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Detailed mechanism of the CH$_2$I + O$_2$ reaction: Yield and self-reaction of the simple Criegee intermediate CH$_2$OO

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The application of a new reaction scheme using CH$_2$I + O$_2$ to generate the simplest Criegee intermediate, CH$_2$OO, has stimulated lively research; the Criegee intermediates are extremely important in atmospheric chemistry. The detailed mechanism of CH$_2$I + O$_2$ is hence important in understanding kinetics involving CH$_2$OO. We employed ultraviolet absorption to probe simultaneously CH$_2$I$_2$, CH$_2$OO, CH$_2$I, and IO in the reaction system of CH$_2$I + O$_2$ upon photolysis at 248 nm of a flowing mixture of CH$_2$I$_2$, O$_2$, and N$_2$ (or SF$_6$) in the pressure range 7.6–779 Torr to investigate the reaction kinetics. With a detailed mechanism to model the observed temporal profiles of CH$_2$I, CH$_2$OO, and IO, we found that various channels of the reaction CH$_2$I + O$_2$ and CH$_2$OO + I play important roles; an additional decomposition channel of CH$_2$I + O$_2$ to form products other than CH$_2$OO or ICH$_2$OO becomes important at pressure less than 60 Torr. The pressure dependence of the derived rate coefficients of various channels of reactions of CH$_2$I + O$_2$ and CH$_2$OO + I has been determined. We derived a rate coefficient also for the self-reaction of CH$_2$OO as $k = (8 \pm 4) \times 10^{-11}$ cm$^3$ molecule$^{-1}$s$^{-1}$ at 295 K. The yield of CH$_2$OO from CH$_2$I + O$_2$ was found to have a pressure dependence on N$_2$ and O$_2$ smaller than in previous reports; for air under 1 atm, the yield of $\sim$30% is about twice of previous estimates. © 2014 AIP Publishing LLC.

I. INTRODUCTION

The reactions of O$_3$ with alkenes are extremely important because they are responsible for the removal of both O$_3$ and unsaturated hydrocarbons, and for the production of OH and organic aerosols in the troposphere. The current model indicates that cycloaddition of O$_3$ to the C=C double bond of unsaturated hydrocarbons forms a primary cyclic ozonide, which rapidly cleaves its C=C and O=O bonds to form a carbonyl molecule and a carbonyl oxide that is commonly referred to as the Criegee intermediate. Previous understanding of the mechanism of these reactions was based on indirect laboratory observations of stable end products because the Criegee intermediates have eluded direct detection until recently.

The recent applications of a new reaction scheme using CH$_2$I + O$_2$ to generate the simplest Criegee intermediate, CH$_2$OO, have stimulated lively research. Using this reaction scheme, CH$_2$OO has been detected with photoionization mass spectrometry, ultraviolet (UV) depletion, UV absorption, infrared (IR) absorption, and microwave spectroscopy. With the use of some of these detection methods, the kinetics of reactions of CH$_2$OO with various compounds have been investigated experimentally. Even though the reaction of CH$_2$I + O$_2$ has been investigated extensively, a detailed mechanism of this reaction still needs to be established. The total rate coefficient for the reaction of CH$_2$I + O$_2$ was reported to be $(1.28\pm0.82) \times 10^{-12}$ cm$^3$ molecule$^{-1}$s$^{-1}$, but the branching of various formation channels was not clearly characterized. The proposed mechanisms in the earlier studies were incomplete because only product channels for the formation of ICH$_2$OO and H$_2$CO + IO, not CH$_2$OO, were considered. The mechanisms employed in more recent reports include the formation of CH$_2$OO but not the rapid self-reaction of CH$_2$OO and various channels of the reaction of CH$_2$OO + I; these reactions become important in some laboratory experiments involving large concentrations of CH$_2$OO and I. A more detailed understanding of the CH$_2$I + O$_2$ system covering experimental conditions over a wide range is thus desirable.

Using transient IR absorption to probe directly the decay of CH$_2$OO, we found that the self-reaction CH$_2$OO + CH$_2$OO was extremely rapid, and estimated the rate coefficient of this self-reaction to be $(4 \pm 2) \times 10^{-10}$ cm$^3$ molecule$^{-1}$s$^{-1}$ at 343 K. According to quantum-chemical calculations, this reaction is rapid because a cyclic dimeric intermediate is formed with large exothermicity ($\sim 375$ kJ mol$^{-1}$) before further decomposition to 2 H$_2$CO + O$_2$ ($^1$Σ$_g^+$). The formation of this dimer, with the terminal O atom of one CH$_2$OO bound to the C atom of the other CH$_2$OO, reflects a unique property of the zwitterionic character of CH$_2$OO in which the

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terminal oxygen atom is partially negatively charged whereas the other oxygen atom and the C atom are partially positively charged. While we were preparing this manuscript, a recent report by Buras et al. indicated that the rate coefficient of this self-reaction of CH2OO, \((6.0 \pm 2.1) \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 297 K, is much smaller than our previous estimate at 343 K.\(^{32}\) The kinetics were investigated with probes of CH\(_2\)OO at 375 nm and I atom at 1315 nm.

We have performed new experiments to probe simultaneously the UV absorption of CH\(_2\)I\(_2\), CH\(_2\)OO, IO, and CH\(_2\)I upon photolysis at 248 nm of a flowing mixture of CH\(_2\)I\(_2\), O\(_2\), and N\(_2\) in the pressure range 7.6–779 Torr. The temporal profiles of CH\(_2\)OO and IO were analyzed simultaneously with a detailed reaction mechanism and the pressure dependence of the yield of CH\(_2\)OO and rate coefficients of various channels of CH\(_2\)I + O\(_2\) and CH\(_2\)OO + I has been characterized. The rate coefficient of CH\(_2\)OO + CH\(_2\)OO at 295 K was determined to be \((8 \pm 4) \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\).

II. EXPERIMENTS

The photolysis cell with transient UV absorption detection has been described previously;\(^{33,34}\) only relevant details are given here. The Criegee intermediate CH\(_2\)OO was produced from the reaction of CH\(_2\)I with O\(_2\); CH\(_2\)I was prepared by photodissociation of CH\(_2\)I\(_2\) at 248 nm.

The photolysis laser beam and the probe light (both diameter 1.8 cm) overlapped collinearly in the reaction cell (length 75 cm, inner diameter 2.0 cm), as shown in Fig. 1. The photolysis laser beam at 248 nm from an excimer laser (Coherent, CompExPro 205F, KrF, \(\sim 50\) mJ, 1 Hz) was introduced into the cell by reflection from an ultra-steep long-pass edge filter (Semrock LP02-257RU-25), which also limited the probe wavelength to be greater than 260 nm. The output of a high-brightness broadband light source (Energetiq, EQ-99) was collimated with a parabolic mirror (\(f = 50.8\) mm) before entering the reaction cell. Another parabolic mirror (\(f = 101.6\) mm) served to focus the light onto the slit of a spectrometer (Andor SR303i) equipped with an intensified charge-coupled detector (iCCD, Andor iStar, DH320T-18F-E3). The resolution of the spectrometer was \(\sim 1.5\) nm. The wavelength was calibrated with the emission spectrum of a low-pressure mercury lamp, with typical errors smaller than 0.5 nm.

The transient absorption spectra were recorded with the array detector at varied delays after photolysis. The delay (duration of reaction) was defined as the interval from the photolysis laser pulse to the center of the detector gate (width \(\sim 1\) \(\mu\)s). The reference spectrum was taken at 1 or 5 \(\mu\)s before the photolysis laser pulse. The integration interval at each delay was 1 \(\mu\)s; the delay was scanned automatically after each photolysis pulse with a computer program written in Andor Basic. The spectrum at a specific delay was typically averaged 60–200 times to achieve an adequate ratio of signal to noise.

A small fraction of CH\(_2\) might be produced through the photolysis of CH\(_2\)I. We have tested the transient absorption spectra with laser pulse energies varied from 30 to 100 mJ pulse\(^{-1}\). A small decrease (2%–4%) in the yield of CH\(_2\)I was observed at laser energy greater than 100 mJ pulse\(^{-1}\), but an insignificant difference in the deduced spectrum of CH\(_2\)OO was found.

Liquid CH\(_2\)I\(_2\) was slightly heated to 305 K to ensure saturation of its vapor pressure and the CH\(_2\)I\(_2\) vapor was carried with a flow of N\(_2\) or O\(_2\). The mixing ratios of the reagent gases (CH\(_2\)I\(_2\), N\(_2\), O\(_2\), SF\(_6\)) were controlled with mass flow controllers (Brooks Instruments, 5850E). These gases were mixed in a Teflon tube before entering the reaction cell. A small stream (1%–2% of the total mass flow) of the N\(_2\)/O\(_2\) mixture gas (with the same ratio as the reagent gas) was introduced to purge both windows of the cell to prevent undesired photochemistry at the window surfaces. This purging also decreased the effective length of the sample from 75 to 72 cm, which was calibrated with the absorbance of CH\(_2\)I\(_2\)/N\(_2\) gas of a known mixing ratio.

The linear flow velocity in the reaction cell was adjusted to be greater than 0.8 \(\text{m s}^{-1}\) to allow refreshment of the sample gas between the photolysis laser pulses at a repetition rate of 1 Hz. The temperature of the reaction cell was 295 \(\pm 1.5\) K. The number density of CH\(_2\)I\(_2\) was determined from its absorption spectrum. The number densities of O\(_2\) and N\(_2\) were deduced with the ideal gas law from the measured cell pressure and their mass flow rates.

III. RESULTS

A. Determination of \(\Delta[\text{CH}_2\text{I}_2], [\text{CH}_2\text{I}], [\text{CH}_2\text{OO}],\) and [IO]

A representative transient difference UV absorption spectrum recorded 9 \(\mu\)s after photolysis of a flowing mixture of CH\(_2\)I\(_2\)/O\(_2\)/N\(_2\) (0.044/10.4/90.7) at 101.1 Torr is shown in Fig. 2. The spectrum was deconvoluted to spectra of CH\(_2\)I\(_2\) (negative due to depletion), IO, CH\(_2\)OO, and CH\(_2\)I, as is discernible from the small residual after subtracting corresponding spectra of these four species. The absorption spectra of CH\(_2\)OO and IO have characteristic progressions, whereas those of CH\(_2\)I\(_2\) and CH\(_2\)I are broad but different in shape. On minimizing the residual between the simulated and experimental spectra in the region 265–480 nm with a least-squares fitting, the number densities of CH\(_2\)OO, IO, and CH\(_2\)I, and the decrease of that of CH\(_2\)I after photolysis, were deduced according to the cross sections of these species (CH\(_2\)I\(_2\) and IO,\(^{35}\) CH\(_2\)I,\(^{23}\) and CH\(_2\)OO).\(^{15}\) The uncertainties in concentration measurements of CH\(_2\)OO, IO, CH\(_2\)I, and CH\(_2\)I\(_2\) from deconvolutions were estimated to be \(\sim 5\%\), 5\%, 10\%, and 5\%,
Our technique has mass selectivity and employs a depletion method to compare with a known reference molecule. This method was proved reliable in the measurements of cross sections of ClOOCl \(^{(38)}\). (2) We utilized both the SO\(_2\) scavenging reaction and the self-reaction of CH\(_2\)OO to extract the CH\(_2\)OO spectrum and obtained consistent results with signal-to-noise ratios superior to other reports. (3) If we used the cross section of Sheps, not only the transient absorption spectra could not be deconvoluted satisfactorily, but also the yield of CH\(_2\)OO from CH\(_2\)I + O\(_2\) at low pressure would become \(-0.25\), much smaller than the values 0.87–1.0 reported by Huang \textit{et al.} \(^{(30)}\) and 0.67–1.0 reported by Stone \textit{et al.} \(^{(31)}\) with the cross section determined by us, the yield 0.72–0.78 agrees with those in previous reports. (4) Buras \textit{et al.} recently reported cross sections of CH\(_2\)OO at 375 nm to be \((7 \pm 1.3) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}\) (Ref. 39) and \((6.2 \pm 2.2) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}\), in satisfactory agreement with our value of \((7.6 \pm 1.1) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}\) with the uncertainty limits overlapping with each other.

B. Temporal profiles of CH\(_2\)OO and IO in experiments with N\(_2\) and O\(_2\)

A summary of experimental conditions and fitted rate coefficients of some representative experiments is presented in Table I; a complete list of a total of 64 experiments is available in Table SI of the supplementary material. \(^{(37)}\)

Representative temporal profiles of CH\(_2\)I, CH\(_2\)OO, and IO recorded upon photolysis of a flowing mixture of CH\(_2\)I\(_2\) (24.3 or 24.5 mTorr), O\(_2\) (both 10.5 Torr), and N\(_2\) (92.7 or 90.4 Torr) in two experiments (nos. 60 and 63 in Table I) near 100 Torr and 295 K with small [CH\(_2\)OO]\(_0\) are shown in Fig. 3. The decrease in concentration of CH\(_2\)I upon laser irradiation, hence [CH\(_2\)I]\(_0\), was \(-\Delta[CH_2I] = [CH_2I]_0 \equiv 1.17 \text{ mTorr} (3.8 \times 10^{13} \text{ molecule cm}^{-2})\). The rapid increase of CH\(_2\)OO and decay of CH\(_2\)I were due to the reaction of CH\(_2\)I + O\(_2\). After approximately 8 \(\mu s\), CH\(_2\)OO began to decay and the concentration of IO gradually increased. In this figure (and all others showing experimental temporal profiles) we also show the simulated temporal profiles of CH\(_2\)I, CH\(_2\)OO, IO, ICH\(_2\)OO, H\(_2\)CO, and I according to the proposed mechanism, as discussed in Sec. IV A.

For comparison, Fig. 4 shows results of two experiments (nos. 49 and 52 in Table I) under similar conditions except for increased [CH\(_2\)OO]\(_0\). The decrease in concentration of CH\(_2\)I upon laser irradiation, hence [CH\(_2\)I]\(_0\), was \(-\Delta[CH_2I] = [CH_2I]_0 \equiv 3.54 \text{ mTorr} (1.16 \times 10^{14} \text{ molecule cm}^{-2})\). In this example, [CH\(_2\)OO] decreased more rapidly than in Fig. 3, indicating the second-order nature of the decay of CH\(_2\)OO. Similarly, [IO] increased more rapidly than in Fig. 3, indicating that some IO was produced from subsequent reactions of CH\(_2\)OO.

The temporal profile of CH\(_2\)I, CH\(_2\)OO, and IO recorded upon photolysis of a flowing mixture of CH\(_2\)I\(_2\) (42.9 mTorr), O\(_2\) (51.1 Torr), and N\(_2\) (354.4 Torr) in an experiment (no. 2 in Table I) at high pressure (405.5 Torr) and 295 K is shown in Fig. S2 of the supplementary material. \(^{(37)}\) In this example, CH\(_2\)OO increased rapidly because of larger [O\(_2\)] employed and the yield of IO (and ICH\(_2\)OO by simulation) relative to CH\(_2\)OO was enhanced, indicating that some IO was produced from secondary reactions of ICH\(_2\)OO of which the concentration was expected to be enhanced at high pressure.
TABLE I. Representative experimental conditions, fitted rate coefficients, yield \( y \) and fraction of survival \( \beta \) of CH\(_2\)OO in the CH\(_2\)I\(+\)O\(_2\) system at 295 K.

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</table>

\( a \) In unit of molecule cm\(^{-3}\).

\( b \) In unit of cm\(^3\) molecule\(^{-1}\) s\(^{-1}\).

\( y = k_{1a}' / (k_{1a}' + k_{1b} + k_{1c}); \beta = k_{1a}' / (k_{1a}' + k_{1c}) \).
yields of CH$_2$OO and IO due to efficient quenching of internally excited ICH$_2$OO were observed.

IV. DISCUSSION

A. Reaction mechanism and simulation of temporal profiles at P > 60 Torr

To describe the CH$_2$I + O$_2$ system in detail, we employed the following scheme:

\[
\begin{align*}
\text{CH}_2\text{I} + \text{O}_2 &\rightarrow \text{CH}_2\text{OO} + \text{I} \\
\text{CH}_2\text{I} + \text{O}_2 &\rightarrow \text{ICH}_2\text{OO} + \text{I} \\
\text{ICH}_2\text{OO} + \text{I} &\rightarrow \text{H}_2\text{CO} + \text{IO}
\end{align*}
\]

in which ICH$_2$OO$^*$ represents an energized adduct ICH$_2$OO initially formed upon reaction of CH$_2$I with O$_2$. ICH$_2$OO$^*$ might decompose to form the original reactants, proceed to form CH$_2$OO + I (reaction (1a)), or become stabilized to ICH$_2$OO (reaction (1b)), with branching ratios $\alpha_1$, $\alpha_2$, and (1 − $\alpha_1$ − $\alpha_2$), respectively. From the steady-state approximation of [ICH$_2$OO$^*$], described in detail in the supplementary material, $\alpha_1$ and $\alpha_2$ were derived as functions of pressure and detailed rate coefficients indicated in grey in the scheme. The grey part in this scheme was not used explicitly in the kinetic fitting; only the effective reactions (solid parts) were used. Because of the large concentration of I atoms and the great reactivity of CH$_2$OO, once produced, CH$_2$OO reacts readily either with I atom (reaction (2)) or with itself (reaction (3)). According to theoretical calculations, the major reactions of CH$_2$OO with I atom proceed via three channels: attack of the terminal O atom of CH$_2$OO by the I atom to form CH$_2$I (reaction (2a)) or stabilization to ICH$_2$OO$^*$ (reaction (2b)) or stabilization to ICH$_2$OO (reaction (2c)). ICH$_2$OO$^*$ further reacts with itself (reaction (4)) or I atoms (reaction (5)) to form ICH$_2$O which subsequently decomposes to H$_2$CO + I (reaction (6)).

The mechanism is summarized below:

\[
\begin{align*}
\text{CH}_2\text{I} + \text{O}_2 &\rightarrow \text{CH}_2\text{OO} + \text{I}, \quad k_{1a} = \alpha_2 k_1, \quad (1a) \\
\text{CH}_2\text{I} + \text{O}_2 &\rightarrow \text{ICH}_2\text{OO}, \quad k_{1b} = (1 - \alpha_1 - \alpha_2) k_1, \quad (1b) \\
\text{CH}_2\text{OO} + \text{I} &\rightarrow \text{CH}_2\text{I} + \text{O}_2, \quad k_{2a} = \alpha_1 k_2, \quad (2a) \\
\text{CH}_2\text{OO} + \text{I} &\rightarrow \text{ICH}_2\text{OO}, \quad k_{2b} = (1 - \alpha_1 - \alpha_2) k_2, \quad (2b) \\
\text{CH}_2\text{OO} + \text{I} &\rightarrow \text{H}_2\text{CO} + \text{IO}, \quad k_{2c}, \quad (2c)
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{OO} + \text{CH}_2\text{OO} &\rightarrow 2\text{H}_2\text{CO} + \text{O}_2 (\Delta_g), \quad k_3, \quad (3)
\end{align*}
\]
\[ \text{ICH}_2\text{OO} + \text{ICH}_2\text{OO} \rightarrow 2\text{ICH}_2\text{O} + \text{O}_2, \quad k_4, \quad (4) \]

\[ \text{ICH}_2\text{OO} + \text{I} \rightarrow \text{ICH}_2\text{O} + \text{IO}, \quad k_5, \quad (5) \]

\[ \text{ICH}_2\text{O} \rightarrow \text{H}_2\text{CO} + \text{I}, \quad k_6, \quad (6) \]

\[ \text{IO} + \text{IO} \rightarrow \text{products} \quad k_7 \quad (7) \]

in which \( k_4 = 9.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), \( k_5 = 3.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), \( k_6 = 1.0 \times 10^{-5} \text{ s}^{-1} \), and \( k_7 = 9.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) were reported.\(^{40}\)

Even though five rate coefficients are listed for reactions (1) and (2), we had to determine only \( k_{1a} \), \( k_{1b} \), and \( k_{2c} \) because \( K^{-1} = k_{2c}/k_{1a} \) or \( k_{2c}/k_{1b} \). As the total rate coefficient for reaction (1), \( k_1 = \alpha_k \), was reported to be (1.28–2.71) \( \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) for pressure up to 250 Torr of Ar,\(^{14,24,26,29,31}\) we used the average value of \( k_{1a} + k_{1b} = 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) in the fitting; this value fits satisfactorily with the experimental decay of CH\(_2\)I, when available, and the initial rise of CH\(_2\)OO in all experiments in SF\(_6\) and those in N\(_2\) and O\(_2\) with \( P \geq 60 \text{ Torr} \). The yield of CH\(_2\)OO, \( \alpha_k = (1 - \alpha_i) = [\text{CH}_2\text{OO}]_0/[\text{CH}_2\text{I}]_0 \), implies that \( k_{1a} = y(k_{1a} + k_{1b}) \) and \( k_{1b} = (1 - y)(k_{1a} + k_{1b}) \); \( k_{1a} \) and \( k_{1b} \) could be determined from \( y \) and \( k_{1a} + k_{1b} \). In the fit, the yield of CH\(_2\)OO was initially estimated with \( y = [\text{CH}_2\text{OO}]_0/[\text{CH}_2\text{I}]_0 \) in which [CH\(_2\)OO] was estimated with a short extrapolation of the decay of [CH\(_2\)OO] to \( t = 0 \) and [CH\(_2\)I] = [CH\(_2\)I] in which \( \Delta [\text{CH}_2\text{I}]_0 \) when we assumed that all photolyzed CH\(_2\)I produced CH\(_2\)I + I. Subsequent fine adjustments of \( y \) were performed on fitting the observed CH\(_2\)OO profile; \( k_{1a} \) and \( k_{1b} \) were thereby derived.

The production of IO resulted mainly from two channels: reaction (2c) from CH\(_2\)OO + I and reaction (5) from CH\(_2\)O + I. At low pressure, [CH\(_2\)OO] is much greater than [ICH\(_2\)OO], so that reaction (2c) is more important than reaction (5); in contrast, at high pressure, [ICH\(_2\)OO] is much greater than [CH\(_2\)OO], so that reaction (5) is more important than reaction (2c). Although the rate coefficient of \( k_{2c} \) was predicted to be \( 5.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \),\(^{21}\) we found that we needed to set \( k_{2c} = 9.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) to fit the rise of IO properly, especially at low pressures. This deviation of \( k_{2c} \) from a previous theoretical prediction is reasonable because this rate coefficient is sensitive to the barrier height and the calculated value of 7.9 kJ mol\(^{-1}\) might have been overestimated. From the sensitivity analysis shown in the supplementary material,\(^{35}\) this rate coefficient has a negligible effect on the rate coefficient \( k_7 \) in fitting the profiles of CH\(_2\)OO.

It should be noted that the reaction

\[ \text{CH}_2\text{OO} + \text{CH}_2\text{I} \rightarrow \text{C}_2\text{H}_4\text{I} + \text{O}_2(3\Sigma_g^-) \quad (8) \]

with \( k_8 \) predicted to be \( 6.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) (Ref. \( 21 \)) is not included in the model because in our experiments O\(_2\) was in excess so that most CH\(_2\)I was readily converted to CH\(_2\)OO or ICH\(_2\)OO. In experiments with significant [CH\(_2\)I], this reaction has to be included in the model.

The fitting procedures thus became systematic on performing the following steps using either the Chemkin II program\(^{41}\) or a fitting program written with MATLAB: the latter was more efficient and convenient to use; its validity was verified with the former. After the initial fitting of \( y \) with \( k_{1a} + k_{1b} \) fixed to \( 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) to derive \( k_{1a} \) and \( k_{1b} \), and subsequently \( k_{2a} \) and \( k_{3a} \) using an initial guess of \( K^{-1} = 70 \), the rate coefficient of self-reaction of CH\(_2\)OO, \( k_3 \), was fitted with least squares to minimize the deviations of the simulated and observed temporal profiles of [CH\(_2\)OO] and [IO]; \( k_{2c} \) and \( k_4-k_6 \) were fixed in the fitting. Values of \( k_4-k_6 \) were taken from the literature, as listed previously, but \( k_7 = 1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) had to be used to account for the decay of IO. The fit yielded \( k_5 = (6.5 \pm 2.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), but \( k_3 \) decreased with pressure for data in the pressure range 60–779 Torr. When \( K^{-1} \) was decreased to 40, we obtained \( k_5 = (10.9 \pm 2.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), with \( k_3 \) increasing with pressure for data in the pressure range 100–779 Torr.

We then varied the value of \( k_5 \) systematically and repeated the fit, all data under varied experimental conditions were fitted satisfactorily to yield \( k_5 \) independent of pressure only when \( k_5 \) was in the range 50–60; the best fits were with \( K^{-1} = 55 \), which yields \( k_5 = (8.2 \pm 1.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) for data in the pressure range 60–779 Torr. The value \( K^{-1} = 55 \) corresponds to \( \Delta G = 9.8 \text{ kJ mol}^{-1} \) for reaction (1a), within expected uncertainties of the value of 10.4 kJ mol\(^{-1}\) predicted with the CCSD(T)/B3LYP/aug-cc-pVTZ-pp method. Using this model, the simulated temporal profiles of CH\(_2\)I, CH\(_2\)OO, IO, ICH\(_2\)OO, I, and H\(_2\)CO for the experiment are shown with thick lines in Figs. 3 and 4; these simulated profiles of CH\(_2\)I, CH\(_2\)OO, and IO agree satisfactorily with experiments. In contrast, the profile simulated for IO in the experiment, shown as a dashed-dotted line (noted as “\( k_{1c} = 0^\circ \)” in Fig. 5 using this model, is significantly greater than the experimental data, to be discussed in Sec. IV B.

B. Decomposition of ICH\(_2\)OO\(^*\) or CH\(_2\)OO\(^*\) at \( P < 60 \text{ Torr} \)

As indicated in Fig. 5, after fitting the profile of CH\(_2\)OO, the experimental temporal profile of IO disagrees with simulations using the mechanism discussed in Sec. IV A. The observed concentration of IO was significantly smaller than that simulated with this model and that of CH\(_2\)OO showed a rise less rapid than simulation. These deviations were observed for all experiments performed below 60 Torr.

As discussed in Sec. IV A, IO could be produced from two channels: CH\(_2\)OO + I (reaction (2c)) and ICH\(_2\)OO + I (reaction (5)). At low pressure, as [ICH\(_2\)OO] is much smaller than [CH\(_2\)OO], most IO was produced from CH\(_2\)OO + I. To reconcile the smaller [IO], we propose that some internally excited ICH\(_2\)OO\(^*\) or CH\(_2\)OO\(^*\) might have decomposed to form products other than CH\(_2\)OO or ICH\(_2\)OO at low pressure because of less efficient quenching. A similar mechanism
was also proposed by Eskola et al. for ICH2OO\(^*\).\(^{29}\) Hence, for experiments below 60 Torr, we modified the original reaction (1a) to include two channels,

\[
\begin{align*}
CH_2 + O_2 &\rightarrow CH_2OO + I, \quad k_{1a} = (1.5 \times 10^{-12} - k_{1b}) \beta, \\
CH_2I + O_2 &\rightarrow \text{products other than CH}_2\text{OO or ICH}_2\text{OO}, \\
&\quad k_{1c} = (1.5 \times 10^{-12} - k_{1b})(1 - \beta)
\end{align*}
\]

in which \(k_{1c} = 0\) and the fraction of survival of CH\(_2\)OO \(\beta = k_{1a} / (k_{1a} + k_{1b})\) is 1 for \(P > 60\) Torr and \(\beta\) decreases with pressure for \(P < 60\) Torr. The decomposition of some ICH\(_2\)OO\(^*\) or CH\(_2\)OO\(^*\) at low pressure consequently accounted for the smaller concentrations of CH\(_2\)OO and IO. The yield of CH\(_2\)OO is consequently revised to be \(\gamma = \beta \times k_{1a} / (k_{1a} + k_{1b})\) to include the data at low pressure; hence \(k_{1a} = (k_{1a} + k_{1b}) \gamma, k_{1b} = (k_{1a} + k_{1b}) (1 - \gamma \beta), \) and \(k_{1c} = (k_{1a} + k_{1b}) \gamma (1 - \beta) / \beta\). This decomposition channel at low pressure is further supported by our observation of infrared absorption bands of CO and CO\(_2\) in the photolytic reaction of CH\(_2\)I\(_2\) + O\(_2\) at 248 nm for pressures below 40 Torr.

With this revised model, we adjusted \(\beta\) and \(\gamma\) to fit the observed temporal profiles of IO and CH\(_2\)OO, with all other parameters determined the same way as in the case at high pressure. Subsequently, rate coefficient \(k_1\) was fitted with least squares. After considering this decomposition channel, the temporal profiles of CH\(_2\)OO and IO were simulated satisfactorily, as shown in thick lines in Fig. 5 with \(\beta = 0.78\) and 0.73 for experiment nos. 29 and 33, respectively. Twenty three experiments performed with total pressure below 60 Torr were fitted satisfactorily using this revised model with \(\beta = 0.73 - 0.92\) or \(k_{1c}\) up to \(3.9 \times 10^{-13}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), 26\% of the total rate coefficient of reaction (1).

The less rapid rise of CH\(_2\)OO might be explained also by the decomposition mechanism. As at low pressure the quenching of ICH\(_2\)OO\(^*\) and CH\(_2\)OO\(^*\) is less facile, the proportion of the internally excited ICH\(_2\)OO\(^*\) or CH\(_2\)OO\(^*\) that decomposes increased, more at the earlier period of reaction. The proportion of the “loss” in CH\(_2\)OO was hence largest at the beginning and decreased at the later stage of reaction. When an efficient quencher SF\(_6\) was employed, even at low pressure this delayed rise of CH\(_2\)OO disappeared, as indicated in Fig. S3 of the supplementary material.\(^{37}\)

C. Fitted rate coefficients and their dependence on pressure

This fitting procedure worked well for 69 sets of data in total in the pressure range 7.6–779 Torr in which the pressure of O\(_2\) was varied from 2.0 to 163.0 Torr, N\(_2\) from 0 to 773.9 Torr, SF\(_6\) from 0 to 62.7 Torr, and [CH\(_2\)I\(_0\)] in the range (2.1–18.4) \(\times 10^{13}\) molecule cm\(^{-3}\). The experimental conditions, the fitted rate coefficients, and the values of \(\gamma\) and \(\beta\) thus derived for some representative experiments are summarized in Table I; a complete list is available in Tables S1 (N\(_2\) and O\(_2\)) and SII (SF\(_6\)) of the supplementary material.\(^{37}\)

FIG. 6. Dependence on pressure of the rate coefficient for the formation of CH\(_2\)OO, \(k_{1a}\). (a) \(k_{1a}\) as a function of total pressure \(P\), the solid line is fitted according to Eq. (9); (b) \((k_{1a} + k_{1b}) / k_{1a}\) as a function of \(P\); \(k_{1a} = k_{1a}' + k_{1c}\).

1. Pressure dependence of \(k_{1a}\) and \(k_{1b}\)

The pressure dependence of \(k_{1a}\) is shown in Fig. 6(a); \(k_{1a}\) represents the rate coefficient for the formation of CH\(_2\)OO from CH\(_2\)I + O\(_2\). As expected, the rate coefficient decreases with pressure as the formation of ICH\(_2\)OO becomes more important. A plot of \((k_{1a} + k_{1b}) / k_{1a}\) as a function of \(P\) is shown in Fig. 6(b); in this case \(k_{1a}\) takes into account the proportion that decomposes at low pressure. According to the rate expression shown in the supplementary material,\(^{37}\)

\[
k_{1a} + k_{1b} / k_{1a} = 1 + \frac{k_q[M]}{k_{-2}}, \quad (9)
\]

The linear relation between \((k_{1a} + k_{1b}) / k_{1a}\) and \([M]\) (=P) and an intercept \(\sim 1\) are satisfactorily demonstrated in Fig. 6(b), supporting the validity of our model. Using this equation, we were able to derive \(k_q / k_{-2} = (1.1 \pm 0.1) \times 10^{-19}\) cm\(^3\) molecule\(^{-1}\).

The dependence of \(k_{1b}\) on pressure is shown in Fig. 7(a); \(k_{1b}\) represents the rate coefficient for the formation of ICH\(_2\)OO from CH\(_2\)I + O\(_2\). A linear rise with pressure is observed for \(k_{1b}\) at low pressure; \(k_{1b}\) levels off at high pressure, characteristic of quenching stabilization of ICH\(_2\)OO. A plot of \((k_{1a} + k_{1b}) / k_{1a}\) as a function of \(P^{-1}\) is shown Fig. 7(b); because this channel is important only at high pressure, we plot data only with \(P \geq 100\) Torr. According to the rate
2. Pressure dependence of \( k_{1c} \)

The dependence of \( k_{1c} \) on pressure is shown in Fig. 8(a) and the dependence of \( \beta \), the fraction of survived CH\(_2\)OO, on pressure is shown in Fig. 8(b); because of the smaller values, the errors in these measurements are greater than others. An initial increase in \( \beta \) with pressure before leveling off, similar to that of \( k_{1b} \), was observed; this is characteristic of quenching stabilization. A decrease with pressure is observed for \( k_{1c} \), the value becomes negligible near 60 Torr. The observed pressure dependence is consistent with a mechanism of stabilization of ICH\(_2\)OO\(^*\) and CH\(_2\)OO\(^*\) by collisional quenching. The \( \beta \) values are fitted to an equation

\[
\beta = 1 - (0.47 \pm 0.11)/[1 + (3.2 \pm 1.2) \times 10^{-18} [\text{M}]].
\]  

(11)

Because of the large uncertainties in \( \beta \), the fitting reproduce \( \beta \) values to only within 0.08.

3. Determination of \( k_3 \)

The fitted rate coefficient for self-reaction of CH\(_2\)OO, \( k_3 \), ranged from 5.6 to 12.0 \( \times 10^{-11} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), with an average of all data \( k_3 = (8.2 \pm 1.4) \times 10^{-11} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for experiments in N\(_2\) and O\(_2\); the error limits represent one standard deviation in averaging. Some representative sensitivity analyses are shown in the supplementary material.\(^{37}\) At high pressure, the analysis clearly shows that reactions (1a), (1b) and (2b) are more sensitive to the variation of [CH\(_2\)OO] than reaction (3), but the factors of reactions (1a) and (1b) have similar values with opposite signs because these reactions are competing with CH\(_2\)I for the formation of either CH\(_2\)OO or ICH\(_2\)OO. The sensitivity of reaction (3), \( \partial x/\partial (\ln k_3) \), in which \( x \) is the mass fraction of CH\(_2\)OO, indicates that \( k_3 \) has greater errors at high pressure than at low pressure, mainly because [CH\(_2\)OO] is small relative to [ICH\(_2\)OO]. At lower pressure [CH\(_2\)OO] is much greater than [ICH\(_2\)OO] and the sensitivity of reaction (3) is greater than of reactions (2a) and (2b), but still smaller than of reactions (1a) and (1b). However, the effect of reactions (1a) and (1b) on \( k_3 \) cancels each other. Even under such conditions and in the critical range 20–150 \( \mu \)s, \( \partial (\ln k_3)/\partial (\ln k_i) \)
Two assumptions were made in these fits: $k_{1a} + k_{1b} = 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $c_1/c_2 = 1$. The former was actually tested with our experimental data, even at high pressure, and we fixed this value simply to minimize the variables in our fitting. The value of $c_1/c_2$ might deviate slightly from 1; a deviation of 30% implies a deviation of $k_{1b}$ by 30%, which translates to ~20% in $k_1$ at low pressure. Considering the estimated relative error of 20% in concentration measurements of CH$_2$OO, which translates to ~60% error in $k_1$ at high pressure and ~30% at low pressure based on sensitivity analysis, 24% error induced by the uncertainty of $K^{-1}$ (=55 ± 15), 17% error in the least-square fit of each individual temporal profile, we report $k_1 = (8 \pm 4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with the error representing the 95% confidence level.

Previously, using IR absorption to monitor CH$_2$OO, we could only roughly estimate the rate coefficient of $k_1$ because of large uncertainties.21 Because the IR probe beam did not follow the UV photolysis beam, the average concentration in the photolysis volume hence differed from that of the IR-probed volume. The conversion between concentrations of CH$_2$OO in the UV-photolyzed volume and the IR-probed volume had large errors. The initial concentration of CH$_2$I in the photolyzed volume was estimated with the UV absorption cross section of CH$_2$I and the laser fluence, which was estimated from the energy and the size of the laser beam. The concentration of CH$_2$OO measured from IR absorption also had large errors because the IR absorption cross section predicted with quantum-chemical computations might have large errors which affect the bimolecular rate coefficient by approximately the same factor. Furthermore, the mechanism employed previously ignored reactions (1b) and (1c), and also employed theoretically predicted rate coefficients for reactions (2a)–(2c). All these factors might result to an underestimated error bar of our previous estimate. The dependence of $k_1$ on temperature is expected to be small, so the previously reported value of $k_1 = (4 \pm 2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 343 K might have been overestimated. Our determination of $k_1 = (8 \pm 4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K in this work agrees with the recently reported value $k_1 = (6.0 \pm 2.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K by Buras et al.32 even though a simplified mechanism was employed in that work.

D. Yield of CH$_2$OO and its dependence on pressure

In Fig. 9 we plot the reciprocal yield of CH$_2$OO, $y^{-1} = (k_{1a} + k_{1b} + k_{1c})/k_{1a} = (k_{1a} + k_{1b})/k_{1a}$, as a function of total density [M] for the pressure range 7.6–779.2 Torr. These data were fitted with the equations

$$y^{-1} = (1.24 \pm 0.03) + (9.13 \pm 0.33) \times 10^{-20} [M], \quad \text{or } \quad M = O_2 \text { or } N_2 \quad (12)$$

in which [M] is the density in molecule cm$^{-3}$; the errors represent one standard deviation in fitting. Our data are compared with previous reports in Fig. 9. The smaller yield of CH$_2$OO (greater $y^{-1}$) at low pressure is due to the decomposition of CH$_2$OO*/ICH$_2$OO*; this reduction of yield would not appear in the experiments with I-atom detection. It is unclear why Huang et al. observed significantly different pressure dependence on $N_2$. Our results for $M = O_2$ and $N_2$ agree satisfactorily with their report for $M = He$ [slope = (0.93 ± 0.13) × 10$^{-19}$] and $O_2$ [slope = (1.1 ± 0.1) × 10$^{-19}$], but are much smaller than for $M = N_2$ [slope = (2.4 ± 0.4) × 10$^{-19}$].30 Our results also have a pressure dependence much less than that reported by Stone et al.31 with $M = N_2$ and $O_2$ [slope = (1.90 ± 0.11) × 10$^{-19}$ for all data].

Our assumption of $-\Delta \text{[CH}_2\text{I]}_2 = [\text{CH}_2\text{I}]_0$ might overestimate [CH$_2$I]$_0$ by as much as 15%, but not significantly enough to explain the discrepancies. When we tested the power dependence of this discrepancy, we found that this discrepancy was not due to secondary photolysis of CH$_2$I; it is likely due to the error of the reported cross section of CH$_2$I. Some uncertainties in these previous reports might have resulted from the indirect methods employed by observation of I atoms and H$_2$CO rather than CH$_2$OO, and the uncertainties in analysis of observed temporal profiles with their models. It should be noted that we performed experiments at 248 nm whereas Huang et al. employed light at 355 nm.30 Weather the difference in internal energy of CH$_2$I affects the stabilization of ICH$_2$OO, even at high pressures, requires further investigation. However, from the results of Stone et al. in which laser light at both 248 nm and 355 nm was used, the effect of photolysis wavelength on yield of CH$_2$OO is insignificant.31

The estimated yields of CH$_2$OO from CH$_2$I + O$_2$ at 298 K and 760 Torr in air, ~15% reported by Huang et al.30 and 18% by Stone et al.31 were proposed to have significant implications for the oxidation chemistry of halogen-containing organic compounds and for the atmospheric chemistry in marine regions with large concentrations of CH$_2$I$_2$. 

![Figure 9](image-url)
Our estimate of a yield $\sim 30\%$ at 295 K and 760 Torr would enhance these effects significantly.

Following the same method to simulate the experimental conditions in the laboratory investigations of the ozonolysis of C$_2$H$_4$ using the revised $k$ value and a model reported previously, we found that, when the self-reaction of CH$_2$OO is included in the model, the simulated yield of hydroperoxymethyl formate [HPMF, CH$_3$(OOH)--O--CHO] and formalic acid anhydride [FA, (HCO)$_2$O] decreased by $\sim 7\%$ and that of HCOOH increased by $\sim 3\%$. The H$_2$CO produced due to the self-reaction of CH$_2$OO accounts for an additional yield $\sim 0.03$. When we increased the rate coefficient for O$_3$ + alkene from $1 \times 10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for C$_2$H$_4$ to $1 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for larger alkenes, the simulated yield of compounds due to the reaction of Criegee intermediate + HCOOH, corresponding to HPMF + FA in O$_3$ + C$_2$H$_4$, decreased by 25%–30%, whereas that of HCOOH increased by 10%–12%. Furthermore, the additional carbonyl compounds produced from the self-reaction of the Criegee intermediates account for a yield 0.11–0.14, explaining the observed stoichiometry ratio larger than unity. Even though the significantly reduced value of the rate coefficient $k_4$ decreases its effect on the laboratory ozonolysis experiments, it might play an important role when the concentration of CH$_2$OO is large.

The rate coefficients $k_{1a}$, $k_{1b}$, $k_{1c}$, $k_{2a}$, $k_{2b}$, $k_{3c}$, $k_3$, and values of $\beta$ (fraction of survival of CH$_2$OO) and $y$ (yield of CH$_2$OO) derived in this work are summarized in Table II.

### V. CONCLUSION

To investigate the detailed kinetics of the CH$_2$I + O$_2$ reaction, we monitored the UV absorption of CH$_2$I$_2$, CH$_2$I, IO, and CH$_2$OO simultaneously in the reaction system of CH$_2$I + O$_2$ at 295 K upon photolysis of a flowing mixture of CH$_2$I$_2$, O$_2$, and N$_2$ (or SF$_6$) at 248 nm. Using a detailed mechanism for the reaction, we simulated the temporal profiles of CH$_2$OO and IO that agreed satisfactorily with experimental data over a wide range of experimental conditions with $P = 7.6$–779 Torr. We found that, at pressure below 60 Torr, some internally excited ICH$_2$OO$^*$ or CH$_2$OO$^*$ decomposed; the fraction of survival $\beta = k_{1a}/(k_{1a} + k_{1b} + k_{1c})$ was determined to be as small as $\sim 0.75$ near 7.8 Torr.

The feature of our mechanism is that we clearly specified three channels for the reaction CH$_2$I + O$_2$, and three channels for CH$_2$OO + I, and include the self-reaction of CH$_2$OO that becomes important when the concentration of CH$_2$OO is large. The dependence of derived rate coefficients on pressure for the formation of CH$_2$OO + I ($k_{1a}$), ICH$_2$OO ($k_{1b}$), and other products ($k_{1c}$) from CH$_2$I + O$_2$ and the formation of CH$_2$I + O$_2$ ($k_{2a}$), ICH$_2$OO ($k_{2b}$), and H$_2$CO + IO ($k_{3c}$) from CH$_2$OO + I was determined; they conform to the expected behavior for enhanced stabilization of ICH$_2$OO at higher pressure. We also determined a rate coefficient $k_3 = (8 \pm 4) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the self-reaction of CH$_2$OO, significantly smaller than our previous estimate at 343 K using IR absorption.

The dependence on pressure of the yield $y$ of CH$_2$OO from CH$_2$I + O$_2$ conforms to the equation $y^{-1} = (1.24 \pm 0.03) + (9.13 \pm 0.33) \times 10^{-20} [M]$ in which [M] = O$_2$ or N$_2$, and IO that is the total density in molecule cm$^{-3}$. This dependence on pressure is smaller than in previous reports; the $\sim 30\%$ yield of CH$_2$OO at 760 Torr much greater than values 15%–18% in previous reports might have a significant impact on the atmospheric chemistry of marine regions.

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