will still be significant formation of isopolyhalomethanes and their associated reactions with water to release strong acids (HX). Using CH\(_2\)I\(_2\) as an example, the HI strong acid and methanediol [CH\(_2\)(OH)\(_2\)] products produced by CH\(_2\)I\(_2\) photolysis will be accompanied...
by some formation of CH$_2$ICl and ClI products/intermediates produced from reactions of the initially formed CH$_2$I radical and I atom photofragments. As the salt concentration increases, it would be reasonable to expect that the production of strong acids and water catalyzed reactions will decrease and more products produced from reactions of the initially formed CH$_2$I radical and I photofragments with the salt (mainly NaCl) in the sea salt particle. Therefore the polyhalomethane photochemistry to produce strong acids and potential halogen activation will likely strongly vary with the level of water or salt in the aqueous sea salt particles. Much more work remains to be done by a number of research groups with a range of expertise to better understand the photochemistry and chemistry of polyhalomethanes in different types of aqueous solutions and in the natural environment. We anticipate this will become an increasing area of investigation.

IV. CONCLUSION

Photochemistry and ps-TR$^3$ experiments were done for the ultraviolet photolysis of CH$_2$I$_2$ in salt water solutions and compared to corresponding results done in aqueous solutions that contain no salt. We found that photolysis of CH$_2$I$_2$ in aqueous environments containing no salt and salt up to 0.5M NaCl produced mostly CH$_2$(OH)$_2$ and HI products. Ps-TR$^3$ experiments showed that CH$_2$I–I is produced within several picoseconds and appears to then react with water in salt and nonsalt aqueous environments. When CH$_2$I$_2$ undergoes photolysis in aqueous solutions containing salt, different products/intermediates were produced (CH$_2$ICl and Cl$_2$) and the amount of CH$_2$(OH)$_2$ and HI products appears to decrease compared to photolysis in nonsalt aqueous solutions. The products/intermediates (CH$_2$ICl and ClI) appear to be formed from reactions of the CH$_2$I radical and I atom photofragments initially produced after CH$_2$I$_2$ photolysis with other species. We briefly discuss possible implications for the photodissociation of CH$_2$I$_2$ and potentially other polyhalomethanes in the natural environment.

ACKNOWLEDGMENTS

This research was supported by grants from the Research Grants Council of Hong Kong (Grant Nos. HKU/7087/01P, HKU/7036/04P, and HKU 1/01C) to D.L.P. W.M.K. would like to acknowledge the University of Hong Kong for the award of a Postdoctoral Fellowship.