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The Reaction of Criegee Intermediate CH$_2$OO with Water Dimer: Primary Products and Atmospheric Impact

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Electronic Supplementary Information (ESI) available: Details of experimental data analysis and global atmospheric model

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Abstract

The rapid reaction of the smallest Criegee intermediate, CH$_2$OO, with water dimers is the dominant removal mechanism for CH$_2$OO in the Earth’s atmosphere, but its products are not well understood. This reaction was recently suggested as a significant source of the most abundant tropospheric organic acid, formic acid (HCOOH), which is consistently underpredicted by atmospheric models. However, using time-resolved measurements of reaction kinetics by UV absorption and product analysis by photoionization mass spectrometry, we show that the primary products of this reaction are formaldehyde and hydroxymethyl hydroperoxide (HMHP), with direct HCOOH yields of less than 10%. Incorporating our results into a global chemistry-transport model further reduces HCOOH levels by 10 – 90%, relative to previous assumptions, which indicates that the reaction CH$_2$OO + water dimer by itself cannot resolve the discrepancy between the measured and predicted HCOOH levels.
Introduction

Criegee intermediates (CI) are carbonyl oxides, formed by ozonolysis of alkenes\textsuperscript{1,2} and long recognized as key players in the Earth’s troposphere through chemically activated decomposition (a dominant non-photolytic source of OH) and bimolecular reactions with trace atmospheric species.\textsuperscript{3} Until recently our knowledge of gas-phase CI reactivity came either from indirect experiments using complex reaction analysis or from computational work.\textsuperscript{4,5} As a consequence, the atmospheric impact of CI reactions was subject to large uncertainties. However, a recent discovery by Taatjes and co-workers of an efficient alternative route\textsuperscript{6,7} to form large quantities of stabilized CI in the lab has opened the door to direct spectroscopic and kinetic studies. The electronic structure and photochemistry of CI are increasingly well characterized by experimental studies\textsuperscript{8} and high-level quantum chemical calculations.\textsuperscript{9,10} Meanwhile, direct kinetics measurements have led to a reassessment\textsuperscript{3} of the role of CI in the oxidizing capacity of the atmosphere and in tropospheric budgets of organic acids, secondary organic aerosols, ozone, NO\textsubscript{x}, NO\textsubscript{y} and HO\textsubscript{x}.\textsuperscript{11-14}

Because Criegee intermediates form during ozonolysis of abundant hydrocarbons such as isoprene, accurate knowledge of product branching in their reactions is important for the understanding of atmospheric oxidative pathways. The simplest CI, CH\textsubscript{2}OO, was found to react much more rapidly with SO\textsubscript{2}, NO\textsubscript{2}, and carboxylic acids than previously assumed.\textsuperscript{6,7,15,16} However, the full impact of its reactivity on the atmosphere depends on the competition among CH\textsubscript{2}OO reactions with trace species and with water vapor. Recent theory\textsuperscript{17,18} and laboratory\textsuperscript{19-22} studies show that although the reaction CH\textsubscript{2}OO + H\textsubscript{2}O is relatively slow, the reaction with water dimer, (H\textsubscript{2}O)\textsubscript{2}, is fast enough to act as the primary removal route of CH\textsubscript{2}OO under most conditions in the atmosphere.

The consensus, based on prior experiments\textsuperscript{23-25} theory,\textsuperscript{17,18} and modeling,\textsuperscript{26-29} was that the reaction of CH\textsubscript{2}OO with water monomer or dimer forms mainly hydroxymethyl hydroperoxide (HMHP), which further reacts to produce formic acid (HCOOH),\textsuperscript{30} H\textsubscript{2}O\textsubscript{2}, and formaldehyde (CH\textsubscript{2}O).\textsuperscript{25,31,32} However, a more recent extensive study by Wennberg and co-workers\textsuperscript{33} concluded that the reaction CH\textsubscript{2}OO + (H\textsubscript{2}O)\textsubscript{2} directly produces formic acid with a yield of 54%. A 2015 review by Millet\textit{ et al.}\textsuperscript{34} showed that formic acid is consistently underpredicted by current models and suggested a large unidentified HCOOH source. The authors considered several possible “missing” sources of HCOOH, including direct biogenic emission, heterogeneous conversion, or reactive formation from multiple sources. The model by Millet\textit{ et al.}\textsuperscript{34} assumed fast conversion of either CH\textsubscript{2}OO or HMHP to HCOOH; however, definitive assessment of the role of CH\textsubscript{2}OO chemistry as a source of HCOOH requires a reliable quantification of the products of its reaction with water.

Previous experimental measurements of the products in the reaction of CH\textsubscript{2}OO with water vapor relied on time-averaged detection of species in quasi-steady state reactors. The derivation of product yields in such studies can be vulnerable to uncertainties in chemical mechanisms, and identification of primary products may be challenging. Here we report direct time-resolved measurements of the reaction of CH\textsubscript{2}OO with water, showing far smaller primary yields of formic acid than suggested by Nguyen\textit{ et al.}\textsuperscript{33} Our results limit the possible direct contribution of CH\textsubscript{2}OO to tropospheric HCOOH and highlight the need to explore the subsequent chemistry of CI reaction products for accurate modeling of organic acid production. We also illustrate the potential impact
of our findings on global atmospheric model predictions of several key species, including OH and formic acid, using a 3-D chemistry transport model, CRI-STOCHEM.

**Experimental methods**

We probed the reaction of CH$_2$OO with water vapor by complementary time-resolved techniques of broadband cavity-enhanced absorption spectroscopy (TR-BB-CEAS) and synchrotron-based photoionization mass spectrometry (PIMS). Both experiments use heatable flow cells, where reactions are initiated by laser photolysis of appropriate radical precursors. Constant T and P in the reactors are maintained by feedback-controlled resistive heaters and downstream throttle valves; sample composition is regulated by precision flow controllers.

The TR-BB-CEAS apparatus$^{35,36}$ is a 1.6 m-long broadband optical cavity that uses continuous “white-light” probe radiation from a Xe arc lamp and operated at probe $\lambda = 300 – 450$ nm simultaneously for this study. The cavity is integrated into a quartz laser photolysis flow reactor with ID = 3 cm, capable of operating up to 650 K and 500 Torr. The optical cavity and photolysis laser overlap length is 80 cm. The time evolution of the cavity output spectrum is recorded by a custom spectrometer for each photolysis laser shot and can be averaged indefinitely to obtain sufficient signal-to-noise ratio. For the present work, the wavelength resolution of the spectrometer was 1.5 nm and the temporal resolution was 35 μs. The effective optical path length $L_{\text{eff}}$ was measured regularly with known NO$_2$ concentrations and was typically ~40 – 70 m, depending on the wavelength. Transient absorption spectra were computed from the difference between photolysis laser ON and OFF images:

$$OD(\lambda, t) = -\ln\left(\frac{I_{\text{ON}}(\lambda, t)}{I_{\text{OFF}}(\lambda, t)}\right) = L_{\text{eff}}(\lambda) \sum_i c_i(t) \sigma_i(\lambda)$$  \hspace{1cm} (E1)

Here $I_{\text{ON}}$ and $I_{\text{OFF}}$ are the measured probe radiation intensities with/without the photolysis laser; the total transient signal $OD(\lambda, t)$ is the sum of contributions by all absorbing species $i$ with concentrations $c_i$ and absorption cross-sections $\sigma_i$.

The multiplexed PIMS apparatus$^{37}$ employs a quartz flow reactor with ID = 1.05 cm, capable of T up to 800 K and P up to 50 Torr. A small orifice (300 μm diameter in this study) samples a portion of the gas mixture into a vacuum chamber, where it is skimmed and ionized. The ions are extracted into a pulsed 50 kHz orthogonal acceleration time-of-flight mass spectrometer, which acquires a complete mass spectrum every 20 μs during a time window -20 ms < t < 130 ms, relative to the arrival of the photolysis laser pulse. For the work described here, ionization was performed with tunable, intense (~$10^{14}$ photons·s$^{-1}$), monochromatic (typical resolution of 20 meV) VUV radiation from the Chemical Dynamics Beamline at the Advanced Light Source, Lawrence Berkeley Lab. The VUV photon energy was scanned over the 9.5 – 11.5 eV range to create a 3-dimensional data set $I(m/z, t, E)$. The PIMS ion signal is described by the formula$^{38}$:

$$I_{m/z}(t, E) = \Lambda \cdot \alpha_{m/z} \cdot \sum_i (\sigma_i(E) \cdot c_i(t))$$  \hspace{1cm} (E2)

The total ion intensity $I_{m/z}(t, E)$ is the sum of signals from all isomers at the mass-to-charge ratio $m/z$. The quantities $\sigma_i(E)$ and $c_i(t)$ are the energy-dependent photoionization (PI) cross-section and the time-dependent concentration of isomer $i$; $\alpha_{m/z}$ is the isomer-independent mass discrimination factor, and $\Lambda$ is the isomer-, mass- and energy-independent sensitivity factor.
values of Λ and α_{m/z}, as well as the experimental mass resolution, were calibrated daily using standard gas mixtures. Time-dependent absolute species concentrations were obtained from raw ion signals using literature absolute photoionization cross-sections, when available, according to a procedure described in detail earlier.39,40
Both experiments generated stabilized CH$_2$OO at room temperature and total pressures 30 – 100 Torr following the scheme developed by Welz et al.6 Chemical reactions were initiated in both flow reactors by photolysis of CH$_2$I$_2$ (99% pure) in either He or N$_2$ bath (both 99.9999%) in the presence of O$_2$ (99.9999%) and varying amounts of H$_2$O. CH$_2$I$_2$ and distilled H$_2$O vapor flows were entrained in bath gas flows using temperature- and pressure-controlled glass bubblers. The experimental H$_2$O concentration was calculated based on the buffer gas flow through the bubbler and the ratio of the H$_2$O vapor pressure to total bubbler pressure. The validity of this approach was assured by gravimetric measurements of the total amount of water that was removed after long periods of stable flows, with typical errors of less than 2%. Photolysis radiation was provided by a fourth harmonic output of a Nd:YAG laser (266 nm, TR-BB-CEAS experiments) or by an Excimer laser (248 or 351 nm, PIMS experiments). The choice of photolysis wavelength had no effect on the observed kinetics or product distributions.

Results and discussion
Reaction kinetics of CH$_2$OO with the water monomer and dimer
We initiated the reaction of CH$_2$OO with water by photolytic production of CH$_2$I in the presence of O$_2$ and H$_2$O in a He or N$_2$ bath. A summary of all conditions used in the PIMS and UV absorption experiments is given in Table 1. Initial CH$_2$OO concentrations, estimated using the measured photolysis laser fluence and the UV absorption cross-section of CH$_2$I$_2$,41,42 were sufficiently low, (5 – 9)$\cdot$10$^{11}$ cm$^{-3}$, to suppress self-reaction.43,44 On the other hand, O$_2$ and H$_2$O were always in excess, so that the observed kinetics were governed by a simple set of four reactions, R1 – R4:

\begin{align*}
\text{CH}_2\text{I}_2 + \text{hv}(266 \text{ nm}) &\rightarrow \text{CH}_2\text{I} + \text{I} \\
\text{CH}_2\text{I} + \text{O}_2 &\rightarrow \text{I} + \text{CH}_2\text{OO} \quad \text{(R1)} \\
\text{CH}_2\text{OO} + \text{H}_2\text{O} &\rightarrow \text{products} \quad \text{(R2)} \\
\text{CH}_2\text{OO} + (\text{H}_2\text{O})_2 &\rightarrow \text{products} \quad \text{(R3)} \\
\text{CH}_2\text{OO} &\rightarrow \text{other losses} \quad \text{(R4)}
\end{align*}

The reaction R4 above collectively refers to CH$_2$OO removal by wall loss and by self-reaction. UV absorption is more sensitive to CH$_2$OO than PIMS; hence, TR-BB-CEAS probing of CH$_2$OO decays at varying [H$_2$O] was used to measure the rate coefficients of R2 and R3. To check the validity of describing our chemical system with the simplified mechanism, R1 – R4, we varied O$_2$ concentration by a factor of ~9.5 and observed no effect on the intensity or decay kinetics of CH$_2$OO UV absorption. Varying the initial radical concentration by a factor of ~4.2 had no apparent effect on the CH$_2$OO formation or decay timescales. A detailed mechanism of the CH$_2$I + O$_2$ reaction system by Lee and Lin44 indicates that radical-radical reactions other than the CH$_2$OO self-reaction are not significant under our conditions. Likewise, the products of R2 – R4 are present in such low concentrations (~10$^{11}$ cm$^{-3}$), that even if their reaction with CH$_2$OO are

Table 1. Experimental conditions used in PIMS and UV absorption probing of the reaction of CH$_2$OO with water. All experiments were conducted at T = 293 K.
## Table

<table>
<thead>
<tr>
<th>Set #</th>
<th>Bath gas</th>
<th>$P$ (Torr)</th>
<th>$[\text{CH}_2\text{OO}] / 10^{11}$ (cm$^{-3}$)</th>
<th>$[\text{O}_2] / 10^{16}$ (cm$^{-3}$)</th>
<th>$[\text{H}_2\text{O}] / 10^{17}$ (cm$^{-3}$)</th>
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<td></td>
<td>3</td>
<td>He 30</td>
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<td>1.3 – 2.6</td>
<td>0 – 2.6</td>
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<tr>
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<tr>
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<td>N$_2$ 50</td>
<td>4.8</td>
<td>2.5</td>
<td>0 – 2.8</td>
</tr>
</tbody>
</table>

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$a$ – CD$_3$I was used instead of CH$_3$I$_2$ as photolytic precursor to CD$_2$OO production  
$b$ – D$_2$O was used in place of H$_2$O

very rapid (as in the case of HCOOH$^{16}$) they do not contribute strongly to its removal. 
The strong B$^1A' \leftrightarrow X^2A'$ absorption of CH$_3$OO has a peak absorption cross-section of $\sim 1 \cdot 10^{17}$ cm$^2$ near 350 nm,$^{45}$ providing a straightforward means of direct measurements of its reaction kinetics. In the present study we averaged the transient absorption between 340 and 380 nm, where other spectral signals from IO (a secondary product)$^{46}$ or from CH$_3$I$_2$ depletion do not contribute significantly. We have previously used the same approach in TR-BB-CEAS probing to investigate the reactivity of CH$_3$OO with SO$_2$,$^{47}$ formic acid,$^{16}$ and isoprene.$^{48}$ Figure 1 shows a representative subset of CH$_3$OO absorption decays at varying [H$_2$O] along with kinetic fits.

**Figure 1.** Representative subset of transient UV absorption traces of CH$_3$OO, taken at $T = 293$ K and total $P = 30$ Torr in a He bath, with [H$_2$O] = (0 – 3.3)·10$^{17}$ cm$^{-3}$. The absorption signals (gray lines) were averaged between probe wavelengths $\lambda = 340$ and 380 nm. Thick black lines are global fitting results to equation E6 (see text).

Within the simple kinetic framework of reactions R1 – R4, the transient CH$_3$OO population can be treated as an intermediate species $B$ in a reaction sequence:
The rise time of $B$ is determined by $k_1'$, the pseudo-first order rate coefficient for the reaction CH$_2$I + O$_2$ (R1). The decay rate coefficient $k'_{\text{decay}}$ is a sum of three (pseudo-) first order rate coefficients for reactions R2 – R4:

$$k_1' = k_1 \cdot [O_2]$$

$$k'_{\text{decay}} = k_2' + k_3' + k_4 = k_2 \cdot [H_2O] + k_3 \cdot [(H_2O)_2] + k_4$$

All of the transient UV absorption signals $S(t)$ were fit to a biexponential expression for the time evolution of $B$ in the equation E3:

$$S(t) = \frac{A k_1'}{k'_{\text{decay}} - k_1'} \left[ e^{-k_1' t} - e^{-k'_{\text{decay}} t} \right] + S_\infty$$

The parameter $S_\infty$ accounts for possible long-time offset due to minor signal contribution from IO or CH$_2$I$_2$. All time traces taken at the same pressure and temperature were fit simultaneously. The fit parameter $k_1'$ was fixed in all fits using the known value$^{49}$ of $k_1 = 1.67 \cdot 10^{-12}$ cm$^3$·s$^{-1}$ and the experimental [O$_2$]. The fit amplitude $A$ and the decay rate coefficient $k'_{\text{decay}}$ were allowed to vary, but $A$ was treated as a global parameter. The fits were convolved with the experimental time resolution (35μs, independently measured). The rise and decay timescales differed by at least a factor of 10 at all conditions. The results of the fits are shown as black lines in Fig. 1.

A plot of all fitted $k'_{\text{decay}}$, corresponding to experimental sets 6 – 10 in Table 1, is presented as a function of [H$_2$O] in Fig. 2. This plot is strongly curved due to the reaction of CH$_2$OO with water dimer, whose concentration scales as the square of the monomer concentration. We then fit $k'_{\text{decay}}$ vs. [H$_2$O] to a 2nd-order polynomial, using the literature value of the water dimer equilibrium constant,$^{50}$ 0.057 atm$^{-1}$ at $T = 293$ K. The quadratic term yields $k_3' = (6.6 \pm 0.7) \cdot 10^{-12}$ cm$^3$·s$^{-1}$, independent of total pressure, 30 – 100 Torr, or bath gas, He vs. N$_2$. The errors listed throughout the manuscript are 1σ. The uncertainty in $k_2$ and $k_3$ is dominated by the scatter in the measured decays (~10%), but also includes the error in [H$_2$O] (~2%) and $K_{eq}$ (~3%). Our value is a
near-perfect match to $k_3 = 6.5 \cdot 10^{-12} \text{ cm}^3\text{s}^{-1}$ by Chao et al.,\textsuperscript{19} which was obtained in a similar way to this study: by direct UV absorption probing of CH$_2$OO, formed via reaction R1. However, our result is lower than the value of Berndt et al.,\textsuperscript{22} $k_3 = 1.13 \cdot 10^{-11} \text{ cm}^3\text{s}^{-1}$, derived from end-product analysis in the ozonolysis of ethene at atmospheric pressure.

The linear term in our fit of $k_{d,\text{decay}}^l$ vs. [H$_2$O] is the rate coefficient $k_2 = (2.4 \pm 1.6) \cdot 10^{-16} \text{ cm}^3\text{s}^{-1}$. Including the linear term in our fit produces noticeable improvement, reducing $\chi^2$ by ~10%, but does not significantly affect $k_3$ outside its error bounds. The reaction of CH$_2$OO with the water monomer had been extensively studied before, mostly by relative rate constant measurements that quantified either the removal of reactants by CH$_2$OO\textsuperscript{51} or the end product yields\textsuperscript{31,49,52,53} as a function of relative humidity. The values of $k_2$, derived from those experiments, spanned about 3 orders of magnitude, $(2.5 - 3200) \cdot 10^{-17} \text{ cm}^3\text{s}^{-1}$. A single study that directly probed CH$_2$OO decays using PIMS by Welz et al.\textsuperscript{6} reported an upper limit of $k_2 < 4 \cdot 10^{-15} \text{ cm}^3\text{s}^{-1}$. Calculated values of $k_2$ similarly vary from $5.8 \cdot 10^{-18} \text{ cm}^3\text{s}^{-1}$ by Ryzhkov et al.\textsuperscript{17} to $3 \cdot 10^{-15} \text{ cm}^3\text{s}^{-1}$ by Anglada et al.\textsuperscript{18} Our present measurements fall roughly in the middle of the range of previous results and refine the earlier result of Welz et al.\textsuperscript{6} Accurate knowledge of $k_2$ is important to this work because it allows a calculation of the partitioning of the reactive flux among R2 – R4 and hence enables determination of absolute yields, based on PIMS measurements of product concentrations.

**Identification of reaction products**

PIMS experiments that use tunable VUV ionizing radiation enable the identification of chemical species with isomeric selectivity (e.g. CH$_2$OO vs. HCOOH) based on their PI spectra. Figure 3 shows a portion of the transient mass spectrum (after subtraction of pre-photolysis signals) with and without H$_2$O, averaged over time $t = 0 – 20$ ms after photolysis. Under dry conditions, CH$_2$OO decays mainly by self-reaction and wall losses, and the mass spectrum in the $m/z = 28 – 66$ range contains two intense ion peaks with $m/z = 30.01$ and 46.01, as shown in Fig. 3. Upon the introduction of water, additional peaks appear at $m/z = 31.02, 47.01, 64.02$. Depletion

![Figure 3](image-url)

**Figure 3.** Transient mass spectra with and without H$_2$O, acquired using ionization energy $h\nu = 11.5$ eV and averaged over kinetic times $t = 0 – 20$ ms. Pre-photolysis ion signals have been subtracted.

of CH$_2$I$_2$ is visible at the mass of parent (CH$_2$I$_2^+$, $m/z = 267.02$) and daughter (CH$_2$I$^+$, $m/z = 140.92$) ions. Ion peaks due to I, HI, and HOI at $m/z = 126.90, 127.91$, and 143.91, respectively, are also present. The time evolution of these latter peaks indicates slow secondary reactions of the I atom.
that do not interfere with the primary chemistry under investigation here; consequently, we omit them from Fig. 3 for clarity.

The minor m/z = 47.01 peak has the molecular formula CH$_3$O$_2$$^+$. However, its PI spectrum does not match the reference spectrum of methyl peroxy (H$_3$COO)$_{54}$ nor is it due to the hydroperoxymethyl (HOOCH$_2$) radical, which is calculated to be highly unstable.$^{55-57}$ The time profile of this peak indicates at least two contributions due to dissociative ionization (DI) of larger compounds, while its lack of dependence on [H$_2$O] suggests that it does not arise from the reaction R3 (see Figs. S2 and S3). In contrast, the remaining peaks come from the products of R3, as we show below.

The time evolution of all ion peaks relevant to the reaction of CH$_2$OO with water, obtained at ionization energy of 11.5 eV, is shown in Fig. 4. The m/z = 46.01 time trace reveals a strong short-lived and a weaker long-lived component, whereas all other peaks have time profiles characteristic of stable reaction products, rising rapidly to a flat plateau. We assign these peaks to four distinct chemical compounds, based on their measured PI spectra (see Fig. 5), time profiles, exact mass, and mass shift when using deuterated reactants, CD$_2$I or D$_2$O, (see Table 1).

The PI spectrum of m/z = 30 (CH$_2$O$_2$$^+$$^+$) ions clearly indicates that it is due solely to formaldehyde and enables its quantification, based on the absolute cross-section measurements of Dodson et al.$^{58}$ The time profile of the m/z = 46 (CH$_2$O$_2$$^+$$^+$) peak suggests two different sources, making its assignment more challenging. The PI spectrum of this peak, averaged over early times, $t = 0 – 5$ ms, agrees very well with a previously measured spectrum of CH$_3$OO$^6$ and contains a minor contribution from HCOOH at energies above 11.3 eV. When averaged over $t = 10 – 80$ ms, after CH$_2$OO decays, the PI spectrum of this peak matches that of HCOOH and enables its quantification using the absolute PI cross-section of Cool et al.$^{59}$ Notably, we find no evidence of dioxirane, which was suggested as a product of R3 in a discharge source.$^{60}$ The calculated adiabatic ionization energy (IE$_a$) of dioxirane is 10.82 eV,$^{61}$ yet we detect no m/z = 46 ions below 11.3 eV at long delay times and thus conclude that dioxirane is not a significant product of stabilized CH$_2$OO reactions.

Time-resolved CH$_2$OO signals in our PIMS experiments have higher noise than the UV absorption time traces, and we could not reliably fit the CH$_2$OO decays in dataset #1. However, $k_{d_{ecay}}$ values obtained from CH$_2$OO ion signals in datasets #2 and #3 (shown in Fig. S1) agree very well with the UV absorption results and are included in Fig. 2.

We assign the remaining ion peaks at m/z = 31 and 64 to the parent cation (HOCH$_2$OOH$^+$) and dissociative ionization (HO$_2$ + HOCH$_2$$^+$) of hydroxymethyl hydroperoxide (HMHP), the main predicted product of R3.$^{17,18}$ Calculations at the CBS-QB3 level show a much longer HOCH$_2$–OOH bond in the parent cation (~162 pm) than in neutral HMHP (~141 pm), implying facile dissociation to HO$_2$ + HOCH$_2$$^+$. The calculated IE$_a$ of HMHP, averaged over four low-lying rotamers of the neutral compound, is ~9.9 eV; the calculated appearance energy of HOCH$_2$$^+$ is ~10.7 eV. These values agree with the observed ionization onsets of the m/z = 31 and 64 peaks. In experiments using deuterated reactants CD$_2$OO + H$_2$O or CH$_3$OO + D$_2$O, the ion peaks assigned to HMHP shift to m/z = 66 and 33 (HOCD$_2$OOH$^+$, HOCD$_2$$^+$) or to m/z = 66 and 32 (DOCH$_2$OOG$^+$, DOCH$_2$$^+$). This supports our assignments and confirms the calculated mechanism of HMHP formation by CH$_2$OO insertion into one of the OH bonds of water.
Figure 4. Time evolution of the $m/z = 30$, 31, 46, and 64 ion peaks, obtained with ionization energy $h\nu = 11.5\,\text{eV}$ at $[\text{H}_2\text{O}] = 2.2\cdot10^{17}\,\text{cm}^{-3}$. All time traces are scaled arbitrarily for visual comparison.

Figure 5. PI spectra of ion peaks, assigned to the products of reactions R1–R4. Panel A: $m/z = 30$ ions, averaged over $t = 10 – 80\,\text{ms}$ (blue dots), along with the literature PI spectrum of CH$_2$O$^{58}$ (black line). Panel B: $m/z = 46$ ions, averaged over $t = 0 – 5$ (red) and 10 – 80 ms (gray dots), along with the literature PI spectrum of HCOOH$^{59}$ (black line). The dotted line at $h\nu = 10\,\text{eV}$ marks the measured ionization energy (IE$_a$) of CH$_2$OO.$^5$ Panel C: $m/z = 31$ and 64, averaged over $t = 10 – 80\,\text{ms}$. Dotted lines at 9.9 and 10.7 eV show the calculated IE$_a$ of HMHP and the appearance energy of the daughter ion (HOCH$_2^+$), respectively, averaged over four rotational conformers.

Determination of reaction yields

The quantification of formaldehyde and formic acid yields by PIMS allows a determination of reaction yields, provided that the relative importance of all CH$_2$OO reaction pathways is known. The calculated branching of the total CH$_2$OO decay into reactions R2 – R4 is shown in Table 2 for experimental sets #1 – 3 (see Table 1). The fractions of the total CH$_2$OO population that reacts with H$_2$O, (H$_2$O)$_2$, or by self-reaction + wall losses ($F_{\text{mono}}$, $F_{\text{dimer}}$, and $F_{S+W}$) are computed as follows:
\[ F_{\text{mono}} = \frac{k_2'}{k_{\text{decay}}} \]
\[ F_{\text{dimer}} = \frac{k_3'}{k_{\text{decay}}} \]
\[ F_{\text{dimer} + w} = \frac{k_4}{k_{\text{decay}}} \]

where the definitions of \( k_2' \), \( k_3' \), \( k_4 \), and \( k_{\text{decay}}' \) are the same as in equation E5. The pseudo-first order rate coefficients \( k_2' \) and \( k_3' \) were determined using the known concentration of water vapor and the fitted values of \( k_2 \) and \( k_3 \) from transient UV absorption results. The wall loss, which in large part determines \( k_4 \), depends on the reactor size and surface quality; hence, \( k_4 \) was directly measured for each of the datasets in Table 2 from the CH2OO decay under zero-water conditions. The wall loss was relatively rapid in dataset #1, which employed an uncoated quartz reactor, with the observed effective loss rate coefficient \( k_4 \) of approximately 480 ± 30 s\(^{-1}\). Subsequent datasets used a reactor coated in halocarbon wax, which significantly reduced wall losses; consequently, \( k_4 \) decreased to ~180 – 190 s\(^{-1}\).

Table 2 shows that as the water vapor concentration in our PIMS experiments increases from 0 to 4.11\( \times \)10\(^{17} \) cm\(^{-3} \) (equivalent to a partial pressure of ~11.5 Torr or relative humidity of ~66% at room temperature), the fraction of CH2OO that is lost via R4 decreases from 1.0 to 0.07. The value of \( F_{\text{dimer}} \) correspondingly increases from 0 to 0.9, while the reaction with water monomers remains a minor channel (\( F_{\text{mono}} < 7\% \)) at all conditions. As a result, the CH2OO removal mechanism shifts from largely by R4 at dry conditions to mostly by R3, reaction with (H\(_2\)O)\(_2\), at maximum [H\(_2\)O]. The measured yields of all stable products, averaged over \( t = 75 – 80 \) ms in our PIMS experiments, are plotted in Fig. 6 as a function of \( F_{\text{dimer}} \). The PI cross-section of HMHP is not known and we therefore plot its relative ion signals in Fig. 6. On the other hand, formaldehyde and formic acid were quantified using known PI cross-sections, which allowed a determination of their branching ratio at [H\(_2\)O] = 0 cm\(^{-3} \) under the assumption that no other products are formed. PIMS spectra taken at dry conditions with ionization energy 11.5 eV showed no stable products other than CH\(_2\)O and HCOOH. Meanwhile, the sum of final concentrations of CH\(_2\)O and HCOOH agreed very well with the initial concentration of CH2OO in the absence of water vapor (see Table 1), supporting our postulate that CH\(_2\)O and HCOOH were indeed the only reaction products. From the ratio of CH\(_2\)O to HCOOH concentrations at [H\(_2\)O] = 0 cm\(^{-3} \), their product branching fractions in the combined CH2OO wall loss and self-reaction are \( \Phi_4(\text{CH}_2\text{O}) = (95 \pm 3)\% \) and \( \Phi_4(\text{HCOOH}) = (5 \pm 3)\% \). Furthermore, the intensity of CH\(_2\)O and HCOOH ion signals at [H\(_2\)O] > 0, relative to that without water vapor, leads directly to their branching ratio as a function of \( F_{\text{dimer}} \) as shown in Fig. 6.

All product intensities vary approximately linearly in Fig. 6 and can be extrapolated to \( F_{\text{dimer}} = 1 \) to determine the branching fractions of R3. The CH\(_2\)O absolute yield at \( F_{\text{dimer}} = 1 \) is computed to be \( \Phi_3(\text{CH}_2\text{O}) = (40 \pm 10)\% \). Formal acid yields as a function of \( F_{\text{dimer}} \) fluctuate between ~2 – 10% of the initial radical concentration, so we settle on a conservative estimate, \( \Phi_3(\text{HCOOH}) < 10\% \). The branching fraction of HMHP is then (55 ± 15)\% as long as no other major products of R3 exist – a good assumption, since the other possible product of R3, dioxirane, should be easily detected by PIMS. The listed errors include uncertainties in the signal normalization procedure and in the extrapolation fit. We note that in principle the branching ratios of R2 can also be derived from the above analysis. However, in our experiments
\(F_{\text{mono}}\) is always small, and the uncertainty in species quantification and in the (H\(_2\)O)\(_2\) concentration make a determination of product yields of R2 impossible.

Our PIMS experiments also reveal a striking observation. Under dry conditions, the observed rate coefficient of the product rise matches the CH\(_2\)OO decay: \(k'_{\text{decay}} \approx 180\) s\(^{-1}\). Yet, although CH\(_2\)OO decays progressively faster with increasing water content (\(k'_{\text{decay}} \approx 2900\) s\(^{-1}\) at highest [H\(_2\)O] used), all products appear with the same rate coefficient of \(\approx 220\) s\(^{-1}\), irrespective of [H\(_2\)O]. This suggests a long-lived CH\(_2\)OO—(H\(_2\)O)\(_2\) complex, whose decomposition controls product formation. Our results suggest a room-temperature decomposition rate coefficient of \(\approx 220\) s\(^{-1}\) for this complex, which, if confirmed, is a benchmark for calculations of R3 and an important insight into its mechanism.

### Table 2. Partitioning of the CH\(_2\)OO reactive flux as a function of [H\(_2\)O] in PIMS experiments.

<table>
<thead>
<tr>
<th>Set #</th>
<th>[H(_2)O]/10(^{-7})</th>
<th>[(H(_2)O)(_2)]/10(^{-4})</th>
<th>rate coefficients (s(^{-1}))</th>
<th>reaction partitioning</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(k_2)</td>
<td>(k_3)</td>
<td>(k_4)</td>
</tr>
<tr>
<td>1</td>
<td>2.73±0.14</td>
<td>1.74±0.17</td>
<td>6.6±44</td>
<td>1150±170</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>480±30</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>4.1±0.2</td>
<td>3.9±0.4</td>
<td>99±66</td>
</tr>
<tr>
<td></td>
<td>2.20±0.11</td>
<td>1.13±0.11</td>
<td>53±35</td>
<td>740±110</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>2.58±0.13</td>
<td>1.55±0.16</td>
<td>6.2±41</td>
</tr>
<tr>
<td></td>
<td>2.34±0.12</td>
<td>1.28±0.13</td>
<td>5.6±38</td>
<td>840±120</td>
</tr>
<tr>
<td></td>
<td>2.30±0.12</td>
<td>1.23±0.12</td>
<td>5.5±37</td>
<td>810±120</td>
</tr>
<tr>
<td></td>
<td>1.05±0.05</td>
<td>0.26±0.03</td>
<td>25±17</td>
<td>170±25</td>
</tr>
<tr>
<td></td>
<td>1.50±0.08</td>
<td>0.52±0.05</td>
<td>36±24</td>
<td>350±50</td>
</tr>
<tr>
<td></td>
<td>2.00±0.10</td>
<td>0.93±0.09</td>
<td>48±32</td>
<td>620±90</td>
</tr>
</tbody>
</table>

\(a\) – \(k_4\), obtained at [H\(_2\)O] = 0, was applied to all PIMS experiments in the same dataset (i.e. performed on the same day).

**Figure 6.** Detected product intensities, averaged over \(t = 75 - 80\) ms, as a function of the CH\(_2\)OO fraction reacting with the water dimer, \(p_{\text{dimer}}\). The branching fractions of CH\(_2\)O and HCOOH (left axis) were determined as described in the text; the relative yields of HMHP (right axis) are the sums of ion counts at \(m/z = 31\) and 64.
The absence of clear experimental signals attributable to such a complex is puzzling. We do not necessarily expect this complex to have an intense UV absorption, especially if its electronic structure differs strongly from bare CH$_2$OO. However, we cannot easily justify the lack of ion signals arising from this species in our PIMS experiments. It is possible, albeit unlikely, that CH$_2$OO$-(\text{H}_2\text{O})_2$ has vanishingly small ionization cross-sections at the VUV photon energy employed in our study. Another possibility is that at least some of the ion signal at \(m/z = 47\) is due to dissociative ionization of CH$_2$OO$-(\text{H}_2\text{O})_2$. Unfortunately, we can’t offer a definitive assignment for the \(m/z = 47\) ions or a simple explanation for the lack of direct signals from the proposed complex.

**Possible influence of wall reactions on measured product yields**

Gas sampling in our PIMS experiments occurs at the reactor wall, and the observed reaction kinetics can potentially be affected by heterogeneous processes, e.g. adsorption/ desorption of chemical species or wall reactions. For homogeneous mixtures in a cylindrical geometry, exact analytical solutions can be found for the spatial distributions of the reactants and their time evolution due to wall losses.\(^6\) These solutions depend only on the reactor size and on the characteristic timescales of mass transport in the bulk and at the reactor boundary, as described in detail in the Supporting Material. The decay of reactants near the PIMS reactor wall can therefore be visualized by using their gas-phase diffusion coefficient \(D\) and wall reaction rate coefficient \(k_{\text{wall}}\). Wall effects at the sampling orifice are no more important than elsewhere in the reactor, because the orifice diameter, 300 \(\mu\)m, far exceeds the mean free path in our sample, \(\sim 1.7\ \mu\)m. Although neither \(D\) nor \(k_{\text{wall}}\) are known for CH$_2$OO or the CH$_2$OO$-(\text{H}_2\text{O})_2$ complex, we can estimate their diffusion coefficients by the method of Fuller et al.\(^6\) and examine certain limiting cases of \(k_{\text{wall}}\) to assess the possible effects of wall reactions on our results.

The details of our diffusion modelling are given in figures S5 and S6 and in the accompanying text of the Supporting Material. The upper limits for the diffusion coefficients \(D(\text{CH}_2\text{OO})\) and \(D(\text{CH}_2\text{OO}(\text{H}_2\text{O})_2)\) are \(\sim 14\) and \(11\ \text{cm}^2\text{s}^{-1}\) in 30 Torr of pure He. In the presence of H$_2$O vapor these diffusion coefficients decrease further to \(\ll 6\ \text{cm}^2\text{s}^{-1}\) at the highest [H$_2$O] employed in this study. The main conclusion that emerges from our analysis is that bulk gas-phase diffusion is far too slow to explain our measured CH$_2$OO or product time traces. We find that any heterogeneous process with greater than \(\sim 100\ \text{s}^{-1}\) rate coefficient yields clear non-exponential time evolution of the reactants, with rapid initial decay on the wall, followed by slow, diffusion-limited decay. Such time evolution is inconsistent with our CH$_2$OO signals in Fig 2, which exhibited unambiguous single-exponential decays up to \(k_{\text{decay}}'\sim 1000\ \text{s}^{-1}\), in excellent agreement with our UV probing results and with literature reports.\(^19\) It is also inconsistent with the 220 \(\text{s}^{-1}\) exponential rise of reaction products. In effect, diffusion places a lower limit on the apparent reactant decay timescales and on the apparent product rise times, since products cannot form any faster than the reactants decay.

In summary, accurate treatment of possible wall effects on the product yields is challenging and we cannot exclude them completely; however, our analysis suggests that such effects are, at most, minor and that our kinetic model consisting of reactions R1 – R4 adequately captures the overall chemistry. Reaction R4 already accounts for the (relatively minor) CH$_2$OO wall losses, and no other wall reactions are required. The fact that product yields determined from dataset #1 agree with those from datasets #2 and #3, despite a marked difference in R4, further bolsters this conclusion.

**Atmospheric impact**
To assess the atmospheric implications of our results, we integrated a global chemistry-transport model CRI-STOCHEM\textsuperscript{64} with and without including our measurements of R3, from which we derived the total CH\textsubscript{2}OO levels and determined their subsequent effects on tropospheric oxidation cycles. The model combines a reduced chemical mechanism (CRI v2-R5) with a 3-dimensional atmospheric module, driven by archived meteorological data. Extensive descriptions of the original model\textsuperscript{65} and subsequent updates,\textsuperscript{66-69} including an augmented chemical scheme and an organic aerosol module, are available in the literature. A detailed summary of the model is also included in the Supporting Material. The base case model contains primary emission and oxidation of ethene, propene, trans-2-butene, isoprene, and \(\alpha-\beta\)-pinene, as well as subsequent CI chemistry. The base case model does not explicitly account for HMHP and assumes rapid conversion of stabilized CI into HCOOH, which therefore represents an upper bound of formic acid production. Conversely, including our measurements of R3 with the assumption that no secondary HCOOH is formed beyond the measured primary yields corresponds to a lower bound of HCOOH production from CI chemistry.

\textbf{Figure 7.} Global impacts of adding the reaction R3 to the CRI-STOCHEM model. \textit{Panel A}: annual average surface mixing ratio of HMHP; \textit{Panel B}: percent change in OH concentrations; \textit{Panel C}: percent change in HCOOH concentrations.

The difference between these two limiting cases of model integration is illustrated in Fig. 7. The global modeled levels of HMHP (Fig. 7A) are in the 10 – 200 ppt range, consistent with field studies.\textsuperscript{70,71} Indeed,
because the reaction CH$_2$OO + water dimer is so rapid, measurements of HMHP might be useful to estimate the tropospheric CH$_2$OO production rate. The effect of including R3 on the hydroxyl radical concentration is minor, reducing surface OH levels by up to ~5%, largely due to lower production from stabilized CI decomposition. On the other hand, the change in HCOOH levels upon including R3 is a dramatic, decreasing the modeled concentration by 10 – 90 %. The reduction of predicted HCOOH is especially pronounced in equatorial and tropical areas, where comparisons of satellite measurements with models show a significant missing source of HCOOH.$^{34,72}$ The model results in Fig. 7 represent an upper bound on the potential atmospheric impact of our measurements, and more studies, especially focusing on the ultimate fate of HMHP, are clearly needed.

**Conclusions**

We report direct experimental measurements of the reaction kinetics and product branching in the reactions of CH$_2$OO with water vapor. Transient UV absorption spectroscopy enables accurate determination of the rate coefficients for the reaction CH$_2$OO + H$_2$O, $k_2 = (2.4 \pm 1.6) \times 10^{-16}$ cm$^3$·s$^{-1}$, and CH$_2$OO + (H$_2$O)$_2$, $k_3 = (6.6 \pm 0.7) \times 10^{-12}$ cm$^3$·s$^{-1}$, at pressures P = 30 – 100 Torr. Our findings resolve the discrepancy in earlier estimates of $k_2$, which varied by over 3 orders of magnitude. Our value of $k_3$ is lower than that of Berndt et al.$^{22}$ using competing kinetics analysis, but matches nearly perfectly the results of Chao et al.$^{19}$ obtained by direct UV probing. Concurrent time-resolved tunable VUV PIMS probing provides isomer-selective quantification of the reaction products and allows determination of their absolute yields. We find that at P = 30 Torr and T = 293 K the reaction CH$_2$OO + (H$_2$O)$_2$ forms (40 ± 10)% formaldehyde, (55 ± 15)% HMHP, and <10% HCOOH.

The link between CH$_2$OO reactions and HCOOH is uncertain at this point, and alternative sources of atmospheric HCOOH have also been proposed, including direct emission from vegetation.$^{73}$ Contrary to the report of Nguyen et al.$^{33}$ our results show that CH$_2$OO + (H$_2$O)$_2$ is not a major direct source of HCOOH, producing mainly HMHP and formaldehyde instead. We measure product yields at low pressure; however, increased P usually tends to favor stabilization products (in this case HMHP) so that its yield may be even higher at 1 atm. As Millet et al. point out,$^{34}$ HMHP itself may ultimately form HCOOH via photo-oxidation or heterogeneous conversion. However, the extent of either process in the atmosphere is not known, and further work is clearly needed to clarify its impact.

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**References**