The UV absorption spectrum of the simplest Criegee intermediate CH$_2$OO†

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SO$_2$ scavenging and self-reaction of CH$_2$OO were utilized for the decay of CH$_2$OO to extract the absorption spectrum of CH$_2$OO under bulk conditions. Absolute absorption cross sections of CH$_2$OO at 308.4 and 351.8 nm were obtained from laser-depletion measurements in a jet-cooled molecular beam. The peak cross section is $(1.23 \pm 0.18) \times 10^{-17}$ cm$^2$ at 340 nm.

Ozonolysis is a major removal mechanism in the troposphere for unsaturated hydrocarbons which are emitted in large quantities from both natural and human sources. Now it is generally accepted that ozonolysis of alkenes proceeds via Criegee intermediates, highly reactive species postulated in 1949 by Rudolf Criegee.1,2 In the troposphere, Criegee intermediates are involved in several important atmospheric reactions,3 including reactions with SO$_2$ and NO$_2$,4–7 or can be photolyzed by near UV light,7–10 as shown for CH$_2$OO in (R1)–(R4).

$$\text{C}_2\text{H}_4 + \text{O}_3 \rightarrow \text{CH}_2\text{OO} + \text{H}_2\text{CO} \quad \text{(R1)}$$

$$\text{CH}_2\text{OO} + \text{SO}_2 \rightarrow \text{SO}_3 + \text{H}_2\text{CO} \quad \text{(R2)}$$

$$\text{CH}_2\text{OO} + \text{NO}_2 \rightarrow \text{NO}_3 + \text{H}_2\text{CO} \quad \text{(R3)}$$

$$\text{CH}_2\text{OO} + \hbar \nu \rightarrow \text{O}^{(1}\text{D}) + \text{H}_2\text{CO} \quad \text{(R4)}$$

The formation of SO$_3$ and NO$_3$, as in (R2) and (R3), plays an important role in atmospheric chemistry,$^{11,12}$ including aerosol and cloud formation. The formation of O($^{1}\text{D}$), as in (R4), will result in OH formation through (R5).

$$\text{O}^{(1}\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \quad \text{(R5)}$$

Because CH$_2$OO absorbs strongly at wavelengths longer than 300 nm,$^{7–9}$ tropospheric photolysis of CH$_2$OO would be quite efficient with an effective photolysis lifetime on the order of 1 second.$^8$ As a result, the OH formation of (R4) + (R5) may contribute significantly to the atmospheric OH concentrations.

Despite their importance, the direct detection of Criegee intermediates was not realized until recently.4,13 Welz et al.$^4$ reported an efficient way to prepare Criegee intermediates. For example, CH$_2$OO can be prepared via (R6) + (R7a).

$$\text{CH}_2\text{I}_2 + \hbar \nu \rightarrow \text{CH}_2\text{I} + \text{I} \quad \text{(R6)}$$

$$\text{CH}_2\text{I} + \text{O}_2 \rightarrow \text{CH}_2\text{OO} + \text{I} \quad \text{(R7a)}$$

Welz et al.$^4$ also demonstrated the direct detection of CH$_2$OO by using vacuum UV photoionization mass spectrometry. The parent ion CH$_2$O$_2$$^+$ was observed when the photon energy exceeded the ionization energy of CH$_2$OO (10.0 eV); other isomers like dioxirane and formic acid were excluded due to their different ionization energies.$^4$ At low pressure, the yield of (R7a) is close to unity,$^{14,15}$ while the adduct formation (R7b) may dominate at near atmospheric pressures.$^{14}$

$$\text{CH}_2\text{I} + \text{O}_2 + \text{M} \rightarrow \text{ICH}_2\text{OO} + \text{M} \quad \text{(R7b)}$$

The kinetics of CH$_2$OO reactions with SO$_2$ and NO$_2$ were investigated by Welz et al.$^4$ and by Stone et al.$^5$ by observing the disappearance of CH$_2$OO and by detecting the H$_2$CO products, respectively. The rate coefficients of these reactions were found to be unexpectedly rapid and imply a substantially greater role of Criegee intermediates in models of tropospheric sulfate and nitrate chemistry.

Beames et al.$^8$ recorded the UV spectrum of CH$_2$OO through observing its depletion in a molecular beam upon laser irradiation (an action spectrum). Based on their laser pulse energy and spot size, Beames et al.$^8$ roughly estimated the peak absorption cross section to be $5 \times 10^{-17}$ cm$^2$ (at 335 nm with FWHM $\sim$ 40 nm). Lehman et al.$^{10}$ measured the angular and velocity distributions of the O($^{1}\text{D}$) photoproduct arising from UV excitation of CH$_2$OO in the 300–365 nm range. From the observed
anisotropic angular distribution ($\beta \approx 0.97$), the authors concluded that the orientation of the transition dipole moment reflects the $\pi^* \leftrightarrow \pi$ character of the electronic transition associated with the COO group. The significant anisotropy of the photofragments also indicates that the dissociation is faster than rotation.

Su et al.\textsuperscript{16} reported an infrared (IR) absorption spectrum of CH$_2$OO. By comparing their experimental results with high-level ab initio calculations, the authors concluded that the observed vibrational frequencies are more consistent with a zwitterion structure rather than a diradical structure. With IR detection, the same group\textsuperscript{17} found that the self-reaction of CH$_2$OO is extremely fast, with a rate coefficient of $(4 \pm 2) \times 10^{-10}$ cm$^3$ s$^{-1}$, which reflects a unique property of the zwitterionic character.

Sheps\textsuperscript{7} used a cavity-enhanced technique to measure the UV absorption spectrum of CH$_2$OO and observed significant vibrational structures at the long wavelength side of the absorption band. Moreover, the absorption spectrum\textsuperscript{7} differs significantly from the action spectrum reported by Beames et al.\textsuperscript{8} Sheps’ argument\textsuperscript{7} is the following: “The difference between the absorption and action spectra likely arises from excitation to long-lived $^4A$ vibrational states that relax to lower electronic states by fluorescence or nonradiative processes, rather than by photodissociation.” However, the measurement of the photoproduct anisotropy\textsuperscript{19} indicates that the photodissociation is faster than rotation which is in the picosecond time scale. Thus, the slower fluorescence process cannot compete with the fast dissociation. Furthermore, there is no theoretical evidence for the nonradiative processes. To investigate the source of this difference, we re-investigate the UV spectrum of CH$_2$OO using two new methods.

CH$_2$OO was prepared in a pulse-photolysis cell following the well-established method of CH$_2$I$_2$/O$_2$ photolysis.\textsuperscript{4,16} CH$_2$I$_2$ mixed with O$_2$ and N$_2$ was photolyzed at 248 nm (KrF excimer laser); transient absorption spectra were recorded using a gated intensified CCD camera (1 $\mu$s gate width) after the probe light was dispersed using a grating monochromator\textsuperscript{19,20} (see ESI for the experimental details). Fig. 1a shows examples of the transient absorption spectra. In Fig. 1a the most significant feature is a strong and broad absorption band peaked at $\sim 340$ nm which showed up quickly upon photolysis and decayed with time. In addition, depletion of the CH$_2$I$_2$ precursor near 290 nm and formation of IO with distinct peaks near 430 nm were clearly observed, especially at long delay times.

Under our experimental conditions, CH$_2$OO reacted quickly with itself\textsuperscript{17} and with I atoms to form H$_2$CO, O$_2$, and IO. Because H$_2$CO and O$_2$ absorb rather weakly, the transient spectra at long delay times mainly consist of the absorption changes of CH$_2$I$_2$ (depletion) and IO (formation). Since the spectra of CH$_2$I$_2$ and IO are very different, their contributions to the transient absorption spectra can be extracted and removed (see ESI for details). The remaining spectra are shown in Fig. 2a. Consistent with ref. 14, we did not observe significant difference in the CH$_2$OO yield for different O$_2$ mixing ratios. The identical shape of these spectra under various experimental conditions (delay times, laser fluences, and O$_2$ pressures) strongly suggests that the spectral carrier is a single species. Based on the high yield of CH$_2$OO from the CH$_2$I$_2$/O$_2$ photolysis at low pressure,\textsuperscript{14,15} it is most reasonable to assign the spectral carrier to CH$_2$OO (see below for discussion on the pressure dependence). If another absorbing species contributes significantly to these spectra, this species must exhibit kinetic behavior similar to that of CH$_2$OO.

It is known that CH$_2$OO reacts quickly with SO$_2$ ($k_2 \sim (3-4) \times 10^{-11}$ cm$^3$ s$^{-1}$).\textsuperscript{4,5} We utilized this kinetic signature of CH$_2$OO to examine the spectral carrier of band A. As shown in Fig. 1c, it is clear that the intensity of band A decreases at higher SO$_2$ concentrations. Because the absorption cross sections of SO$_2$, H$_2$CO and SO$_3$ in the 316–450 nm range are much smaller
the estimated number density and the observed absorbance of

the number density of CH$_2$OO can be estimated based on the

above assignment.

Fig. 2b. The good agreement between Fig. 2a and b confirms

normalized curves of such difference spectra are shown in

should be mostly due to the absorption of CH$_2$OO. The height-

density of CH$_2$I can be estimated. Under the high O$_2$ pressures used,

published quantum yield of (R7a) ($\Phi$CH$_2$I = 0.86% at 11 Torr).$^{14}$ From

the estimated number density and the observed absorbance of

CH$_2$OO, its absolute peak cross section can be deduced to be

($1 \times 10^{-19}$ cm$^2$) than those of CH$_2$OO (peak cross section

$>1 \times 10^{-17}$ cm$^2$),$^8$ the differences between the spectra of Fig. 1c

should be mostly due to the absorption of CH$_2$OO. The height-

normalized curves of such difference spectra are shown in

Fig. 2b. The good agreement between Fig. 2a and b confirms

the above assignment.

When O$_2$ was absent in the photolysis cell, the absorption of

CH$_2$I was present and band A could not be observed. With the

published absorption cross sections of CH$_2$I,$^{21}$ the initial number
density of CH$_2$I can be estimated. Under the high O$_2$ pressures used,

CH$_2$I reacted with O$_2$ within a few microseconds.$^{5,7,14,15}$ Therefore

the number density of CH$_2$OO can be estimated based on the

published quantum yield of (R7a) ($\Phi$CH$_2$I = 86% at 11 Torr).$^{14}$ From

the estimated number density and the observed absorbance of

CH$_2$OO, its absolute peak cross section can be deduced to be

$(1.26 \pm 0.25) \times 10^{-17}$ cm$^2$ at 340 nm. The overall error bar is

estimated to be ±20% mostly due to the uncertainty in

$\Phi$CH$_2$OO.$^{14,15}$ (see ESI† for details).

In Fig. 2a we can see that the shape of band A does not depend

on the total pressure in the range of 8–100 Torr.

This observation excludes the contribution of ICH$_2$OO because

its formation is a termolecular process which has strong pressure

dependence.$^{14,15}$ At higher pressures (100 Torr < P < 760 Torr),

the yield of CH$_2$OO was found to decrease with pressure (see

Table S1 (ESI†) for a typical example) and an additional (weaker)

absorption band was observed at $\lambda < 290$ nm, indicating the

formation of a new species (likely ICH$_2$OO).$^{21,22}$ The absorption

of ICH$_2$OO seems to be much weaker than that of CH$_2$OO, such

that the change in spectral shape (not including the yield) with

pressure is not very obvious.

The IO peaks are absent in short delay times while the absorption of CH$_2$OO is very significant, indicating that IO is

not a primary product. Based on our signal-to-noise ratio, we

further constrain the primary IO yield to be less than 1%,

resolving some debate among published results.$^{23–26}$ The formation

of IO is likely due to (R8).$^{5,14}$

\[
\text{CH}_2\text{OO} + I \rightarrow \text{H}_2\text{CO} + \text{IO} \quad (\text{R8})
\]

Detailed kinetic analysis is beyond the scope of this paper

and will be published elsewhere.

To further quantify the absolute value of the absorption cross

section of CH$_2$OO, we measured the depletion of CH$_2$OO in a

molecular beam upon laser irradiation at 308.4 and 351.8 nm.

CH$_2$OO was detected using a quadrupole mass spectrometer

equipped with an electron impact ionizer. This method$^{27–29}$ has

been demonstrated to be efficient in determining the photo-
dissociation cross section of a species in a mixture without the

knowledge of its concentration. Under our experimental condi-
tions, the number of molecules $N$ after laser irradiation can be

described by eqn (1).

\[
\frac{N}{N_0} = e^{-\sigma \phi} \frac{\Delta N}{N_0} = 1 - e^{-\sigma \phi}
\]

Where $N_0$ is the number of molecules before the laser irradia-
tion, $I$ is the laser fluence in photons per cm$^2$, $\sigma$ is the

absorption cross section in cm$^2$, $\phi$ is the dissociation quantum

yield and $\Delta N = N_0 - N$. For CH$_2$I$_2$, the excitations at 351.8

and 308.4 nm correspond to repulsive (unbound) excited states

which dissociate in picosecond time scales,$^{30–32}$ resulting in

100% dissociation ($\phi = 1$).

Fig. 3a shows the arrival-time profiles of CH$_2$OO at various

laser fluences at 308.4 nm. Fig. 3b shows the corresponding

saturation curve. A nice fit of eqn (1) to the experimental data

indicates that the measurement corresponds to a single species

(or multiple species having the same cross section, which is

unlikely). The results at 351.8 nm are similar (see ESI†). The

complete depletion of CH$_2$OO indicates that its dissociation

yield is unity. The absolute cross section of CH$_2$OO can be

obtained by comparing its saturation curve with that of CH$_2$I$_2$,

for which the cross section is known. A summary of the cross

section measurement is shown in Table 1.

With the absolute cross sections of CH$_2$OO (Table 1), we may

set the spectra of Fig. 2 on the absolute scale. However, we need
to consider the temperature effect of the absorption cross

sections because the temperature of the molecular beam is

lower than room temperature. Since the cross section of CH$_2$I$_2$
of Fig. 2 and to plot the scaled spectra in Fig. 4. We believe that the SO$_2$ scavenging method would give a more reliable spectrum of CH$_2$OO (see Table S3 (ESI†) for numerical values) while the result of the self-reaction method is very similar. The peak value of the scaled spectrum is $(1.23 \pm 0.18) \times 10^{-17} \text{cm}^2$ at 340 nm. We assume an error bar of $\pm 15\%$ to include possible variations due to the temperature effect. This value is consistent with the peak cross section of $(1.26 \pm 0.25) \times 10^{-17} \text{cm}^2$ obtained in the transient absorption experiment of this work based on the estimated CH$_2$OO number density.

Previous UV absorption 7 and action spectra 8 of CH$_2$OO exhibit significant differences. Beames et al. 8 measured the laser depletion of CH$_2$OO in a similar molecular beam and obtained an action spectrum of CH$_2$OO. However Beames et al. 8 only estimated the laser fluence from their laser (a dye laser) pulse energy and spot size. The beam spot of a dye laser is usually highly non-uniform. Without using a laser beam profiler, it is difficult to quantify the actual laser fluence. Beames et al. 8 might underestimate their laser fluence and thus overestimate the CH$_2$OO cross section. In this work, we utilized a reference molecule to effectively calibrate the laser fluence and to cancel the effect of non-uniform laser spot. Therefore, our results should be more accurate.

Fig. 4 compares our results with those of Sheps 7 and Beames et al. 8. The scaled spectrum of Beames et al. 8 is weaker in this wavelength range. Another possibility mentioned by Sheps 7 is a decrease in the dissociation yield at long wavelengths. Although this might explain the discrepancy between the absorption and action spectra, it is inconsistent with the product anisotropy measurement by Lehman et al. 10 which shows that the UV photodissociation of CH$_2$OO is faster than its rotation ($\sim$picosecond). Thus, a non-uniaxial dissociation yield would require a fast process that can compete with photodissociation. Fluorescence is too slow to fulfill this condition. Other fast non-radiative processes are unlikely but cannot be fully ruled out at this moment. More evidence and investigations are needed.

Sheps’ used a newly-built cavity-enhanced absorption spectrometer to measure the transient absorption spectra of the CH$_2$I$_2$/O$_2$ photolysis system. Sheps 7 determined the absolute CH$_2$OO spectrum based on the measured CH$_2$I spectrum (when O$_2$ was absent) and an estimated ($90 \pm 10\%$) yield of transforming CH$_2$I to CH$_2$OO at 5 Torr. Qualitatively, the shape of Sheps’ spectrum 7 is similar to ours, particularly the structures at the long-wavelength side (the peak positions are matched). However, the short-wavelength side of Sheps’ spectrum 7 decays much faster than that in this work. Furthermore, the reported peak cross section and position of the CH$_2$OO spectrum by

Table 1  Summary of the cross section measurements of CH$_2$OO in a jet-cooled molecular beam

<table>
<thead>
<tr>
<th>Wavelength [nm]</th>
<th>$\sigma_{\phi}(\text{CH}_2\text{OO})$</th>
<th>$\sigma_{\phi}(\text{CH}_2\text{I})$</th>
<th>$\sigma\text{(CH}_2\text{I}_2)$</th>
<th>$\sigma\text{(CH}_2\text{OO})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>308.4</td>
<td>$2.52 \pm 0.28^b$</td>
<td>$3.21 \times 10^{-18}$</td>
<td>$8.09 \pm 0.90 \times 10^{-18}$</td>
<td></td>
</tr>
<tr>
<td>351.8</td>
<td>$47.6 \pm 5.2$</td>
<td>$2.34 \times 10^{-16}$</td>
<td>$1.21 \pm 0.13 \times 10^{-17}$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The error bar is 2 standard deviation. $^b$ Average values of ref. 33 and 34 at $T = 273$ K. The temperature dependence of the UV absorption cross section of CH$_2$I$_2$ is very weak at 308.4 nm, but moderate at 351.8 nm. The actual cross section at 351.8 nm would be smaller for CH$_2$I$_2$ in a jet-cooled molecular beam.

Fig. 3 (a) Arrival-time profiles of CH$_2$OO at various laser fluences at 308.4 nm. The parent ion of CH$_2$OO was detected at $m/z = 46$ amu. (b) Saturation curve for the laser depletion of CH$_2$OO ($m/z = 46$) and CH$_2$I$_2$ ($m/z = 141$, CH$_2$I, a daughter ion of CH$_2$I$_2$) at 308.4 nm. The x-axis is the laser pulse energy which is proportional to the laser fluence. The lines are the fit of eqn (1). The nice fit indicates that the laser depletion experiments are single-photon processes.

at 308.4 nm does not change with temperature, 33,34 we can use the near-room-temperature value for the cross section of CH$_2$I$_2$ in a molecular beam. The UV absorption band of CH$_2$OO can be assigned to the intense B $\rightarrow X$ transition 8,22 which is analogous to the Hartley band of O$_3$. The cross section of the O$_3$ Hartley band has a quite weak temperature dependence. 18,35 The peak cross section (at 254 nm) of O$_3$ increases by $\sim 1.5\%$ when the temperature decreases from 293 K to 203 K. For the main region of the Hartley band (215–288 nm, $1 \times 10^{-18} \text{cm}^2 < \sigma < 1.1 \times 10^{-17} \text{cm}^2$), the temperature effect is within $5\%$ (203–293 K). 18,35 Similarly, it is expected that the temperature dependence of the CH$_2$OO cross sections is weak near the peak. Therefore, we choose the cross section at 308.4 nm to scale the average spectra
Sheps$^7$ [(3.6 ± 0.9) × 10^{-17} cm^2 at 355 nm] are different from our values. The source of the discrepancies is not clear. It might arise from the complexity of the cavity-enhanced measurement.

There are at least 7 vibrational peaks observable on the long-wavelength side of the UV absorption band of CH$_2$OO (Fig. 2 and 4). The widths of these vibrational peaks are significantly wider than the instrument resolution of 2 nm. Similar structures have been reported by Sheps$^7$ at a slightly lower resolution and signal-to-noise ratio. The positions of the most well-defined peaks are 363.7, 372.0, 380.7, 389.2, 399.0, 409.3, 420.5 nm (27495, 26882, 26267, 25694, 25063, 24432, 23781 cm$^{-1}$). The average peak separation is about 620 cm$^{-1}$. Analogous to the Huggins band of O$_3$, these vibrational structures may arise from some periodic motions on the excited potential energy surface, most likely the Α′ (A′) surface. The widths of the vibrational peaks may originate from congested vibrational structures (vibrational modes involving O–O stretching and C–O–O bending)$^{22}$ or rotational contours at room temperature. For the O$_3$ Huggins band, the widths of the vibrational peaks become narrower at low temperatures.$^{18,35}$ It will be interesting to see how the peak structures change at lower temperatures for CH$_2$OO.

In summary, more accurate UV absorption cross sections of the simplest Criegee intermediate CH$_2$OO are reported. The peak cross section is determined to be (1.23 ± 0.18) × 10^{-17} cm$^2$ at 340 nm. This value is significantly smaller than previous reports,$^7,8$ implying slower photolysis rates in the atmosphere than previously expected. Nonetheless, this intense absorption band of CH$_2$OO overlaps well with the incoming solar spectrum, resulting in efficient photolysis of this Criegee intermediate. The clear vibrational structures on the long-wavelength side of the CH$_2$OO spectrum provide a fingerprint feature for spectroscopic identification of this elusive intermediate.

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