

Formation of Iodine Monoxide Radical from the Reaction of CH₂I with O₂

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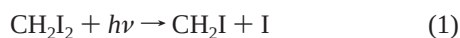
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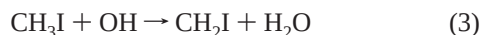
The rate constants of IO radical formation from the reaction of CH₂I with O₂ were determined in the pressure range of 5–80 Torr with N₂ diluent at 278–313 K, using cavity ring-down spectroscopy. The room temperature rate constant is $(4.0 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 30 Torr total pressure. No significant dependences on temperature and total pressure were observed. The yield of IO from CH₂I + O₂ was estimated to be unity in 100 Torr total pressure of N₂ diluent.

Introduction

The atmospheric chemistry of iodine monoxide radicals has attracted attention for its potential effect on the oxidizing capacity of the troposphere in the NO_x and HO_x budget and toward dimethyl sulfide (DMS).^{1–3} DMS accounts for 75% of natural sulfur emission. According to a recent kinetic measurement, the reaction rates of IO/BrO radicals with DMS are much faster than those previously reported, and hence the importance of those reactions in the marine boundary layer is comparable with that of the OH radical.² Iodine atoms from the photodissociation of CH₂I₂, CH₂IBr, and CH₂ICl are considered to be the main source of IO in the marine boundary layer.^{4,5} CH₂I₂ is, for example, photodissociated by the solar flux with a lifetime of a few minutes.^{6,7} The IO radical is produced by the reaction of an I atom with ozone:



Another reactive iodine compound in the atmosphere is CH₃I originating from marine algae species.⁸ In the daytime atmosphere, although the lifetime of CH₃I is controlled almost entirely by photodissociation, OH- and Cl-initiated attack could account for 10–20% of the removal of CH₃I.⁹



Under atmospheric conditions it has been believed that the CH₂I radical produced via reactions 1 and 3 reacts with O₂ to generate CH₂IO₂ in analogy to other halogenated alkyl radicals:^{10–12}



However, Masaki et al. found that the rate constants of the CH₂I + O₂ reaction did not depend on the total pressures in the range of 2–15 Torr and considered the following two-body process:¹³



Although they suggested the possibility of formation of IO from CH₂I + O₂, there has been no direct evidence of the IO formation. If IO radicals are produced from CH₂I produced in reactions 1 and 3 followed by reaction 5 with an appreciable yield, the IO formation mechanism in the atmosphere should be altered. In the present work, we have investigated the rate constants and the IO yield for the reaction of CH₂I with O₂ by monitoring the absorption of IO radicals with cavity ring-down spectroscopy (CRDS).^{2,14}

Experimental Section

After the CRDS technique was introduced by O’Keefe and Deacon, it has been widely applied to spectroscopy and chemical reactions.^{15–18} Applicability of the CRDS apparatus to kinetic study was discussed.^{19,20} The CRDS apparatus used in the present study has been described elsewhere.² The system employs photolysis and probe pulsed lasers. After the photolysis laser beam traverses the glass tube reactor, the probe laser beam is injected nearly collinear to the axis of the photolysis laser through one of two high-reflectivity mirrors (Research Electro-Optics, reflectivity of 0.9994 at 435 nm), which make up the ring-down cavity of 1.04 m. The length of the reaction region is 0.40 m. Light leaking from the end mirror is detected by a photomultiplier tube through a narrow band-pass filter. The decay of the light intensity is recorded using a digital oscilloscope and transferred to a personal computer.

CH₂I₂ is injected into the cell using a bubble tube with N₂ buffer gas, the concentration of which is monitored at 253.7 nm before the entrance, typically $1 \times 10^{14} \text{ molecules cm}^{-3}$. The 266 nm output of a Nd³⁺:YAG laser is used to dissociate CH₂I₂ to give an I atom and a CH₂I radical. The dissociation yield of CH₂I₂ by the 266 nm photolysis laser is estimated to be below a few percent from its absorption cross section and the laser intensity. The IO radical concentration is monitored at 435.63 nm, the band head of the A²Π_{3/2} ← X²Π_{3/2} (3,0) transition, with a dye laser (Spectra Physics, PDL-3, spectral resolution < 0.01 nm). The IO absorption cross section was previously measured to be $5.9 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at this

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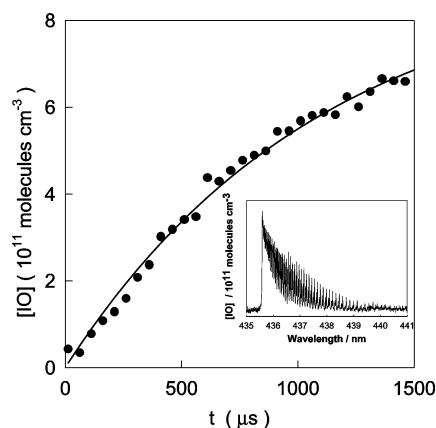


Figure 1. A typical rise profile of the IO radical monitored at 435.63 nm after the initial pulse (time = 0 μ s) of the 266 nm output of an Nd³⁺:YAG laser. The inset shows the A $\leftarrow$ X (3, 0) band of IO.

wavelength.^{2,14} The signal baseline is taken at 435.51 nm, a region in which there is no IO absorption. The IO concentration profile is measured between 30 and 2500 μ s after the photolysis laser pulse. A large excess amount of O₂, 10¹⁵–10¹⁶ molecules cm⁻³, is used to maintain the pseudo-first-order reaction conditions. CH₂IBr and CH₂ICl are also used as alternative sources of CH₂I to confirm the measured rate constants. To estimate the branching ratio of the IO radical formation from CH₂I + O₂, the reactions of CH₃I and CF₃I with O atoms in the presence of O₂ are performed. In this experiment, the 266 nm photolysis of O₃ generates O(³P) atoms under N₂ diluent.

The reaction cell consists of a Pyrex glass tube (21 mm i.d.). The temperature of the gas flow region is controlled over 278–313 K. The difference between the temperature of the sample gas at the entrance and exit of the flow region is <0.4 K. The total flow rate is adjusted so that the gas in the cell is completely replaced under 2 Hz laser operation.

Results and Discussion

Reaction Kinetics of CH₂I with O₂. The rate constants for reaction 5 are determined by the rise time profiles of the IO signal intensity (Figure 1). The monitored IO absorption spectrum is shown in the inset. Under conditions with a large excess O₂ concentration over that of CH₂I, the rise profile followed pseudo-first-order kinetics. The formation of the IO radicals are analyzed using the following equations:

$$[\text{IO}]_t = [\text{CH}_2\text{I}]_0 \{1 - \exp(-k't)\} \quad (\text{I})$$

$$k' = k_5[\text{O}_2] + k_d \quad (\text{II})$$

where [IO]_t is the concentration of IO radicals at time *t* and [CH₂I]₀ is the concentration of CH₂I radicals at time *t* = 0. *k*₅ and *k'* are the second-order and pseudo-first-order rate constants for reaction 5, respectively. *k*_d is mainly the rate constant for diffusion out of the photolysis volume. Figure 1 shows a typical rise profile of the IO concentration with O₂ of 1.1 × 10¹⁵ molecules cm⁻³ at 298 K, which is fitted to eq I. Figure 2 shows a plot of *k'* vs [O₂] at room temperature in 30 Torr total pressure of N₂ diluent. The second-order rate constant *k*₅ is obtained from a linear least-squares analysis of the data; *k*₅ = (4.0 ± 0.4) × 10⁻¹³ cm³ molecule⁻¹ s⁻¹. In this run, *k*_d is 720 s⁻¹. This value is in reasonable agreement with our previous experiments, e.g., *k*_d = 500–1000 s⁻¹ for 20–100 Torr total pressure.²

When the concentration of CH₂I₂ is increased by 3 times, no change of the rate constant *k*₅ is observed. Since the initial

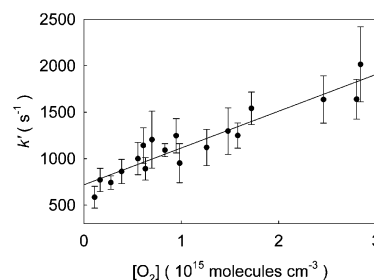
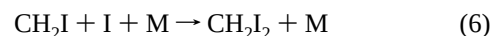


Figure 2. Second-order plots for the reaction of CH₂I radicals with O₂ at 30 Torr of N₂ diluent at 298 K. The solid line is a linear least-squares fit.

concentrations of the radicals are low, the radical–radical reactions do not affect the determination of the rate constant *k*₅. For example, CH₂I radicals are not consumed by the reaction with I atoms:²¹



The rate constants are also measured using CH₂ICl and CH₂I–IBr as precursors of the CH₂I radical, which yield the same rate constant as for CH₂I₂. On the basis of these results, any secondary reactions are not significant in the present experiment. Masaki et al. determined *k*₅ = (1.6 ± 0.2) × 10⁻¹² cm³ molecule⁻¹ s⁻¹ from the decay profile of the CH₂I signal using a combination of pulsed laser photolysis and photoionization mass spectrometry, which is 4 times larger than our value.¹³ Since their initial concentrations of CH₂I were low, the radical–radical reactions would not enhance the decay rate in their experiment. Thus, the reason for the discrepancy between their rate constant and ours is not clear. As will be described below, the evolution curve of IO from the reaction of CH₃I + O(³P) in the presence of O₂ can be reproduced by our rate constant, while not by their rate constant.

The rate constants, *k*₅, measured for the range of 278–313 K at 30 Torr are found to be essentially temperature-independent: *k*₅ in units of 10⁻¹³ cm³ molecule⁻¹ s⁻¹ are 3.6 ± 0.3 at 278 K, 4.0 ± 0.2 at 288 K, 4.0 ± 0.4 at 298 K, and 3.7 ± 0.5 at 313 K. Furthermore, *k*₅ at room temperature does not show any pressure dependence for the range of 5–80 Torr with N₂ diluent. These results suggest that the two-body reaction mechanism is dominant in CH₂I + O₂, or possibly the CH₂IO₂ formation path reaches already its high-pressure limit with a very limited yield. As will be discussed below, the formation yield of IO from CH₂I + O₂ is estimated to be unity. Thus, CH₂IO₂ formation can be neglected under our experimental conditions. Sehested et al. reported, however, the formation of CH₂IO₂ under 1000 mbar total pressure of SF₆ diluent.¹² They measured the absorption of CH₂IO₂ at 220–400 nm 2 μ s after the electron pulse initiation with spectral resolution of 0.8 nm. The UV absorption at that region could also be due to IO and/or HCHO from reaction 5 because IO and HCHO have the UV absorption in the wavelength region similar to the reported CH₂IO₂ spectrum. In the present experiment, our spectral resolution is less than 0.01 nm, which enables us to separate completely the IO spectrum from other species including CH₂IO₂ and HCHO. In addition, the heats of reaction for CH₂X + O₂ → XO + HCHO are –30.6, –36.0, and –48.0 kcal mol⁻¹ for X = Cl, Br, and I, respectively.²² Since the iodine channel is highly exothermic, CH₂IO₂ is not stabilized even under the high-pressure condition while the formation of CH₂ClO₂ and CH₂BrO₂ was reported.^{10,11} In general, the IO formation from reaction 5 is considered to occur via the four-centered intermediate. Because CH₂I has a low ionization potential (<8.6

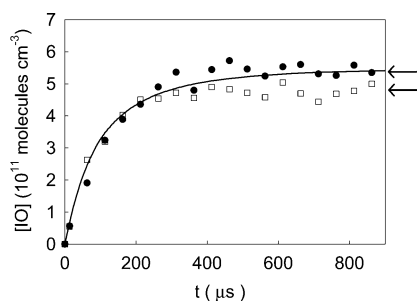


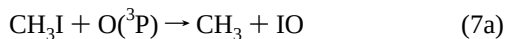
Figure 3. Rise profiles of IO radicals produced from the reactions of O(³P) with CH₃I (filled circle) and CF₃I (open square) in the presence of O₂. [CH₃I] = [CF₃I] = 8 × 10¹⁴, [O₂] = 1 × 10¹⁶, [O₃] = 4 × 10¹² molecules cm⁻³. The solid curve is a simulated one. See text for details. The vertical arrows show the asymptotic values.

eV)¹³ and hence the electron of the I atom could flow into the binding O₂, the O–O bond is weakened followed by the IO formation via reaction 5.

Furthermore, to check the IO formation from reaction 5, we test 355 nm photolysis of CH₃I/Cl₂/O₂/N₂ mixture at room temperature; [CH₃I] = 5.1 × 10¹⁴, [Cl₂] = 1.1 × 10¹⁵, and [O₂] = 3.9 × 10¹⁶ molecules cm⁻³ in 30 Torr total pressure of N₂ diluent. The photoproducted Cl atom abstracts an H atom from CH₃I to produce a CH₂I radical that reacts with O₂. The formation of IO is confirmed by observing the IO (3,0) band with our CRDS apparatus.²³

Estimation of the Yield of the IO Radical from the Reaction of CH₂I with O₂. To measure the formation yield of IO from CH₂I + O₂, two different experiments are performed. First, the concentration of IO radicals produced from the reaction of O(³P) atoms with CH₃I is measured. This reaction is initiated by the 266 nm photolysis of CH₃I/O₂/O₃/N₂ mixtures; [CH₃I] = 8.1 × 10¹⁴, [O₂] = 1.1 × 10¹⁶, and [O₃] = 3.9 × 10¹² molecules cm⁻³ in 100 Torr total pressure of N₂ diluent. Although O(¹D) atoms are produced from the O₃ photolysis, they are efficiently quenched by N₂ to O(³P) before reacting with CH₃I.

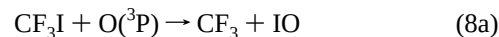
The following reactions were proposed by Gilles et al.:²⁴



They reported that product yields at 100 Torr with N₂ diluent are Y(IO)_{7a} = 0.44 ± 0.04, Y(CH₂I)_{7b} = 0.16 ± 0.05, Y(H)_{7c} = 0.07 ± 0.02, Y(CH₃O)_{7d} < 0.03, and Y(HI)_{7e} < 0.05. Under our experimental conditions the contribution of IO formation from I + O₃ is estimated to be less than 1% because of the low O₃ concentration.²⁵ The reaction channels (7c and 7d) do not contribute to the IO radical formation under the present low O₃ concentration. Thus, the IO radicals are generated exclusively through reaction channels (7a and 7b) and the subsequent reaction 5 with O₂. Figure 3 shows the rise profile of the IO radicals, which goes up to (5.4 ± 0.2) × 10¹¹ molecules cm⁻³.

As a reference experiment, the concentration of IO radicals produced from the reaction of O(³P) atoms with CF₃I is measured. This reaction is initiated by the 266 nm photolysis of CF₃I/O₂/O₃/N₂ mixtures ([CF₃I] = 8.0 × 10¹⁴, [O₂] = 1.1 × 10¹⁶, [O₃] = 4.0 × 10¹² molecules cm⁻³ in 100 Torr total pressure of N₂ diluent). With these experimental conditions,

O(³P) atoms react with CF₃I through the following reaction channels:



The reported product yields at 100 Torr with N₂ diluent are Y(IO)_{8a} = 0.83 ± 0.09, Y(CF₃O)_{8c} < 0.01, and Y(IF)_{8d} < 0.01.²⁴ The IO radicals are generated exclusively through reaction 8a under our experimental conditions. Figure 3 shows the rise profiles of IO radicals. The concentration of IO generated from O(³P) + CH₃I, [IO]_{CH₃I}, is compared with [IO]_{CF₃I} from O(³P) + CF₃I. The ratio of two asymptotic values in Figure 3 is [IO]_{CH₃I}/[IO]_{CF₃I} = 1.15 ± 0.14. Hence, the IO production yield from the reaction channels (7a and 7b) is estimated to be 0.95 ± 0.20. Subtracting the reported yield of reaction 7a for direct IO production Y(IO)_{7a} = 0.44 ± 0.04 from the present IO production yield of 0.95 ± 0.20, the IO yield from reaction 5 through reaction 7b is estimated to be Y(IO)_{5-7b} = 0.51 ± 0.20, which should be the same as the CH₂I yield in reaction 7b. Gilles et al.²⁴ reported a much smaller value, Y(CH₂I)_{7b} = 0.16 ± 0.05. When the relatively large errors in two different experiments are taken into account, it is safe to say that the yield efficiency of the IO radical from reaction 5 is unity. From the reaction of CH₂I + O₂, formation of HCOOH + I or CHIO + OH is energetically possible. However, these reactions do not occur.

The evolution curve for IO from reaction 5 in Figure 3 reproduces the experimental data, which is simulated with the present rate constant for k₅, the reported rate constant k₇ = 1.71 × 10⁻¹¹,²³ and the estimated one k_{7b} = k₅Y(IO)_{5-7b} = 6.0 × 10⁻¹² cm³ molecule⁻¹ s⁻¹. The rate constant for O(³P) + O₂ is adopted to be k_{O+O₂} = 1.96 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹.²² The absolute concentration of O(³P) atoms is estimated from the maximum concentration of IO.

Searching for another possible reaction channel of the IO formation in the present experimental conditions, we test the 266 nm photodissociation of mixture gases of 9 × 10¹⁴ molecules cm⁻³ of CH₃I or CF₃I and 3 × 10¹⁵ molecules cm⁻³ of O₂ in 100 Torr of N₂ diluent without O₃. IO radicals are not detected. These results suggest that the following reactions do not produce IO radicals:



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