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Formation of Iodine Monoxide Radical from the Reaction of CH_2I with O_2

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The rate constants of IO radical formation from the reaction of CH_2I with O_2 were determined in the pressure range of 5−80 Torr with N_2 diluent at 278−313 K, using cavity ring-down spectroscopy. The room temperature rate constant is $(4.0 \pm 0.4) \times 10^{-13}$ cm^3 molecule^{-1}s^{-1} at 30 Torr total pressure. No significant dependences on temperature and total pressure were observed. The yield of IO from $CH_2I + O_2$ was estimated to be unity in 100 Torr total pressure of N_2 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 CH_2I_2, CH_2IBr, and CH_2ICl are considered to be the main source of IO in the marine boundary layer.[4,5] CH_2I_2 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:

$$CH_2I_2 + h\nu \rightarrow CH_2I + I \qquad (1)$$

$$I + O_3 \rightarrow IO + O_2 \qquad (2)$$

Another reactive iodine compound in the atmosphere is CH_3I originating from marine algae species.[8] In the daytime atmosphere, although the lifetime of CH_3I is controlled almost entirely by photodissociation, OH- and Cl-initiated attack could account for 10−20% of the removal of CH_3I.[9]

$$CH_3I + OH \rightarrow CH_2I + H_2O \qquad (3)$$

Under atmospheric conditions it has been believed that the CH_2I radical produced via reactions 1 and 3 reacts with O_2 to generate CH_2IO_2 in analogy to other halogenated alkyl radicals:[10−12]

$$CH_2I + O_2 + M \rightarrow CH_2IO_2 + M \qquad (4)$$

However, Masaki et al. found that the rate constants of the $CH_2I + O_2$ reaction did not depend on the total pressures in the range of 2−15 Torr and considered the following two-body process:[13]

$$CH_2I + O_2 \rightarrow IO + HCHO \qquad (5)$$

Although they suggested the possibility of formation of IO from $CH_2I + O_2$, there has been no direct evidence of the IO formation. If IO radicals are produced from CH_2I 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 CH_2I with O_2 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.

CH_2I_2 is injected into the cell using a bubble tube with N_2 buffer gas, the concentration of which is monitored at 253.7 nm before the entrance, typically 1×10^{14} molecules cm^{-3}. The 266 nm output of a Nd^{3+}:YAG laser is used to dissociate CH_2I_2 to give an I atom and a CH_2I radical. The dissociation yield of CH_2I_2 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 $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ (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 5.9×10^{-17} cm^2 molecule^{-1} at this

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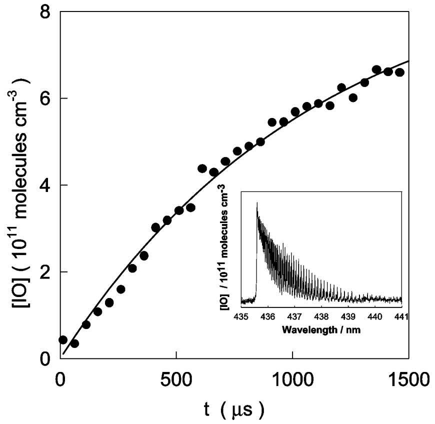

Figure 1. A typical rise profile of the IO radical monitored at 435.63 nm after the initial pulse (time = 0 μs) of the 266 nm output of an Nd^{3+}:YAG laser. The inset shows the A ← X (3, 0) band of IO.

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 μs after the photolysis laser pulse. A large excess amount of O_2, $10^{15}-10^{16}$ molecules cm^{-3}, is used to maintain the pseudo-first-order reaction conditions. CH_2IBr and CH_2ICl are also used as alternative sources of CH_2I to confirm the measured rate constants. To estimate the branching ratio of the IO radical formation from $CH_2I + O_2$, the reactions of CH_3I and CF_3I with O atoms in the presence of O_2 are performed. In this experiment, the 266 nm photolysis of O_3 generates $O(^3P)$ atoms under N_2 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 CH_2I with O_2. 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 O_2 concentration over that of CH_2I, the rise profile followed pseudo-first-order kinetics. The formation of the IO radicals are analyzed using the following equations:

$$[IO]_t = [CH_2I]_0\{1 - \exp(-k't)\} \tag{I}$$

$$k' = k_5[O_2] + k_d \tag{II}$$

where $[IO]_t$ is the concentration of IO radicals at time t and $[CH_2I]_0$ is the concentration of CH_2I 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 O_2 of 1.1×10^{15} molecules cm^{-3} at 298 K, which is fitted to eq I. Figure 2 shows a plot of k' vs $[O_2]$ at room temperature in 30 Torr total pressure of N_2 diluent. The second-order rate constant k_5 is obtained from a linear least-squares analysis of the data; $k_5 = (4.0 \pm 0.4) \times 10^{-13}$ cm^3 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 CH_2I_2 is increased by 3 times, no change of the rate constant k_5 is observed. Since the initial concentrations of the radicals are low, the radical−radical reactions do not affect the determination of the rate constant k_5. For example, CH_2I radicals are not consumed by the reaction with I atoms:[21]

$$CH_2I + I + M \rightarrow CH_2I_2 + M \tag{6}$$

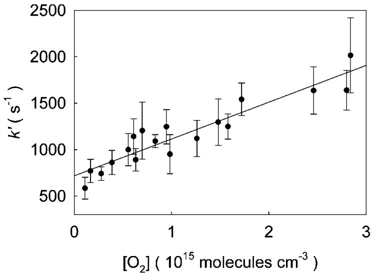

Figure 2. Second-order plots for the reaction of CH_2I radicals with O_2 at 30 Torr of N_2 diluent at 298 K. The solid line is a linear least-squares fit.

The rate constants are also measured using CH_2ICl and CH_2IBr as precursors of the CH_2I radical, which yield the same rate constant as for CH_2I_2. On the basis of these results, any secondary reactions are not significant in the present experiment. Masaki et al. determined $k_5 = (1.6 \pm 0.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} from the decay profile of the CH_2I 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 CH_2I 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 $CH_3I + O(^3P)$ in the presence of O_2 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} cm^3 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 N_2 diluent. These results suggest that the two-body reaction mechanism is dominant in $CH_2I + O_2$, or possibly the CH_2IO_2 formation path reaches already its high-pressure limit with a very limited yield. As will be discussed below, the formation yield of IO from $CH_2I + O_2$ is estimated to be unity. Thus, CH_2IO_2 formation can be neglected under our experimental conditions. Sehested et al. reported, however, the formation of CH_2IO_2 under 1000 mbar total pressure of SF_6 diluent.[12] They measured the absorption of CH_2IO_2 at 220−400 nm 2 μs 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 CH_2IO_2 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 CH_2IO_2 and HCHO. In addition, the heats of reaction for $CH_2X + O_2 \rightarrow XO + HCHO$ 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, CH_2IO_2 is not stabilized even under the high-pressure condition while the formation of CH_2ClO_2 and CH_2BrO_2 was reported.[10,11] In general, the IO formation from reaction 5 is considered to occur via the four-centered intermediate. Because CH_2I has a low ionization potential (<8.6

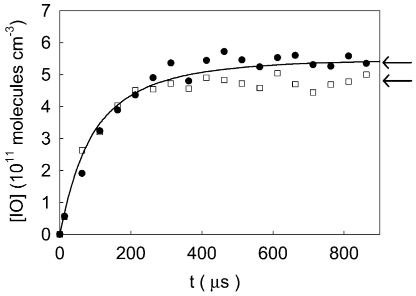

Figure 3. Rise profiles of IO radicals produced from the reactions of $O(^3P)$ with CH_3I (filled circle) and CF_3I (open square) in the presence of O_2. $[CH_3I] = [CF_3I] = 8 \times 10^{14}$, $[O_2] = 1 \times 10^{16}$, $[O_3] = 4 \times 10^{12}$ molecules cm^{-3}. The solid curve is a simulated one. 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 O_2, 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 $CH_3I/Cl_2/O_2/N_2$ mixture at room temperature; $[CH_3I] = 5.1 \times 10^{14}$, $[Cl_2] = 1.1 \times 10^{15}$, and $[O_2] = 3.9 \times 10^{16}$ molecules cm^{-3} in 30 Torr total pressure of N_2 diluent. The photoproduced Cl atom abstracts an H atom from CH_3I to produce a CH_2I radical that reacts with O_2. 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 CH_2I with O_2. To measure the formation yield of IO from of $CH_2I + O_2$, two different experiments are performed. First, the concentration of IO radicals produced from the reaction of $O(^3P)$ atoms with CH_3I is measured. This reaction is initiated by the 266 nm photolysis of $CH_3I/O_2/O_3/N_2$ mixtures; $[CH_3I] = 8.1 \times 10^{14}$, $[O_2] = 1.1 \times 10^{16}$, and $[O_3] = 3.9 \times 10^{12}$ molecules cm^{-3} in 100 Torr total pressure of N_2 diluent. Although $O(^1D)$ atoms are produced from the O_3 photolysis, they are efficiently quenched by N_2 to $O(^3P)$ before reacting with CH_3I.

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

$$CH_3I + O(^3P) \rightarrow CH_3 + IO \tag{7a}$$

$$\rightarrow CH_2I + OH \tag{7b}$$

$$\rightarrow H + I + HCHO \tag{7c}$$

$$\rightarrow I + CH_3O \tag{7d}$$

$$\rightarrow HI + HCHO \tag{7e}$$

They reported that product yields at 100 Torr with N_2 diluent are $Y(IO)_{7a} = 0.44 \pm 0.04$, $Y(CH_2I)_{7b} = 0.16 \pm 0.05$, $Y(H)_{7c} = 0.07 \pm 0.02$, $Y(CH_3O)_{7d} < 0.03$, and $Y(HI)_{7e} < 0.05$. Under our experimental conditions the contribution of IO formation from $I + O_3$ is estimated to be less than 1% because of the low O_3 concentration.[25] The reaction channels (7c and 7d) do not contribute to the IO radical formation under the present low O_3 concentration. Thus, the IO radicals are generated exclusively through reaction channels (7a and 7b) and the subsequent reaction 5 with O_2. Figure 3 shows the rise profile of the IO radicals, which goes up to $(5.4 \pm 0.2) \times 10^{11}$ molecules cm^{-3}.

As a reference experiment, the concentration of IO radicals produced from the reaction of $O(^3P)$ atoms with CF_3I is measured. This reaction is initiated by the 266 nm photolysis of $CF_3I/O_2/O_3/N_2$ mixtures ($[CF_3I] = 8.0 \times 10^{14}$, $[O_2] = 1.1 \times 10^{16}$, $[O_3] = 4.0 \times 10^{12}$ molecules cm^{-3} in 100 Torr total pressure of N_2 diluent). With these experimental conditions, $O(^3P)$ atoms react with CF_3I through the following reaction channels:

$$CF_3I + O(^3P) \rightarrow CF_3 + IO \tag{8a}$$

$$\rightarrow I + F + CF_2O \tag{8b}$$

$$\rightarrow I + CF_3O \tag{8c}$$

$$\rightarrow IF + CF_2O \tag{8d}$$

$$\rightarrow CF_3IO \tag{8e}$$

The reported product yields at 100 Torr with N_2 diluent are $Y(IO)_{8a} = 0.83 \pm 0.09$, $Y(CF_3O)_{8c} < 0.01$, 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 $O(^3P) + CH_3I$, $[IO]_{CH_3I}$, is compared with $[IO]_{CF_3I}$ from $O(^3P) + CF_3I$. The ratio of two asymptotic values in Figure 3 is $[IO]_{CH_3I}/[IO]_{CF_3I} = 1.15 \pm 0.14$. 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 $Y(IO)_{7a} = 0.44 \pm 0.04$ from the present IO production yield of 0.95 ± 0.20, the IO yield from reaction 5 through reaction 7b is estimated to be $Y(IO)_{5-7b} = 0.51 \pm 0.20$, which should be the same as the CH_2I yield in reaction 7b. Gilles et al.[24] reported a much smaller value, $Y(CH_2I)_{7b} = 0.16 \pm 0.05$. 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 $CH_2I + O_2$, 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 k_5, the reported rate constant $k_7 = 1.71 \times 10^{-11}$,[23] and the estimated one $k_{7b} = k_5 Y(IO)_{5-7b} = 6.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. The rate constant for $O(^3P) + O_2$ is adopted to be $k_{O+O_2} = 1.96 \times 10^{-15}$ cm^3 $molecule^{-1}$ 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 9×10^{14} molecules cm^{-3} of CH_3I or CF_3I and 3×10^{15} molecules cm^{-3} of O_2 in 100 Torr of N_2 diluent without O_3. IO radicals are not detected. These results suggest that the following reactions do not produce IO radicals:

$$CH_3O_2 + I \rightarrow IO + CH_3O \tag{9}$$

$$CF_3O_2 + I \rightarrow IO + CF_3O \tag{10}$$

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