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PAPER

Kinetic study of the reaction of OH with CH₂I₂

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Flash photolysis (FP) coupled to resonance fluorescence (RF) was used to measure the absolute rate coefficients (k_1) for the reaction of OH($X^2\Pi$) radicals with diiodomethane (CH₂I₂) over the temperature range 295–374 K. The experiments involved time-resolved RF detection of the OH ($A^2\Sigma^+ \rightarrow X^2\Pi$ transition at $\lambda = 308$ nm) following FP of the H₂O/CH₂I₂/He mixtures. The OH($X^2\Pi$) radicals were produced by FP of H₂O in the vacuum-UV at wavelengths $\lambda > 120$ nm. Decays of OH radicals in the presence of CH₂I₂ are observed to be exponential, and the decay rates are found to be linearly dependent on the CH₂I₂ concentration. The results are described by the Arrhenius expression $k_1(T) = (4.2 \pm 0.5) \times 10^{-11} \exp[-(670 \pm 20)K/T]$ cm³ molecule⁻¹ s⁻¹. The implications of the reported kinetic results for understanding the atmospheric chemistry of CH₂I₂ are discussed.

1. Introduction

The tropospheric importance of iodine was first suggested in 1980 by Chameides and Davis.¹ Major sources of atmospheric iodine are believed to be of macroalgal origin releasing organoiodine compounds into the Marine Boundary Layer (MBL).^{2,3} Other sources of atmospheric iodine are believed to be volatile organoiodine compounds (VOIC), namely CH₃I, CH₂I₂ and CH₂ICl that are produced photochemically at the sea–air interface.^{2–5} Recently, a new and purely chemical VOIC source was proposed that is independent of biological generation and that depends on the presence of atmospheric ozone, dissolved iodide and dissolved organic matter.⁶ Martino *et al.* showed that very reactive VOICs, namely CH₃I, CH₂I₂ and CH₂ICl are produced by the sea surface reaction of ozone with dissolved iodide and subsequent reaction of HOI with organic constituents.⁶ Diiodomethane (CH₂I₂) is one of the key organoiodine compounds of biogenic and photochemical origin that appears to be of central importance to understanding MBL iodine chemistry. Field observations suggest CH₂I₂ average mixing ratios ranging from 0.05 to 0.46 ppt.^{2,7} Since the CH₂I₂ absorption wavelengths overlap well with the actinic flux wavelength distribution, the atmospheric fate of CH₂I₂ is mainly governed by photodissociation ($\tau_{\text{photolysis}} = 3$ to 12 minutes).^{8–10} Other tropospheric CH₂I₂ loss processes include the gas-phase reactions with O(³P),¹¹ NO₃,¹² Cl¹³ and

OH radicals.¹⁴ Atmospheric CH₂I₂ destruction leads to the formation of reactive iodine compounds that are now known to be involved in the depletion of ozone in the troposphere and the polar regions.⁸ Further, CH₂I₂ itself and its reactive products are implicated in the generation of aerosols in coastal areas.^{8,15}

In addition to atmospheric interest, the reactivity of CH₂I₂ has recently gained increased interest in the nuclear industry in order to better understand chemical processes responsible for the formation of molecular iodine and iodine oxides resulting from a severe nuclear power plant accident. Among all of the possible “released” fission products, volatile iodine has the highest radiological health impact, *i.e.*, the isotope ¹³¹I that is known to bind to the thyroid gland. The quantity of volatile iodine containing compounds, namely I₂, organic iodides and iodine oxides, that would be released into the environment is, therefore, a major security and public health issue.

Iodine radiochemistry is particularly complex and many international research programs have been launched over the years to predict iodine behavior during a severe accident scenario. As a result, the International Phebus Fission Product program (Phebus) was launched in 1988 to study the degradation of a core reactor, the transport of fission products and their release into the reactor containment volume.^{16–22} Its objective is to reduce the uncertainty in the speciation and quantity of fission products that may be released into the environment if a major nuclear power plant accident were to occur, releasing some fission products in the environment. One of the results of this program was that short chain organic iodides are formed such as CH₃I and CH₂I₂, henceforth RI, under irradiation from the painted surfaces of the reactor containment and then partly destroyed by radiations through complex mechanisms involving air and steam radiolytic products such as OH and O

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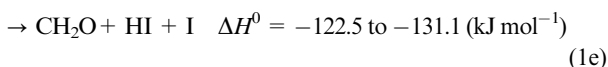
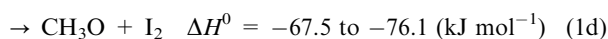
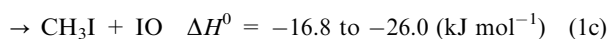
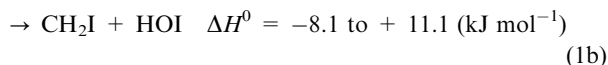
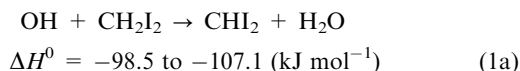
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radicals among others. The products of RI destruction are thought to be iodine oxides even if their speciation, mechanisms and kinetics of formation have never been formally determined and measured under “real” or representative accident conditions. The ability of the field measurement community to accurately determine the concentrations of reactive free radicals has evolved to the point where detailed comparisons of field data with photochemical models are limited by the accuracy of rate coefficients for key reactions. For this reason, new kinetic studies of important chemical processes that focus on high accuracy are needed. Since one of the major oxidant products from the air radiolysis under accident conditions is a hydroxyl radical, there is a need for carrying out kinetic and mechanistic studies of the reaction of a OH radical with CH₂I₂.

2. Background

The photodissociation and gas-phase reactions of NO₃ and O(³P) radicals with CH₂I₂ have been investigated by several authors.^{8–12} The adduct formation from the gas-phase reaction of Cl radicals with CH₂I₂ was studied by Enami *et al.*¹³ To date no kinetic data are available for the reaction of OH radicals with CH₂I₂ and only one theoretical study reports on the mechanism for the title reaction. The reaction of OH radicals with CH₂I₂ can occur *via* a number of reactive pathways:



Thermochemical information used to obtain the above heats of reaction is taken from JPL Publication 06-2²³ and Louis *et al.*¹⁴ and references therein. The literature enthalpy values used to calculate the enthalpies of reaction (1) are shown in Table 1.

In this work we report the results of a kinetic study of reaction (1). Total rate coefficients for OH radical removal by CH₂I₂, $k_1(T)$, are reported as a function of temperature (295–373 K) in 188 Torr of He; this represents the first measurement at any temperature and the first temperature-dependent kinetics study of OH + CH₂I₂ reaction. Details of the experimental approach that was employed to study k_1 are given below.

3. Experimental approach

The experiments were performed at two places, the University of Bayreuth, Germany, and the University of Provence, France. At both universities, the experimental approach is similar to one employed in a number of other studies of OH reactions of atmospheric interest.²⁸ The experiments involved time-resolved detection of OH radicals by resonance fluorescence

Table 1 Literature heats of formation values used to calculate enthalpies for reaction (1) at $T = 298 \text{ K}$

Compound	$\Delta H^0/\text{kJ mol}^{-1}$	References
OH	38.987 ± 1.21	24
	37.28 ± 0.29	23
CH ₂ I ₂	108.1	25
	118.4 ± 0.1	23
H ₂ O	-241.826 ± 0.042	24
HOI	-59.2 ± 3.3	26
	-69.6 ± 5.4	23
IO	115.9 ± 5.0	23
I ₂	62.42 ± 0.08	23
HI	26.50 ± 0.10	23
I	106.76 ± 0.04	23
CHI ₂	290.4	25
CH ₃ I	14.4 ± 0.5	27
	13.76 ± 3.8	23
CH ₃ O	17.15 ± 3.8	23
CH ₂ O	-108.7 ± 0.05	23

($A^2\Sigma^+ \rightarrow X^2\Pi$) at $\lambda = 308 \text{ nm}$ following vacuum-UV flash photolysis of H₂O/CH₂I₂/He and H₂O/He mixtures.²⁹ The schematic of the FPRF apparatus is shown in Fig. 1. Details of the approach are provided below.

A black anodized aluminium reaction cell was used in all experiments carried out under precise temperature, pressure and flow conditions. The reaction cell at the University of Bayreuth is described in detail by Witte *et al.*³⁰ and was maintained at a constant temperature ($\pm 1 \text{ K}$) by circulating silicone oil from a thermostated bath. A platinum resistance thermometer Pt-100 with a stainless steel jacket was inserted into the reaction zone through a vacuum seal, allowing measurement of temperature under precise pressure and flow conditions of the experiments. The reaction cell at the University of Provence was maintained at a constant temperature ($\pm 1 \text{ K}$) using a heating ribbon (FGR Series, Newport Omega) connected to a temperature controller (CN400 Series, Newport Omega), and the temperature within the reactor was monitored using a Type-J thermocouple. The reaction cell used at the University of Provence and the gas saturation system used both at the University of Provence and the University of Bayreuth have been described in detail by Wahner and Zetzsch.³¹ The geometry of the reaction vessel was such that it allowed for the vacuum UV (VUV) beam and the resonance lamp beam to enter perpendicular to one another and to the photomultiplier, *i.e.*, the RF detector, to be orthogonal to each of the overlapping beams. The direction of gas flow was perpendicular to the direction of propagation of both the photolysis VUV beam and the probe radiation beam.

In all experiments, a Perkin Elmer FX 1165 short arc xenon flashlamp with a $> 200 \text{ ns}$ flash jitter served as the photolytic light source. The reactant OH($X^2\Pi$) was generated *via* FP of H₂O. Flash energies ranged from ~ 60 to $\sim 540 \text{ mJ}$. Flash energy was calculated based on the discharge capacitance and input voltage. The VUV beam entered the reaction cell through a MgF₂ window. A resonance lamp mounted at right angle to the VUV photolysis excited the photolytically produced OH radicals in the reaction cell by resonance fluorescence. The resonance lamp at the University of Provence consisted of a 150 mm by 12 mm outer diameter fused silica tube fitted with a silver plated microwave cavity³²

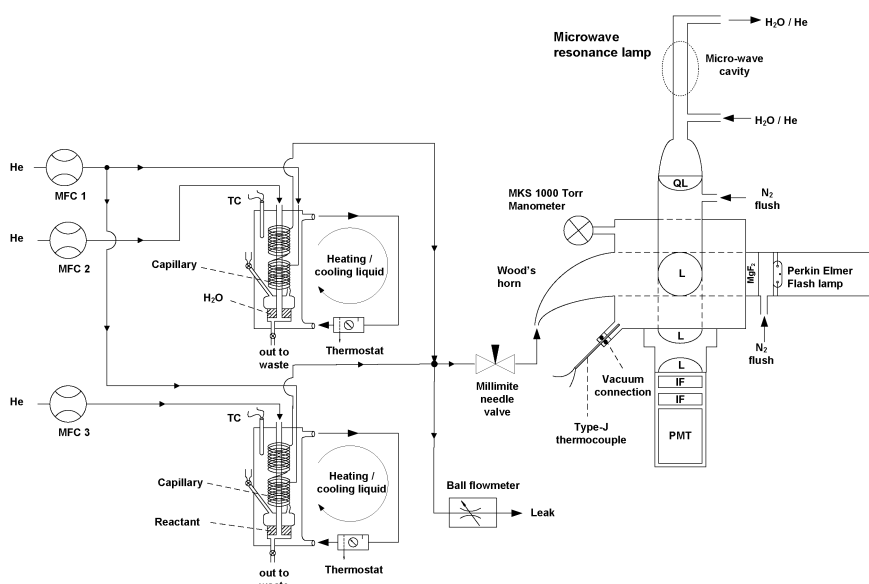


Fig. 1 Schematic representation of the Flash Photolysis Resonance Fluorescence (FPRF) apparatus used to study the reaction of OH radicals with CH_2I_2 . PMT: photomultiplier tube; L: quartz lenses anti-reflection coated for 308 nm; IF: 308 nm interference filters; QL: quartz lens; MFC: mass flow controller; TC: type J thermocouple.

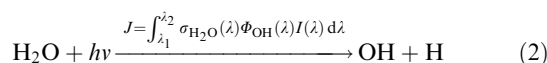
(Ophos Instruments, Inc.) powered by a microwave generator (Muegge, Reichelsheim, MW-GPRYJ1511-300-01, 2.45 GHz, 300 W) and operated at ~ 70 W. A gas mixture of $\text{H}_2\text{O}/\text{He}$ at a pressure of a few Torr total pressure was allowed to flow through the resonance lamp. The electrodeless microwave discharge dissociates H_2O and creates OH radicals. These radicals are then electronically excited to the $A^2\Sigma^+$ state *via* collisions with either electronically excited helium or free electrons. Since fluorescence is resonant, the $A^2\Sigma^+ \rightarrow X^2\Pi$ radiation leaving the lamp electronically excites OH($X^2\Pi$) radicals present in the reaction vessel. The resulting resonant fluorescence ($A^2\Sigma^+ \rightarrow X^2\Pi$) at 308 nm is coupled out of the lamp through a quartz lens (Heraeus, Suprasil, $f_{\text{VIS}} = 50$ mm) into the reaction cell. The resonance fluorescence light is collected by another anti-reflection coated quartz lens (Heraeus, Suprasil, $f_{\text{VIS}} = 50$ mm) and passes through two 308 nm interference filters (FWHM, 9 nm each) which block any impurity emissions from the resonance lamp radiation and stray light on the axis normal to both the photolysis VUV beam and the resonance lamp beam and is imaged by another quartz lens (Heraeus, Suprasil, $f_{\text{VIS}} = 50$ mm) onto the photocathode of a photomultiplier tube (Thorn-EMI, 9789QB). Dry nitrogen gas was used to prevent room air from entering the volume between the flash lamp and the reaction cell. The signal was processed using photon-counting techniques in conjunction with multichannel scaling (EG&G Ortec, model ACE MCS) and accumulated in a PC.

All experiments were carried out under “slow flow” conditions with a linear flow rate of about 1.2 cm s^{-1} and a VUV repetition rate of 0.8 Hz, so the gas mixture within the detection volume was replenished between VUV flashes. The reactor temperature was varied from 295 K to 373 K in 188 Torr He buffer.

The gases used in this study had the following stated minimum purities: University of Provence—He (Linde Gas)—99.9999%; University of Bayreuth—He (Riessner)—99.999%; N_2 (Linde Gas)—99.9995%. The liquid CH_2I_2 (Sigma Aldrich) had the

stated minimum purity of 99% and contained copper as a stabilizer. To limit CH_2I_2 decomposition, the sample was stored under dark conditions. Further, to test for possible I_2 contamination, the CH_2I_2 samples were scanned in the UV-visible region for the presence of I_2 lines. No I_2 absorption was observed under the experimental conditions employed. At the University of Provence deionized water (resistivity $> 18 \text{ M}\Omega$) was prepared by passing tap water through a reverse osmosis demineralization filter (ATS Groupe Osmose) followed by a commercial deionizer (Milli-pore, Milli-Q). At the University of Bayreuth, deionized water was doubly distilled by a quartz still.

Concentrations of H_2O and CH_2I_2 in the reaction mixture were calculated from the given vapor pressures, mass flow rates and total pressure. The Antoine equation for H_2O used in this study is $\log_{10}[P(\text{bar})] = 5.40221 - [1838.675/(T(\text{K}) - 31.7)]$.³³ The vapor pressure of CH_2I_2 is reported to be 1.2 Torr at $T = 298 \text{ K}$.^{34,35} and the saturator was kept exactly at $T = 298 \text{ K}$. The initial OH radical concentration was not directly measured but was determined experimentally at room temperature using the water-vapor UV-photolysis calibration technique and oxygen actinometry as described in detail by Dusanter *et al.*³⁶ and Falona *et al.*³⁷ Briefly, this technique uses direct photolysis of water vapor at atmospheric pressure. It was assumed that the photolysis of water leads to the production of equal amounts of OH radicals and H atoms (reaction (2)).



The initial hydroxyl radical concentration, $[\text{OH}]_0$, was calculated from the following relationship:^{36,37}

$$[\text{OH}]_0 = \Phi_{\text{OH}} \times \sigma_{\text{H}_2\text{O}} \times [\text{H}_2\text{O}] \times (F \times t) \quad (1)$$

where Φ_{OH} is the quantum yield for OH production from VUV photolysis of H_2O , $\sigma_{\text{H}_2\text{O}}$ is the absorption cross section for H_2O , F is the flash lamp fluence and t is the photolysis

time. It was assumed that $\Phi_{\text{OH}} = 1$.²³ The absorption cross section for H_2O , $\sigma_{\text{H}_2\text{O}}$, varies between 0.5×10^{-18} and $8 \times 10^{-18} \text{ cm}^2$ in the wavelength range from 120 to 180 nm.³⁸ Similar to the work of Rinke and Zetzsch,³⁹ we used $\sigma_{\text{H}_2\text{O}} = 5 \times 10^{-18} \text{ cm}^2$.

In eqn (I) above, the product ($F \times t$) is derived from oxygen actinometry by measuring the concentration of ozone using a commercial ozone analyzer (Environment s.a., O_3 41 M) following VUV photolysis of a 20% O_2/N_2 reaction mixture:^{40,41}

$$[\text{O}_3] = \Phi_{\text{O}_2} \times \sigma_{\text{O}_2} \times [\text{O}_2] \times (F \times t) \quad (\text{II})$$

where $\Phi_{\text{O}_2} = 2$ is the photolysis quantum yield and σ_{O_2} is the absorption cross section for O_2 .

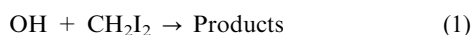
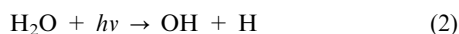
Eqn (II) above can be rewritten to give the product ($F \times t$):

$$(F \times t) = \frac{[\text{O}_3]}{2[\text{O}_2]\sigma_{\text{O}_2}} \quad (\text{III})$$

The absorption cross section for O_2 , σ_{O_2} , varies between 2×10^{-17} and $8 \times 10^{-17} \text{ cm}^2$ in the wavelength range from 120 to 180 nm.³⁸ In this work, σ_{O_2} was taken to be $5 \times 10^{-17} \text{ cm}^2$.³⁸ Substituting the product ($F \times t$) from eqn (III) into eqn (I) gives $[\text{OH}]_0$. We conservatively estimate a maximum value of $[\text{OH}]_0 \approx 2 \times 10^{10} \text{ cm}^{-3}$ under the experimental conditions employed.

4. Results and discussion

All experiments were carried out under pseudo-first order conditions with CH_2I_2 , H_2O and He bath gas in excess over OH radicals where $10^3 \times [\text{OH}]_0 \approx [\text{CH}_2\text{I}_2]$. Data were obtained over the temperature range 296–374 K in 175 and 188 Torr He. The OH radical temporal evolution was monitored following VUV flash photolysis of $\text{H}_2\text{O}/\text{CH}_2\text{I}_2/\text{He}$ reaction mixtures. The processes that control the temporal evolution of OH are the following:



Since $[\text{CH}_2\text{I}_2]$ was much larger than $[\text{OH}]_0$, it was assumed that the observed OH temporal profiles followed the pseudo-first-order rate law:

$$\ln \frac{[\text{OH}]_0}{[\text{OH}]} = (k_1[\text{CH}_2\text{I}_2] + k_0)t \quad (\text{IV})$$

In eqn (IV), the decay rate k_0 is the OH disappearance rate in the absence of CH_2I_2 . The value of k_0 is basically the sum of the first order rate coefficients for the reaction of OH radicals with its precursor, H_2O , and any impurities in the He bath gas, reaction with background impurities that find their way into the reaction mixture *via* small leaks and/or *via* diffusion through a small amount of Teflon tubing in the apparatus plumbing, and the diffusion of OH radicals out of the detection zone. $\text{OH}(X^2\Pi)$ is unreactive toward He and does not react readily with H_2O .⁴²

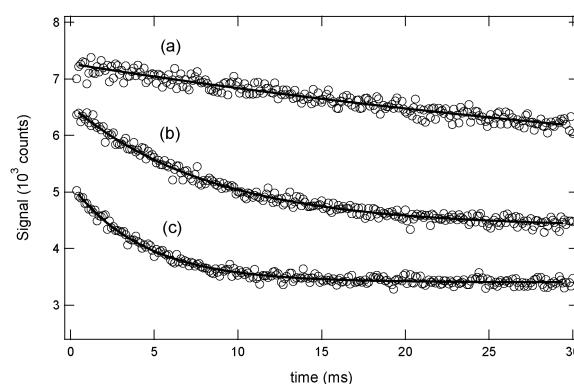


Fig. 2 Typical OH radical decay profiles as a function of $[\text{CH}_2\text{I}_2]$. Experimental conditions: $T = 304 \text{ K}$; $[\text{H}_2\text{O}] = 1.7 \times 10^{15} \text{ cm}^{-3}$; $[\text{CH}_2\text{I}_2]$ in units of 10^{13} cm^{-3} : (a) 0; (b) 1.5; (c) 3.4. Number of flashes averaged: 200. Solid lines are obtained from least-squares analyses that give the following best fit parameters k' in units of s^{-1} : (a) 25; (b) 110; (c) 209. The plots have been displaced vertically for clarity.

Some typical $\text{OH}(X^2\Pi)$ temporal profiles, observed following flash photolysis of $\text{H}_2\text{O}/\text{CH}_2\text{I}_2/\text{He}$ mixtures are shown in Fig. 2.

For the kinetic experiments carried out at the University of Provence, the observed OH signal in the presence and absence of the reactant (CH_2I_2) was exponential. However, the kinetic experiments carried out on the flash photolysis system at the University of Bayreuth showed a second exponential component on time scales greater than 100 ms when CH_2I_2 was added to the system. This secondary component was measured to be 2 to 3 s^{-1} and was observed to be independent of the amount of CH_2I_2 used. We believe that this secondary exponential component associated with the OH signal is actually the diffusion of OH from the reaction zone and/or secondary reactions of OH with CH_2I_2 impurities. However, further studies into the origin of this secondary component would be of interest. The bimolecular rate coefficients for removal of OH radicals by CH_2I_2 , $k_1(T)$, were obtained from the variation of k' with $[\text{CH}_2\text{I}_2]$ at constant $[\text{H}_2\text{O}]$ and $[\text{He}]$. The Arrhenius expression $k_1 = A \exp(-E_a/RT)$ was used to deduce the temperature-dependencies of reaction (1), where k_1 is the bimolecular rate coefficient, A is the pre-exponential factor, E_a is the activation energy, and R is the gas constant. A linear relationship is obtained by taking the natural log of the Arrhenius expression listed above and plotting $\ln k$ vs. $1/T$. The values of A and E_a are obtained from the intercept and slope, respectively. Typical first-order plots for the reaction of OH with CH_2I_2 are shown in Fig. 3.

The results of all studies of reaction (1) are summarized in Table 2 and an Arrhenius plot for the title reaction is shown in Fig. 4.

The following Arrhenius expression is derived from the data:

$$k_1(T) = (4.2 \pm 0.5) \times 10^{-11} \exp[-(670 \pm 20)K/T] \quad (\text{V})$$

Uncertainties in the above expression are 2σ and represent precision only (all data points weighted equally). The uncertainties in the above expression refer to the Arrhenius parameters only. We believe that systematic errors in the

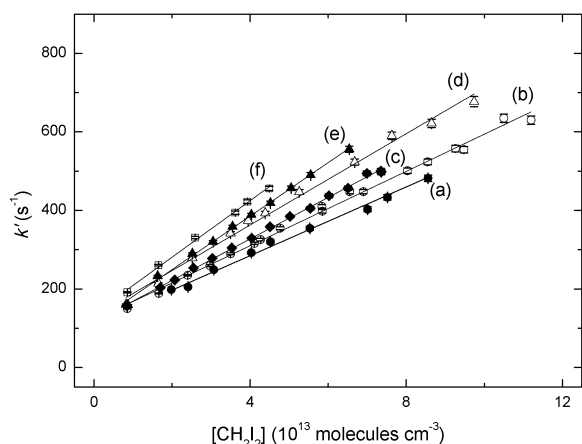


Fig. 3 Plots of k' versus $[\text{CH}_2\text{I}_2]$ for data obtained at three different temperatures. Fits are obtained from linear least squares analyses and give the following bimolecular rate coefficients in units of $10^{-12} \text{ cm}^3 \text{ s}^{-1}$: (a) 4.45 ± 0.32 at 296 K, (b) 4.73 ± 0.16 at 305 K, (c) 5.28 ± 0.11 at 323 K, (d) 5.81 ± 0.74 at 336 K, (e) 6.59 ± 0.23 at 359 K, (f) 7.19 ± 0.72 at 374 K.

Table 2 Summary of kinetic data for the reaction of OH with CH_2I_2 in 188 Torr of He

T^a	$[\text{CH}_2\text{I}_2]^a$	k_0^a	$k_1^{a,b,c}$
296	1.48–8.56	30	4.45 ± 0.32
304	1.05–3.50	40	$4.82 \pm 0.20^{d,e}$
305	0.12–11.0	40	4.73 ± 0.16
323	0.83–7.36	40	5.28 ± 0.11
336	0.82–9.74	40	5.81 ± 0.74
336	0.78–5.71	40	5.63 ± 0.74^f
359	0.86–6.54	40	6.59 ± 0.23
374	0.85–4.49	25	7.19 ± 0.72

^a Units are: T (K), concentration ($\times 10^{13} \text{ cm}^{-3}$), k_0 (s^{-1}) is the OH radical disappearance rate in the absence of CH_2I_2 , k_1 ($\times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$).

^b Uncertainty is $\pm 2\sigma$, precision only. ^c Flash energy = 540 mJ; $[\text{H}_2\text{O}] = 1.5 \times 10^{15} \text{ cm}^{-3}$. ^d Flash energy = 400 mJ; $[\text{H}_2\text{O}] = 1.7 \times 10^{15} \text{ cm}^{-3}$. ^e $p = 175 \text{ Torr}$. ^f Flash energy = 60 mJ; $[\text{H}_2\text{O}] = 1.5 \times 10^{15} \text{ cm}^{-3}$.

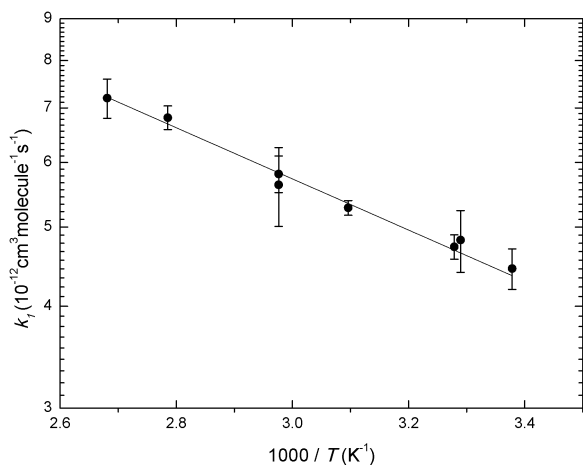


Fig. 4 Arrhenius plot for the reaction of OH with CH_2I_2 obtained in this work. The solid line is Arrhenius expression fitted to the rate constant k_1 obtained in this work.

Table 3 Comparison of Marine Boundary Layer (MBL) lifetimes of CH_2I_2 toward photolysis and attack by different atmospheric constituents, namely $\text{O}(^3\text{P})$, Cl, NO_3 and OH, at 298 K

Reference	Method	Radical	Lifetime
4	UV-Vis	Photolysis	5–9 min ^a
11	PLP-RF	$\text{O}(^3\text{P})$	19 hours ^b
13	CRDS	Cl	46 hours ^c
12	CRDS	NO_3	58 hours ^d
This work	FPRF	OH	62 hours ^e

^a $J = 1.90 \times 10^{-3} \text{ s}^{-1}$. ^b $[\text{O}(^3\text{P})] = 2 \times 10^5 \text{ cm}^{-3}$, $k_{\text{O}_3\text{P}} = 7.36 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. ^c $[\text{Cl}] = 2 \times 10^5 \text{ cm}^{-3}$, $k_{\text{Cl}} = 3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. ^d $[\text{NO}_3] = 1.2 \times 10^7 \text{ cm}^{-3}$, $k_{\text{NO}_3} = 4 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. ^e $[\text{OH}] = 1 \times 10^6 \text{ cm}^{-3}$, $k_{\text{OH}} = 4.48 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$.

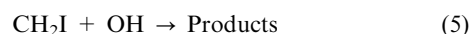
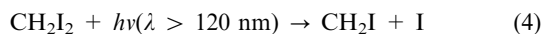
determination of k_1 are small, and conservatively estimate the absolute accuracy of each reported rate coefficient to be $\pm 15\%$ at the 95% confidence level. Assumed contributions to the overall uncertainty are precision, uncertainty in the CH_2I_2 vapor pressure, and small systematic errors in temperature ($\pm 1 \text{ K}$), pressure ($\pm 1 \text{ Torr}$), and mass flow rates ($\pm 1\%$).

It is clearly evident in Fig. 3 and in Table 3 that the observed kinetics of the reaction of OH radicals with CH_2I_2 yield a very high intercept when CH_2I_2 is added to the system. As shown in Fig. 3 and in Table 3 the intercept is about 100 s^{-1} when CH_2I_2 is present in the system whereas measurements in the absence of CH_2I_2 give an intercept in the range 25 to 40 s^{-1} . This difference is likely due to an accumulation of highly reactive reaction products, for example IO radicals, which increase the background reactivity. However, we believe that this background reactivity is independent of CH_2I_2 (see model calculations below).

There is no kinetic data in the literature with which to compare the rate coefficients reported in this work. The obtained rate coefficient for reaction (1) increases slightly with increasing temperature over the range measured. From the Arrhenius plot shown in Fig. 4 an activation energy of $5.5 \pm 0.3 \text{ kJ mol}^{-1}$ for reaction (1) was calculated.

Only one mechanistic study of reaction (1) reported to date was carried out by Louis and coworkers.¹⁴ These authors used the *ab initio* DK-CCSD(T)/ANO-RCC approach to compare the H-atom abstraction and I-atom abstraction channels for reaction pathways (1a) and (1b), respectively. Louis and coworkers calculated that the H atom abstraction channel (1a) is strongly exothermic (-80 to -90 kJ mol^{-1}) and the I atom abstraction channel (1b) is endothermic ($+20$ to $+40 \text{ kJ mol}^{-1}$).¹⁴ The difference may be best explained in terms of C–H and C–I bond strengths that are 431 and 239 kJ mol^{-1} , respectively.¹⁴ While no theoretical information is available regarding other exothermic reaction channels (1c)–(1e), these channels are thermochemically probable. Clearly, more research is warranted to enhance our understanding of the kinetics of these interesting reactions.

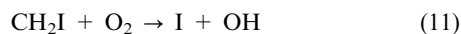
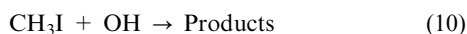
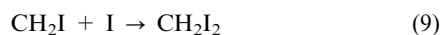
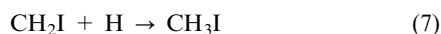
One potential source of error in the measured rate coefficient is the potential loss of CH_2I_2 due to VUV photolysis to produce CH_2I radicals and I atoms.



The concentrations of a CH_2I radical and a I atom following VUV flash photolysis of the $\text{CH}_2\text{I}_2/\text{H}_2\text{O}/\text{He}$ mixtures are estimated from the photoabsorption cross-sections in the wavelength range of interest.¹²

$$[\text{CH}_2\text{I}]_0 \approx [\text{I}]_0 \approx [\text{OH}]_0 \frac{\sigma_{\text{CH}_2\text{I}_2} [\text{CH}_2\text{I}_2]}{\sigma_{\text{H}_2\text{O}} [\text{H}_2\text{O}]} \quad (\text{VI})$$

In eqn (VI) above, $\sigma_{\text{CH}_2\text{I}_2}$ and $\sigma_{\text{H}_2\text{O}}$ are assumed to be $1.48 \times 10^{-17} \text{ cm}^2$ ⁴³ and $5 \times 10^{-18} \text{ cm}^2$,³⁸ respectively. The $[\text{CH}_2\text{I}]_0$ and $[\text{I}]_0$ are calculated to be $1.9 \times 10^9 \text{ molecules cm}^{-3}$ under the experimental conditions employed. To estimate the influence of reactions (5) and (6) on the $[\text{OH}]_0$, the OH temporal decays were simulated using the Gepasi Biochemical Simulation software package. In addition to reactions (4)–(6) listed above, the following reactions (7)–(12) were used to simulate the OH radical temporal decay.



There is no kinetic data available in the literature for reaction (5). Similar to the work of Nakano *et al.*,¹² it was assumed that the room temperature rate coefficient for reaction (5) is the same as the corresponding reaction of the CH_3 radical with the I atom ($k_{\text{CH}_3+\text{I}} = 7.31 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).⁴⁴ Further, there are no room temperature rate coefficient values reported in the literature for reactions (6) and (7). It was assumed that the room temperature rate coefficients for reactions (6) and (7) are the same as that for $\text{Br} + \text{OH}$ ($k_{\text{Br}+\text{OH}} = 1.09 \times 10^{-24} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)⁴⁵ and $\text{CH}_3 + \text{H}$ ($3.21 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$),⁴⁶ respectively. The room temperature rate coefficients for reactions (8)–(12) are taken to be $k_{\text{CH}_2\text{I}+\text{CH}_2\text{I}} = 4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,⁴⁷ $k_{\text{CH}_2\text{I}+\text{I}} = 1.33 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,⁴⁸ $k_{\text{CH}_3\text{I}+\text{OH}} = 9.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,⁴⁹ $k_{\text{CH}_2\text{I}+\text{O}_2} = 1.39 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,⁵⁰ and $k_{\text{OH}+\text{OH}} = 1.48 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,⁵¹ respectively. Based on model calculations, OH radicals were observed to be consumed in majority by reactions (1) and (3) and OH radical loss *via* reactions (5)–(11) was calculated to be less than 1%.

The effect of photolysis of CH_2I_2 on the kinetics of reaction (1) was further verified by varying the flash energy used to produce OH radicals. The flash energy was intentionally reduced by turning down the flash lamp discharge voltage and placing a stack of quartz plates in the flash path to demonstrate that the obtained results did not depend on the initial radical concentration. The flash energy was varied by a factor of more than 9. By varying the flash energy we cannot conclude that secondary processes resulting from the photolysis of CH_2I_2 did not occur, however, we feel that this secondary chemistry was not important under the experimental conditions employed. The influence of photolysis of CH_2I_2 on the kinetics of reaction (1) was further verified by

changing the type of window on the flash lamp side of the reactor. We did not observe any pronounced effects on the OH radical kinetics when the MgF_2 window was replaced with the UV grade fused silica window.

5. Conclusions

The results reported in this work demonstrate that $k_1(T)$, the rate coefficient for the reaction of OH radicals with CH_2I_2 , is $k_1(296\text{--}374 \text{ K}) = (4.2 \pm 0.5) \times 10^{-11} \exp[-(670 \pm 20)K/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the measured temperature range. For reaction of CH_2I_2 with OH radicals this work represents the first rate coefficient determination reported at any temperature and the first study of the temperature dependence. Comparison of different atmospheric residence times toward photolysis and attack by different atmospheric constituents is shown in Table 3. As shown in Table 3, the Marine Boundary Layer (MBL) loss of CH_2I_2 is predominantly governed by photolysis, where the photolytic lifetime of CH_2I_2 is calculated to be about 5 minutes at midday. In the marine atmosphere, a typical diurnally global averaged OH, Cl, and $\text{O}(^3\text{P})$ number density is 1×10^6 radicals per cm^3 , 1×10^5 atoms per cm^3 and 2×10^5 atoms per cm^3 , respectively.^{52–54} Under these conditions, the lifetime of CH_2I_2 toward destruction by OH (k_1 , this work), Cl ($k_{\text{Cl}+\text{CH}_2\text{I}_2} = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and $\text{O}(^3\text{P})$ ($k_{\text{O}(^3\text{P})+\text{CH}_2\text{I}_2} = 7.36 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is approximately 62 hours, 46 hours and 19 hours, respectively. Not surprisingly, photolysis constitutes the major atmospheric sink for CH_2I_2 on a global scale. A nighttime reaction of CH_2I_2 with NO_3 ($k_{\text{NO}_3+\text{CH}_2\text{I}_2} = 4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) does not represent a significant nighttime sink for CH_2I_2 since its residence time is ~ 58 hours toward the attack by NO_3 . However, under certain confined industrial conditions, *i.e.*, typical of a major nuclear central accident scenario, the OH number density can be as high as 1×10^9 radicals per cm^3 within the nuclear core confinement area.⁵⁵ Under these conditions, the lifetime of CH_2I_2 toward destruction by OH is approximately 220 seconds, *i.e.*, about 4 minutes, at room temperature. In the absence of photolysis and any other radiation in such a confined environment, the reactivity with OH would represent one of the major destruction channels for CH_2I_2 . It appears, therefore, that reaction with OH removes CH_2I_2 from the confined environment under accident conditions that is faster than photolysis. Reaction (1) should be included in model calculations to better assess possible “released” fission products during a major nuclear accident scenario.

It has to be noted that in the case of a nuclear power reactor, the photolysis is replaced by more energetic beta and gamma radiations. Even if a direct link of the effect of both types of rays is not obvious, this work represents a good way to start studying these types of reactions. A following step would be to study the reactions of interest under beta/gamma radiation in order to validate the observed reaction kinetics.

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