

Observational evidence for Criegee intermediate oligomerization reactions relevant to aerosol formation in the troposphere

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Supplementary Note 1: Field measurements.

1.1 TOF-CIMS technique.

1.1.1 Calibrations and background measurements.

Mass calibration was performed using 5 known masses (I^- , $\text{I}^-\cdot\text{H}_2\text{O}$, $\text{I}^-\cdot\text{HC}(\text{O})\text{OH}$, I_2^- and I_3^-) that cover a range of m/z 127 to 380. The mass calibration was accurate to within 1 ppm, ensuring peak identification for all species was accurate below 1 ppm. The Tofware-specific FIGAERO-CIMS analysis software (version 3.1) was utilized to attain high-resolution 1 Hz time series of all of the species identified here, in both the gas- and particle-phases. Further analysis was done using software developed in-house.

Gas-phase background measurements were made once every 30 minutes for 30 seconds by overflowing the IMR just above the pinhole with wetted high-purity nitrogen. Data was background-subtracted using an interpolation of the two background measurements recorded either side of data collection. An example of the data processing for an arbitrary mass is shown in Figure S1.

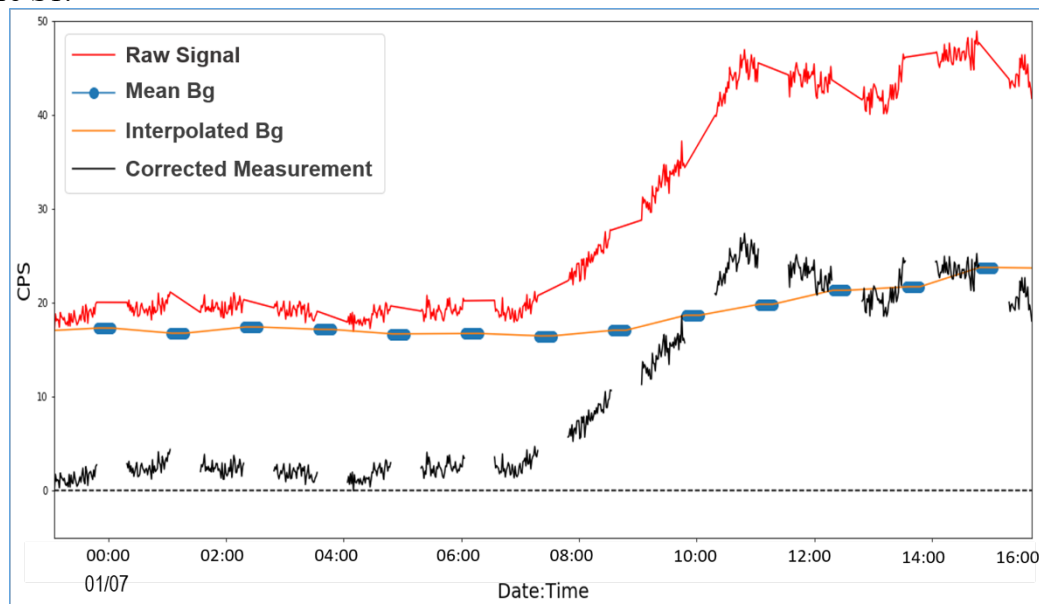


Fig. S1. Retrieval of background-corrected data from raw data for a subset of the measurement campaign for an arbitrary mass. The background counts obtained during the background period (blue dots) are interpolated to yield the interpolated background data (orange line). This is subtracted from the raw signal (red line) to obtain the corrected measurement (black line). All data are in units of counts per second (CPS).

Background filter measurements comprised a ramp, soak and cool cycle matching that of the ambient air sampling method. Each background measurement was applied to the thermogram measurements made until the next background filter measurement was recorded. In the event of a break in FIGAERO-CIMS measurements (i.e., due to temporary failure or power shortages), a new filter was placed into the instrument. The new filter was cleaned by ramping the temperature to 200°C for a duration of 20 minutes and subsequently cooled, with a complete cycle immediately after. Where there was no break in the measurements for ~2 days, the cleaning process was undertaken for the existing installed filter.

The result of high-resolution peak-fitting confirmed the presence of species with elemental compositions consistent with those of species in the proposed insertion sequence (bound to I⁻ from the ionization process) as shown in Figure S3. There are no calibration standards for the proposed insertion sequence, thus reported concentrations in this study are presented relative to the formic acid calibrations regularly performed throughout the measurements. These formic acid calibrations were carried out regularly throughout the campaign and utilized formic acid permeation tubes. An average (mean) formic acid calibration factor of 2.2 c ppt⁻¹, with a $\pm 5\%$ variation was obtained throughout the campaign and this sensitivity was applied to the measured species presented here. All sensitivities utilized herein were deduced assuming a linear response between reported and formic acid calibrations in the field (where day-to-day calibrations were performed). A range of other species were calibrated for after the campaign, and relative calibration factors were derived using the measured formic acid sensitivity during these calibrations, as has been performed previously ^{1,2}. An estimated uncertainty of $\pm 100\%$ is applied to reported concentrations of species for which no direct calibration source is available, *e.g.*, the insertion sequence products.

1.1.2 Supporting measurements.

Several supporting measurements were made that allow for interpretation of the TOF-CIMS measurements. These include gas-phase measurements of biogenic volatile organic compounds (BVOCs) from a proton transfer time-of-flight mass spectrometer (PTR-TOF-MS; Ionicon Analytik) and particle-phase measurements using an aerosol chemical speciation monitor (ACSM) ³. Operation and analysis procedures are outlined elsewhere for the PTR-TOF-MS ⁶ and for the ACSM ⁴. The chemical composition of submicrometer aerosols was measured on-line by mass spectrometry using an ACSM. The aerosol mass spectrometer ³ was used to characterize a wide range of non-refractory sub-micron aerosol particles such as organics, nitrate, sulfate, ammonium, and chloride in real-time with time-resolution of <15 minutes. Sulfur dioxide, NO_x and O₃ mixing ratios were monitored at both sites using trace gas analyzers (Thermo 43i-TLE, Thermo 42i and Thermo 49i, respectively). Meteorological parameters were measured using two different automatic weather stations (HOBO U30 Station GSM-UDP). Meteorological measurements comprised: temperature (± 0.3 °C), humidity ($\pm 3\text{--}5\%$), rain amount ($\pm 5\%$ for daily accumulation), wind speed (0.3–0.5 ms⁻¹) and direction ($\pm 3^\circ$), where the resolution and accuracy are stated in parenthesis.

1.2. Additional TOF-CIMS data.

Formic acid concentrations measured over the duration of the campaign are shown in Extended Data Figure 1. Formic acid concentrations up to 444 ppt were observed and show consistent evidence of secondary photochemical production based on the diurnal profiles. A good correlation is observed between ozone and formic acid, except during times of rain where it is anticipated that formic acid is washed out (Figure S2).

The peak fitting of the mass spectra for the insertion products $n=2-6$ identified in the campaign are shown in Figure S3, with pertinent data tabulated in Table S1.

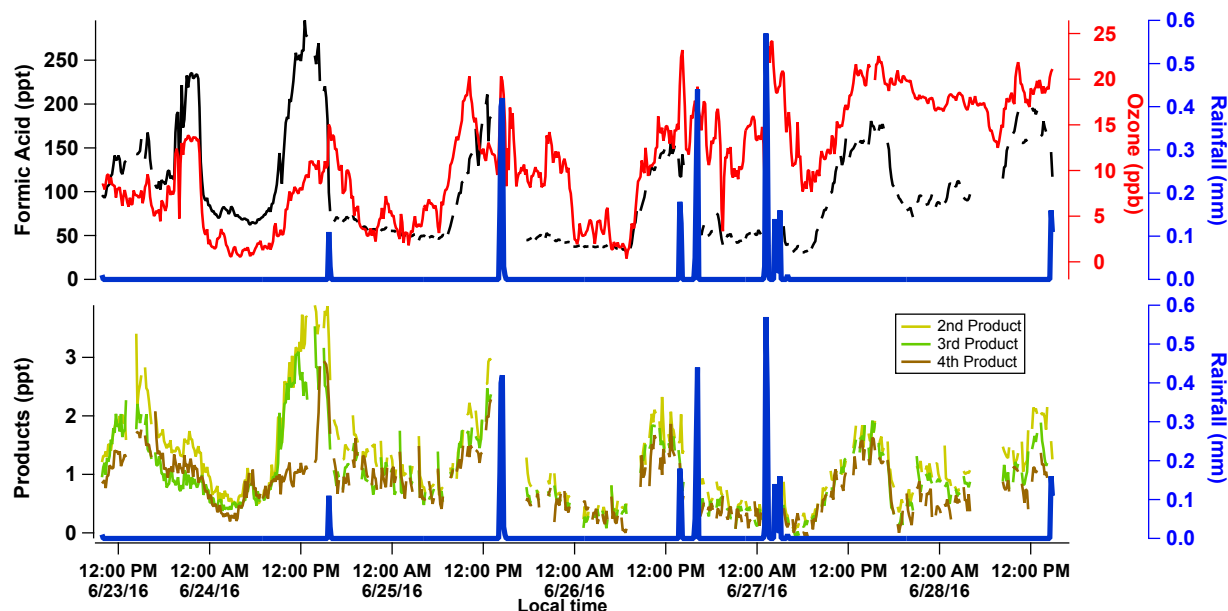


Fig. S2. Occurrences of rain (blue) and measured time series of (*upper*) formic acid (black), ozone (red) and (*lower*) gas-phase insertion products from $n=2-4$, over a selected time period.

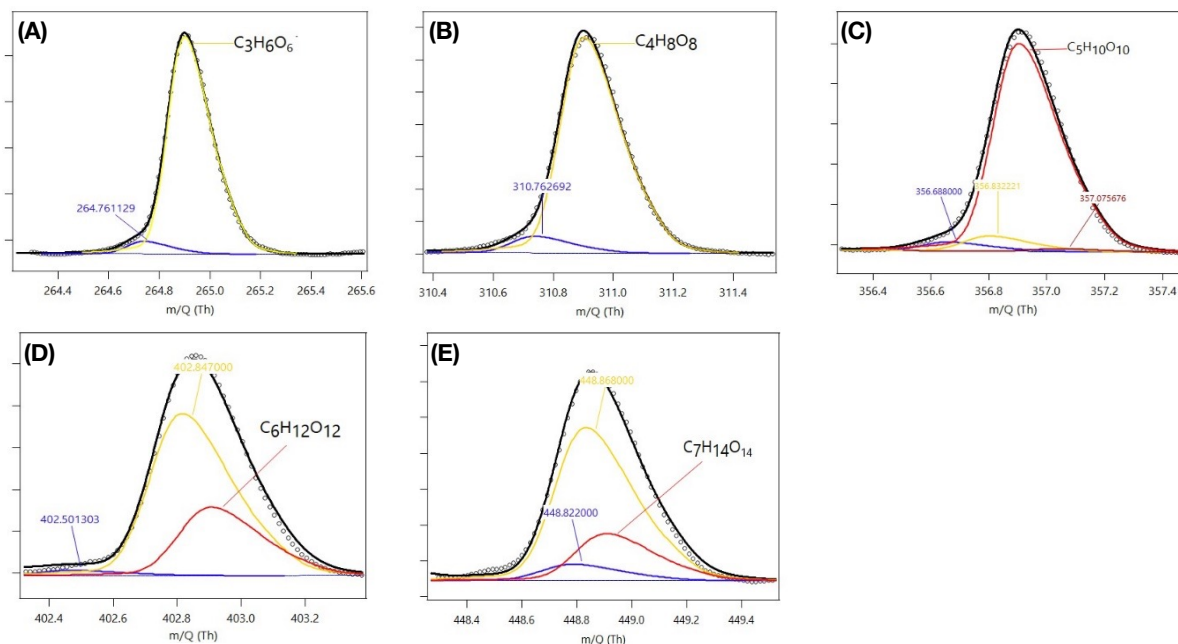


Fig. S3. Peak fittings for the products identified in the gas-phase ambient spectra for (A) $n=2$, (B) $n=3$, (C) $n=4$, (D) $n=5$ and (E) $n=6$ insertion products. The data is taken as the averaged (mean) gas phase spectra from the entire data set. The y-axes are arbitrary units of signal amplitude (scaled for visualization). The average (mean) peak shape for the tuning utilized for this campaign was used to calculate the mass resolution and optimization of the baseline fit. Mass calibration error shows a <1 ppm error for each calibrant throughout the entire campaign, giving confidence that m/z variation does not induce an error in identification. Each unknown peak was assigned, and accurate fitting was characterized by a ppm error of less than 1 and subsequent accurate fittings of isotopic peaks. The contribution of each product to the total signal at each mass reduces with increasing size.

Table S1. Exact masses and statistics from multipeak fits (see Figure S3) to the gas-phase field data measured over the Amazonian troposphere using iodide TOF-CIMS.

Insertion species	Nominal m/z of ion signal	Exact m/z of ion signal from multipeak fits	Chemical formula assigned to detected species	Contribution % of species to overall mass feature intensity	Precision %	Other mass features identified from multipeak fit
$n = 2$	265	264.921459	IC ₃ H ₆ O ₆	82	6	264.761129
$n = 3$	311	310.926939	IC ₄ H ₈ O ₈	83	6	310.762692
$n = 4$	357	356.932418	IC ₅ H ₁₀ O ₁₀	89	4	356.68000, 356.832221, 357.075676
$n = 5$	403	402.937897	IC ₆ H ₁₂ O ₁₂	29	12	402.501303, 402.847000
$n = 6$	449	448.943377	IC ₇ H ₁₄ O ₁₄	22	19	448.8222000, 448.868000

Diagnostics associated with multi-peak fitting, based on Cubison and Jimenez,⁵ were performed using the Tofware analysis software. The uncertainty from the accuracy of the multi-peak fitting was determined to be 4-19 % depending on the relative intensities and other masses at each peak, with the precision error generally rising with increasing m/z. The low uncertainties associated with the multi-peak fitting demonstrate the sufficient resolving power of the CIMS used in this study to report measurements of these products. This calculated uncertainty is however unique to this instrument and rely on accurate mass calibrations and so may differ for other I-CIMS instruments.

1.3 Observation of insertion products in the particle phase.

Maximum thermal desorption temperatures (Tmax), obtained from multiple repeated thermogram measurements can be correlated into the volatility of measured aerosol-phase species. The increase of Tmax with insertion number along the sequence with increasing molecular weight and oxygen content is consistent with decreasing volatility. Using the method outlined previously by Bannan *et al.*⁶, the measured Tmax values of the *n*=3-5 insertion products in the aerosol phase have been converted to approximate species vapor pressures using E1, as summarized in Table S2.

$$Vp = 0.2612 \cdot e^{(-0.071 \cdot Tmax)} \quad \text{E1}$$

Where Vp is the vapor pressure in Pa, and Tmax is the measured maximum thermal desorption temperature in C.

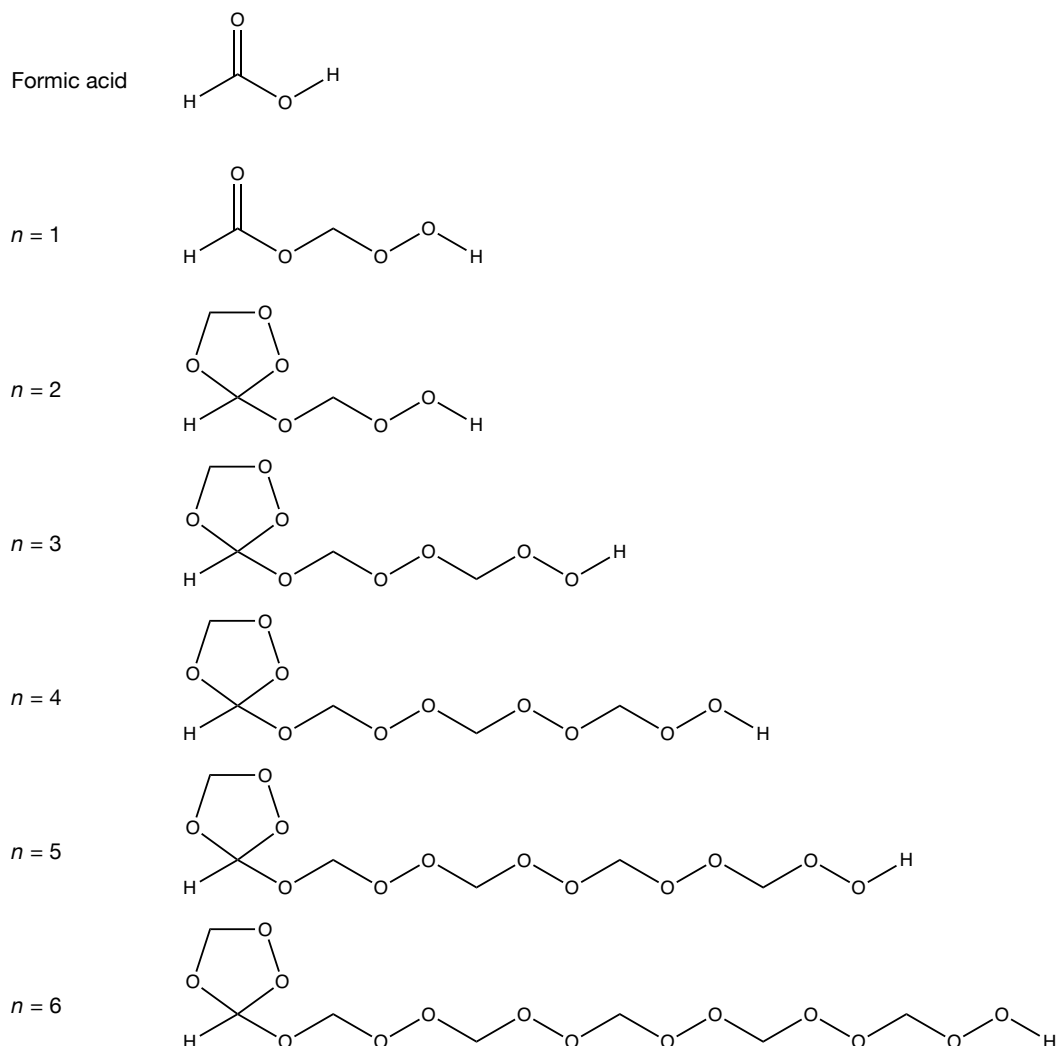
Table S2. Calculated vapor pressures for the *n*=3-5 insertion products in the aerosol phase using the median Tmax values and E1.

Insertion number, <i>n</i>	Measured Tmax (median) / C	Calculated vapor pressure / Pa
3	174.4	10.9×10^{-7}
4	178.8	8.0×10^{-7}
5	183.3	5.8×10^{-7}

The potential instability of organic peroxide species within the FIGAERO desorption method, when integrated with CIMS, has been previously demonstrated by Wang *et al.*⁷ This substantiates the qualitative presentation of the aerosol measurements in this study.

1.4 Proposed chemical structures of the CH₂OO + formic acid sequence.

Based on high-level theoretical analysis of the first three insertions of CH₂OO into formic acid (see main text and later sections herein), and following on this sequence, the anticipated chemical structures of the sequence up to $n=6$ are shown in Scheme S1.



Scheme S1. Proposed structures of the sCI + ROOH insertion sequence initiated by insertion of CH₂OO into formic acid. The structures of the $n=1-3$ products are based on high-level theoretical calculations (see main text and Supplementary Note 3), while the postulated structures of $n=4-6$ are based on assuming the same insertion pattern proceeds.

Supplementary Note 2: Jet-stirred reactor (JSR) measurements.

2.1 Masses from multipeak fitting in the JSR experiments.

Table S3. Exact masses and assignments extracted from multipeak fits (see Fig. 2A in the main text) to the JSR O₃ + ethene laboratory data measured using photoionization mass spectrometry.

Nominal m/z of signal	Exact m/z from multipeak fits	Chemical formula assigned to detected species
46	46.005	CH ₂ O ₂
92	92.007	C ₂ H ₄ O ₄
	92.042	C ₃ H ₈ O ₃
138	138.01	C ₃ H ₆ O ₆
	138.02	C ₄ H ₁₀ O ₅

Supplementary Note 3: Multiplexed photoionization mass spectrometer (MPIMS) experiments.

3.1 Species concentration experiments.

3.1.1. H₂O₂ concentration measurements.

Hydrogen peroxide (H₂O₂) was produced by heating urea hydrogen peroxide in a temperature- and pressure-controlled glass bubbler, whereby it was entrained into He flow. H₂O₂ concentrations were established in separate measurements recorded at a photoionization energy of 11.0 eV and that were performed back-to-back with the kinetics measurements. The procedure for these measurements is outlined in Supplementary Note 1 of Caravan *et al.*⁸, and thus described here only in brief. A commercially prepared sample of alkenes in Ar, including propene, is flowed alongside H₂O₂ and He at total flow rates and reactor pressures, such that the H₂O₂ concentration is identical to that used in the kinetics experiments recorded immediately prior and/or afterward. Using the known photoionization cross-sections of H₂O₂ from Dodson *et al.*⁹ and of propene from Nicole and Person^{10,11}, and the known concentration of propene in the reactor, [H₂O₂] is extracted, using E2. Further details regarding E2 are given in the supplementary information of Rotavera *et al.*¹², but in brief, S is the ion signal σ is the photoionization cross-section at a given photoionization energy, and m is the mass. β is the mass discrimination factor that accounts for mass-dependent sampling efficiencies of the instrument, and is characterized in separate calibration experiments using a commercially prepared standard mixture of rare gases diluted in He¹¹. The subscripts x and y denote the species of interest (H₂O₂ in this case) and the reference species (propene), respectively.

$$N_x = \left(\left(\frac{S_x/\sigma_x}{S_y/\sigma_y} \right) \cdot \left(\frac{m_y}{m_x} \right)^{\beta(p,T)} \right) \cdot N_y \quad \text{E2}$$

In addition to single energy measurements at 11.0 eV, experiments whereby the photoionization energy was scanned between 9.4 and 11.5 eV were also recorded and utilized to verify the identity and concentration of H₂O₂. The PI cross-sections of propene and H₂O₂ at the exact photoionization energy (established by measurement of the Xe resonance, section 3.2.4.) were used in determining [H₂O₂] in the 11.0 eV back-to-back measurements with each kinetics measurement.

3.1.2. $(\text{CH}_3)_3\text{COOH}$ concentration measurements.

A solution of t-BuOOH in water (70% wt. in H_2O) was delivered to the reactor via a temperature- and pressure-controlled glass bubbler using He carrier gas. For safety reasons, it was not feasible to work with 100% t-BuOOH. The concentration of t-BuOOH was established in separate measurements recorded at a photoionization energy of 11.0 eV, performed back-to-back with the kinetics measurements, as described in section 3.1.1 for H_2O_2 . To our best knowledge, the photoionization cross sections of t-BuOOH have not previously been measured, therefore, we measured the photoionization cross section of t-BuOOH using the method described herein.

A known concentration of propene, He bath gas, and the output of the t-BuOOH/water solution bubbler was delivered to the MPIMS reactor (298 K, and either 10 or 40 Torr).

Separate characterization measurements were performed to establish the fraction of the vapor from the t-BuOOH/water solution bubbler that is t-BuOOH ($\gamma_{\text{t-BuOOH}}$) and that is H_2O ($\gamma_{\text{H}_2\text{O}}$, where $\gamma_{\text{t-BuOOH}} + \gamma_{\text{H}_2\text{O}} = 1$) under our experimental conditions (see section 3.1.4.) via simultaneous laser absorption measurements of water and of t-BuOOH.

To establish [t-BuOOH] output from the bubbler in our photoionization cross-section measurements, we performed online water absorption measurements of the output of the t-BuOOH/water solution bubbler using a highly sensitive, time-resolved spectrometer (see section 3.1.3.). [t-BuOOH] was determined using these measurements in combination with $\gamma_{\text{t-BuOOH}}$.

Absolute PI spectra were recorded from 9.0-11.5 eV, using a known concentration of propene as a reference. The PI cross-section of propene is known over this entire energy range^{10,11}. The measured PI signal of t-BuOOH was scaled to the PI cross-section of propene at 11.0 eV using the value of Person and Nicole¹⁰. The PI spectrum of t-BuOOH was recorded four times – twice each using the two water spectrometers described in section 3.1.3. An average (mean) PI cross-section of 1.15 ± 0.32 Mb at 11.0 eV was established, where the uncertainty is 2 standard deviations of the mean value.

The PI cross-sections of propene and t-BuOOH at the exact photoionization energy (established by measurement of the Xe resonance, section 3.2.4.) were used in determining [t-BuOOH] in the 11.0 eV back-to-back measurements with each kinetics measurement.

Due to the significant uncertainties in the PI cross-section of t-BuOOH, $\gamma_{\text{t-BuOOH}}$, and in the water spectrometer measurements, we estimate an uncertainty of $\pm 50\%$ in [t-BuOOH] for the experiments reported here. This is reflected in the reported bimolecular rate coefficient for $\text{CH}_2\text{OO} + \text{t-BuOOH}$.

3.1.3. Water absorption measurements.

Water concentrations were measured using a tunable laser spectrometer (TLS) downstream of the H_2O bubbler needle valve. Two versions of the water spectrometer were used in this work, operating at different Mid-IR wavelengths, however the general construction of the two units was identical. Light from a tunable diode laser was directed through a glass flow-cell, with anti-reflective-coated calcium fluoride windows, and collected onto a mercury-cadmium-telluride (MCT) detector, operated at room temperature. Signals from the MCT were amplified and read into a computer using a fast digitizer. The pressure and temperature of the gas flow were measured using a baratron and Pt resistance temperature detector probe, respectively.

The diode lasers were operated isothermally ($\sim 29^\circ\text{C}$), and the wavelengths were tuned by ramping the diode supply current. The first iteration used a laser centered at 2632 nm (3800 cm^{-1}) probing one H_2O spectral line. In the second iteration, the laser was centered at 3447 nm

(2901 cm^{-1}) probing four H_2O spectral lines.

Using the temperature and pressure, along with line parameters from the HITRAN¹³ database, the H_2O lines were fit in real-time using a Voigt profile estimation, using the HITRAN application programming interface (HAPI¹⁴) to calculate the line cross-sections. One hundred co-added spectra were averaged (mean) before fitting (0.1 Hz data rate). Figure S4 shows an example H_2O spectrum recorded at 21 Torr, 20 sccm with a fitted concentration of $1.87 \times 10^{17} \text{ cm}^{-3}$ using the second iteration of the H_2O spectrometer.

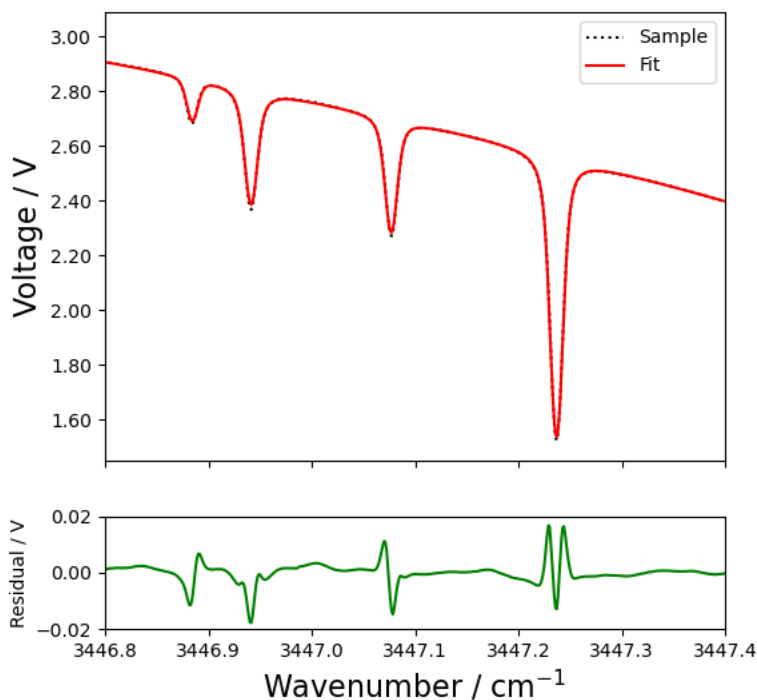


Fig. S4. (*Upper*) Example recorded H_2O spectrum (dotted black), fit using HITRAN line parameters (red). (*Lower*) The residual of the fit (green).

Uncertainties in the H_2O measurement originate from the uncertainties in the following: the listed HITRAN line parameters, the conversion of the laser drive current to wavenumber, the pathlength of the cell and the quality of the fit (systematic), in addition to the noise in the collected signal from the electronic components, and fluctuations in the laser beam intensity (precision). All quoted uncertainties are $\pm 2\sigma$. The precision uncertainties in this case are minimal ($\sim 1\%$) and were estimated from the standard error in the calculated concentration over time. The mA conversion and pathlength were measured using the introduction of known pressures of pure N_2O into the spectrometer in a static experiment. The N_2O spectrum has several lines within the operating region used for H_2O measurements that enabled the uncertainty associated with the pathlength ($\sim 2\%$) and the mA conversion ($\sim 3\%$) to be minimized. The fit quality was judged by the residual, which systematically showed some residual spectral features, as shown in Figure S4 (*lower*). This was likely due to the Voigt line shape approximation used for the fitting routine not capturing biases introduced by speed dependent effects, *e.g.* Dicke effects. However, the uncertainty caused was deemed negligible for this application as the error in the integrated area

was <1%. The largest uncertainty in the measurements was that associated with the HITRAN line parameters. Loos *et al.*¹⁵ conducted a suite of experiments using these parameters, with quoted minimized uncertainties in the H₂O line parameters on the order of ~5-10%. We therefore establish an upper limit uncertainty of the [H₂O] measurements of ±11%.

3.1.4. (CH₃)₃COOH absorption measurements.

Experiments were conducted at JPL to validate the fraction of t-BuOOH evolved from the t-BuOOH/water solution bubbler. The apparatus used replicated the experimental conditions (*e.g.* bubbler pressures, flow rates, temperatures) used in the absolute PI spectrum measurements of t-BuOOH using the MPIMS apparatus at the ALS (section 3.1.2.). Helium bath gas was flowed through two MKS mass flow controllers: one main flow (1000 sccm) and one bubbler flow (100 sccm). The pressure of the main flow (750 sccm total) was maintained at 12 Torr. Gas eluting from the temperature-controlled bubbler (19 ± 1 °C, 48 Torr, 5 sccm), containing a solution of (CH₃)₃COOH in water (70% wt. in H₂O), was passed through the H₂O spectrometer, followed by a UV absorption cell, both located after the bubbler needle valve, before being mixed with the main flow.

The UV absorption cell (50 cm length, 2.54 cm O.D, 185 nm) utilized light from a Hg-Ar lamp combined with a photomultiplier tube (PMT) and two 185 ± 3 nm bandpass filters. Concentrations of (CH₃)₃COOH were determined using the value of Baasandorj *et al.*¹⁶, $\sigma_{185\text{nm}} = (4.24 \pm 0.32) \times 10^{-19}$ cm², subtracting the minor absorption of H₂O using the H₂O spectrometer and the recommended cross section at 185 nm ($(7.22 \pm 0.22) \times 10^{-20}$ cm², Burkholder *et al.*¹⁷). Three repeated measurements of [t-BuOOH] and [H₂O] were conducted, bypassing the bubbler flow in between measurements. An observed mean t-BuOOH fraction ($\Upsilon_{\text{t-BuOOH}}$) of 0.28 ± 0.07 (2 σ precision) was obtained. Systematic uncertainties come from the H₂O measurement, reported cross sections and the UV cell pathlength. As we report in section 3.1.3, the uncertainty in the H₂O measurement is 11%, the uncertainties in the reported cross sections were 7.5% (t-BuOOH) and 3% (H₂O), and the pathlength uncertainty was estimated at 3%. Based on this we assign an uncertainty of ±14% on the t-BuOOH fraction.

The value of $\Upsilon_{\text{t-BuOOH}}$ reported here is lower than that of Baasandorj *et al.*¹⁶ (0.56 ± 0.08 at 23 °C). The reason for this discrepancy is unclear. The reported fraction from Baasandorj *et al.*¹⁶ was measured from a gas sample expanded into a glass bulb, rather than in a bulk flow experiment through a bubbler, although it is not clear how this would affect the observed results. The fraction of t-BuOOH eluting from the bubbler was observed to increase over time; a sample bubbled through for ~1 week was observed to exhibit a fraction ~0.4, however this is still outside of the uncertainty range of the Baasandorj *et al.* study¹⁶.

3.2 Data analysis procedure.

3.2.1 Instrument response function.

The time-resolved detection of ions in the multiplexed photoionization mass spectrometry (MPIMS) instrument is subject to an inherent delay and broadening, known collectively as the instrument response time. This delay is due to the transportation time between the regions at which the ions are created and detected. It causes a perturbation on the time profile of detected ions – the observed kinetics is a convolution of the ‘true’ kinetics with the instrument response function, which has been parameterized by Moore and Carr¹⁸ and Taatjes¹⁹. Using the methodology described in the supplementary online material of Welz *et al.*²⁰, we have utilized the reaction of $\text{CH}_2\text{I} + \text{O}_2$ to determine the instrument response function parameters. The resultant characterized parameters were utilized in the fitting of CH_2OO decay kinetics and reaction products growth kinetics.

3.2.2 Kinetic fitting equations.

Loss rate coefficients for CH_2OO were retrieved by fitting with a single exponential decay expression, convolved with the instrument response function. The parameters of the latter were determined from the calibration outlined above. Rate coefficients for the formation of potential product species were retrieved by fitting time traces with a single exponential growth expression, convolved with the instrument response function. Examples of typical fitted time profiles of CH_2OO and a reaction product are shown in the main text, Figure 2C. Fits to the data returned first order rate coefficients and associated 95 % confidence intervals of the fit. Bimolecular rate coefficients were obtained from a linear fit to a plot of the first order rate coefficients vs. $[\text{ROOH}]$, weighted by the 95 % confidence interval error bars. The reported errors in the bimolecular rate coefficients are the 95 % confidence intervals of the linear fit.

3.2.3 Mass axis calibration.

The mass axis was calibrated using the measured flight times of ethene, propene and 1-butene ionized at 10.6 eV²¹. Further mass axis calibration checks were performed during the kinetics experiments by using the exact masses and flight times of the Criegee intermediate precursor (CH_2I_2), iodine (produced from CH_2I_2 photolysis), CH_2OO and the peroxide (H_2O_2 or $(\text{CH}_3)_3\text{COOH}$).

3.2.4 Photoionization energy calibration.

The photoionization energy was calibrated using the Xe $5p \rightarrow 8s$ resonance at 12.5752 eV²², and the photoionization efficiency curve of propene^{10,11}.

3.2.5 $\text{CH}_2\text{OO} + \text{water vapor}$ in $\text{CH}_2\text{OO} + (\text{CH}_3)_3\text{COOH}$ kinetics measurements.

Due to the introduction of water vapor ($[\text{H}_2\text{O}] < 5.2 \times 10^{15} \text{ cm}^{-3}$) with t-BuOOH (section 3.2.2), the impact of $\text{CH}_2\text{OO} + \text{H}_2\text{O}$ and $\text{CH}_2\text{OO} + (\text{H}_2\text{O})_2$ must be considered in the kinetic measurements of $\text{CH}_2\text{OO} + \text{t-BuOOH}$. Using the recommended rate coefficients for $\text{CH}_2\text{OO} + \text{H}_2\text{O}$ and $\text{CH}_2\text{OO} + (\text{H}_2\text{O})_2$ ^{17,23}, the maximum loss rate for CH_2OO under our experimental conditions due to these reactions is $< 2 \text{ s}^{-1}$, which is significantly slower than the observed loss due to reaction with t-BuOOH. Because of the presence of water vapor in our experiments on $\text{CH}_2\text{OO} + \text{t-BuOOH}$, complexation of t-BuOOH with water is a possibility. Water effects on CH_2OO insertion reactions should be investigated in future work but are anticipated to be minimal under our experimental conditions due to low $[\text{H}_2\text{O}]$.

3.3 Additional MPIMS data.

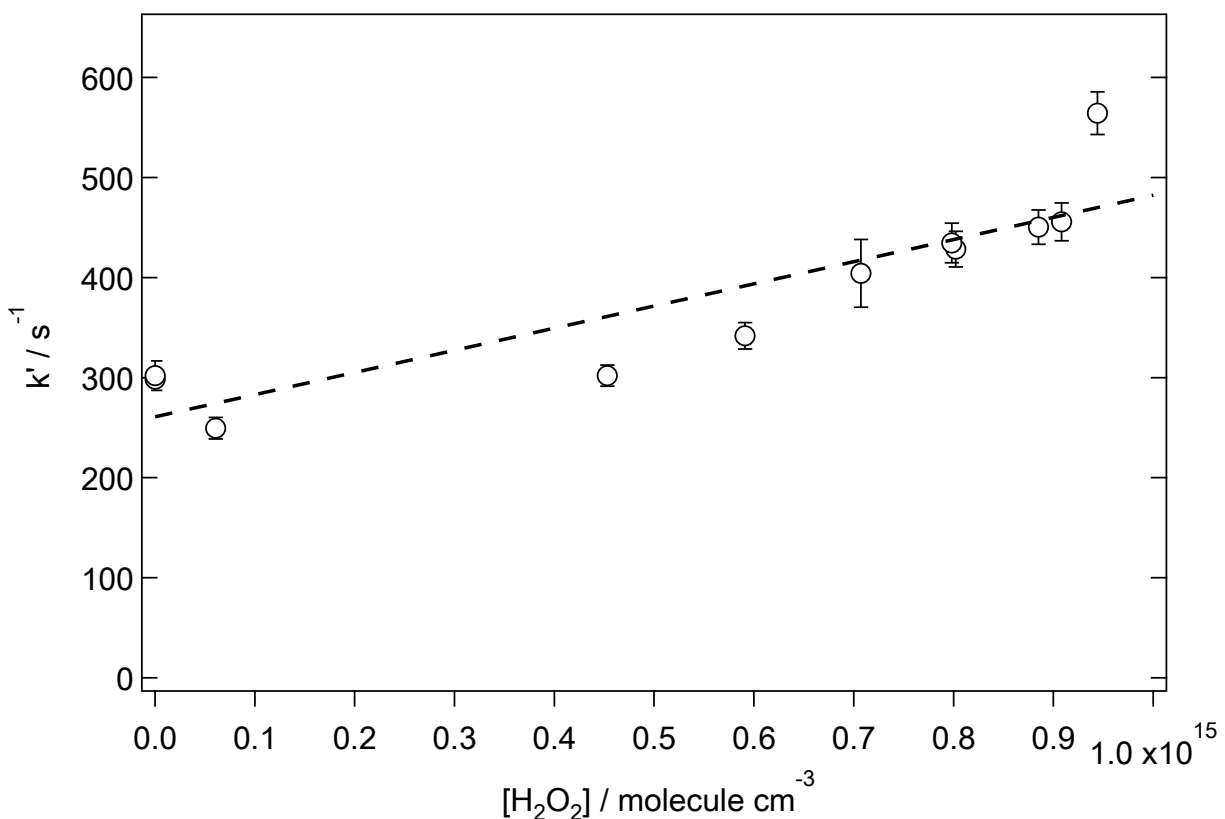


Fig. S5. First order rate coefficients for CH_2OO loss (open circles) in the presence of H_2O_2 plotted as a function of $[\text{H}_2\text{O}_2]$. First order rate coefficients are obtained from fits to the m/z 46 time-traces of a single exponential decay expression convolved with the instrument response function. Each data point corresponds to a single first-order decay measurement. Error bars are 2σ errors from the fits. A non-weighted linear fit to the data returns the bimolecular rate coefficient of $(2.2 \pm 0.9) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ (95 % confidence interval).

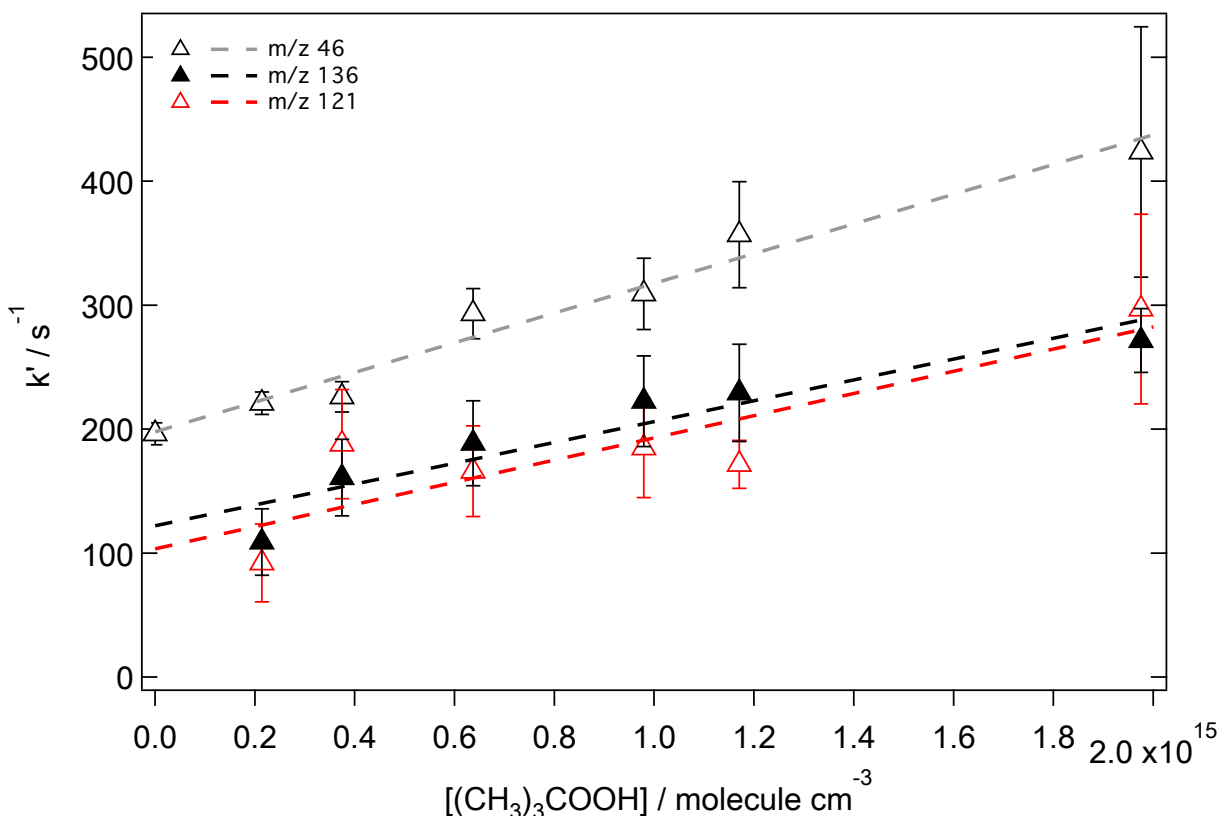


Fig. S6. First order rate coefficients for m/z 46 (CH_2OO) loss (open grey triangles) and m/z 136 (closed black triangles) and m/z 121 (open red triangles) growths in the presence of $(CH_3)_3COOH$ (t-BuOOH), plotted as a function of $[(CH_3)_3COOH]$. First order rate coefficients are obtained from fits to the time-traces using single exponential decay or growth expressions convolved with the instrument response function. Each data point corresponds to a single first-order decay measurement. Error bars are 2σ errors from the fits. Non-weighted linear fit to the m/z 46 data returns the bimolecular rate coefficient of $(1.2^{+1.2}_{-0.6}) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, where the reported errors are due to the $\pm 50\%$ 2σ uncertainty in $[(CH_3)_3COOH]$ (see section 3.1.2.). The bimolecular rate coefficient is consistent with the values obtained from fits to the product data.

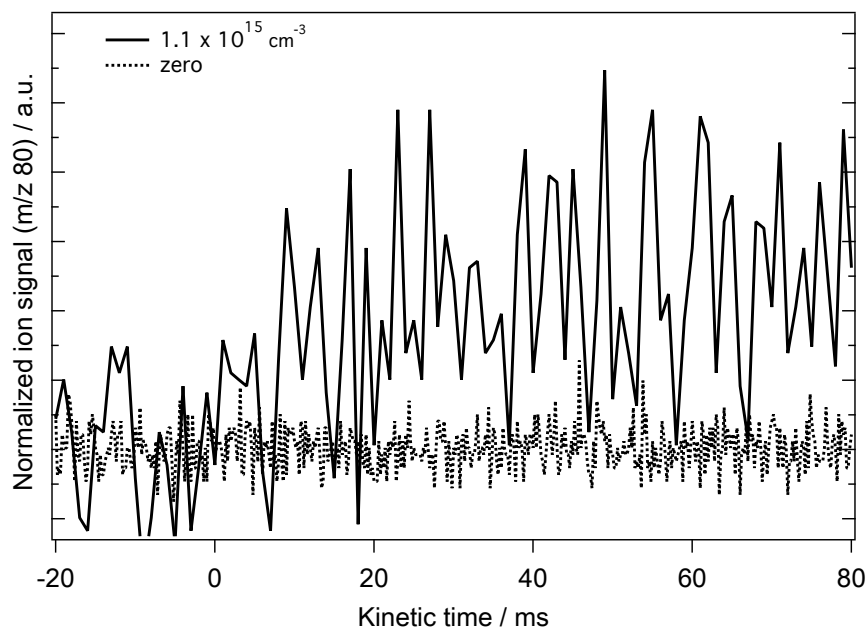


Fig. S7. Time profile of m/z 80 in the absence (dotted line) and presence (full line) of H_2O_2 from MPIMS study of the reaction of $\text{CH}_2\text{OO} + \text{H}_2\text{O}_2$. Signals are normalized for the number of laser shots and measured photocurrent of the photoionizing radiation.

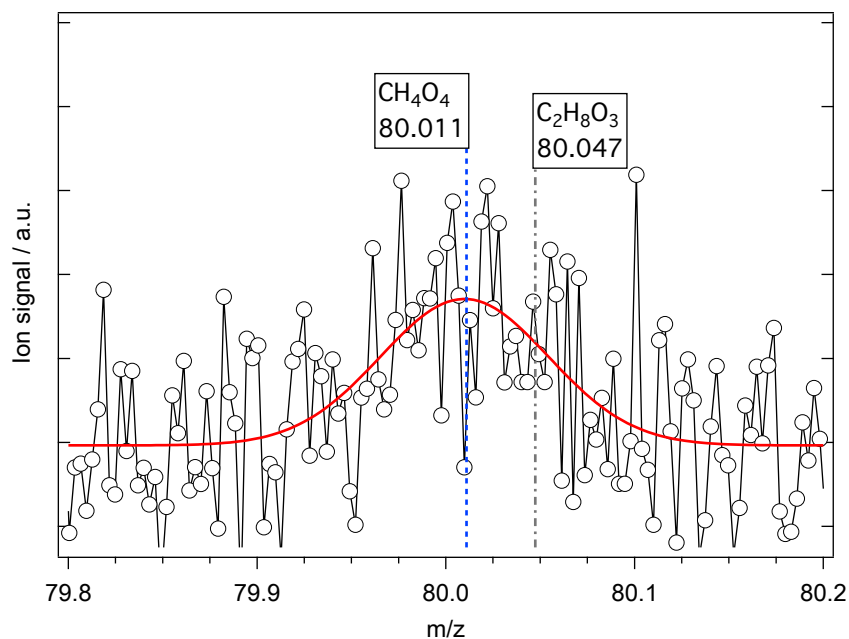


Fig. S8. Gaussian fit (red line) to determine the exact mass of the reaction product $\sim m/z$ 80 formed from the reaction of $\text{CH}_2\text{OO} + \text{H}_2\text{O}_2$. The Gaussian fit retrieved a value of (80.010 ± 0.006) amu, consistent with the exact mass of the proposed insertion product, CH_4O_4 , as illustrated by the blue dashed line. The observed mass is inconsistent with that of other possible chemical formulae, for example $\text{C}_2\text{H}_8\text{O}_3$ (grey dotted/dashed line).

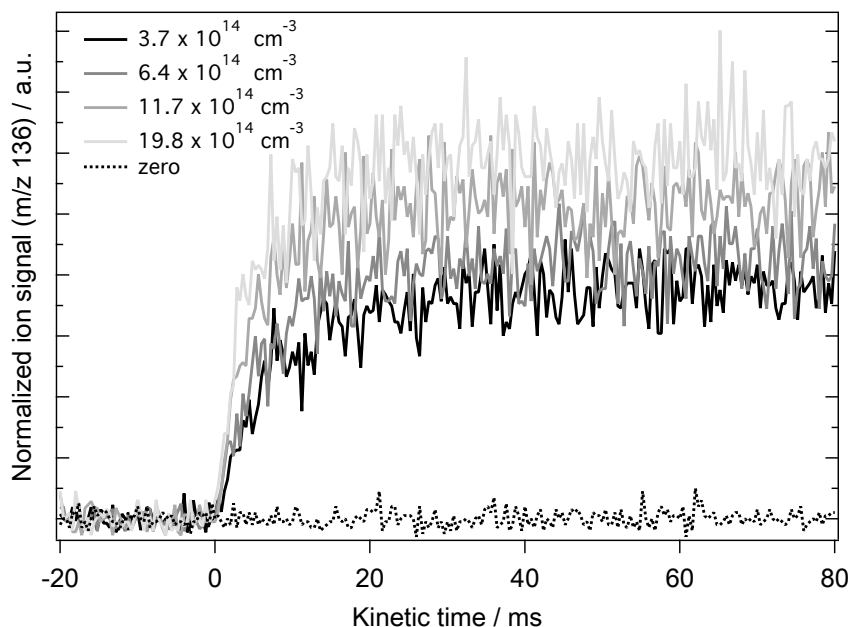


Fig. S9. Time profile of m/z 136 in the absence (dotted line) and presence (full lines) of $(\text{CH}_3)_3\text{COOH}$ from MPIMS study of the reaction of $\text{CH}_2\text{OO} + (\text{CH}_3)_3\text{COOH}$. Signals are normalized for the number of laser shots and measured photocurrent of the photoionizing radiation. Note that the signal amplitudes and rise time, which increase and decrease respectively, with $[(\text{CH}_3)_3\text{COOH}]$, are consistent with formation from the reaction of interest.

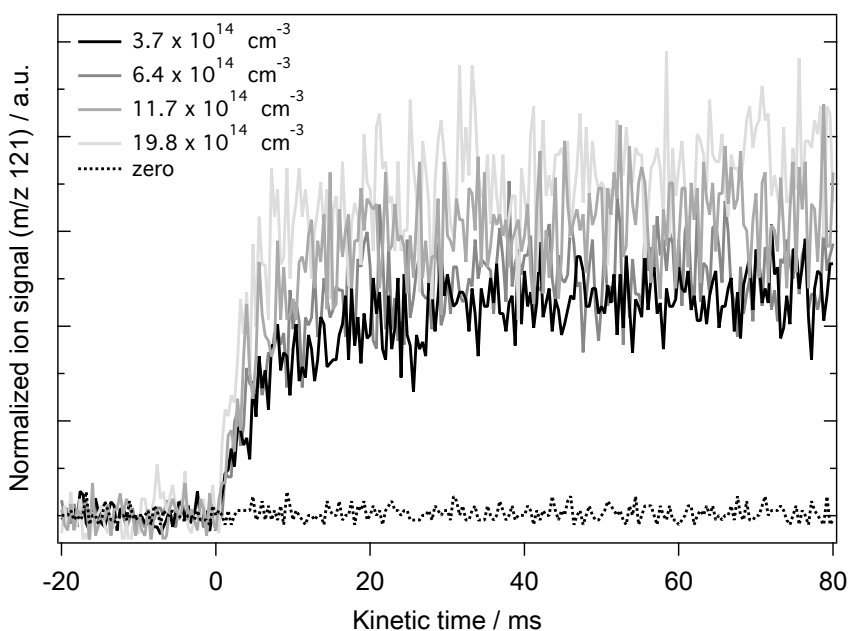


Fig. S10. Time profile of the proposed product daughter ion at m/z 121 in the absence (dotted line) and presence (full lines) of $(\text{CH}_3)_3\text{COOH}$ from MPIMS study of the reaction of $\text{CH}_2\text{OO} + (\text{CH}_3)_3\text{COOH}$. Signals are normalized for the number of laser shots and measured photocurrent of the photoionizing radiation. Note that the signal amplitudes and rise time, which increase and decrease respectively, with $[(\text{CH}_3)_3\text{COOH}]$, are consistent with formation from the reaction of interest and with m/z 136.

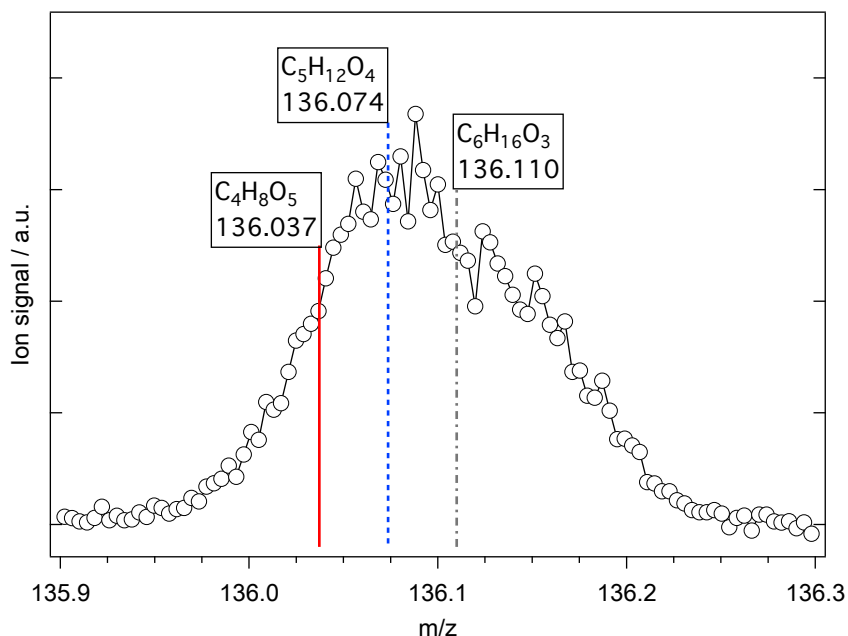


Fig. S11. High-resolution mass spectrum extraction showing the mass peak of the reaction product $\sim m/z$ 136 formed from the reaction of $\text{CH}_2\text{OO} + (\text{CH}_3)_3\text{COOH}$. The maximum amplitude in the mass peak is consistent with the exact mass of the proposed insertion product, $\text{C}_5\text{H}_{12}\text{O}_4$, as illustrated by the blue dashed line. The center of the mass peak is inconsistent with that of other possible chemical formulae, for example $\text{C}_4\text{H}_8\text{O}_5$ (red solid line) or $\text{C}_6\text{H}_{16}\text{O}_3$ (grey dotted/dashed line).

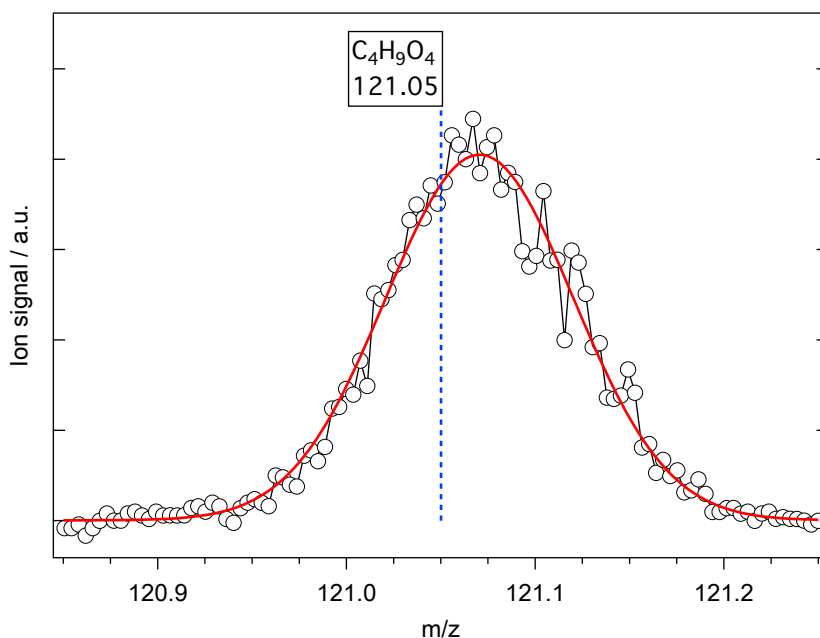


Fig. S12. Gaussian fit (red line) to determine the exact mass of the proposed daughter ion at $\sim m/z$ 121 from the product $\sim m/z$ 121 formed from the reaction of $\text{CH}_2\text{OO} + (\text{CH}_3)_3\text{COOH}$. The Gaussian fit retrieved a value of 121.07 amu, consistent with the exact mass of the proposed daughter ion of the insertion product, $\text{C}_4\text{H}_9\text{O}_4$, as illustrated by the blue dashed line.

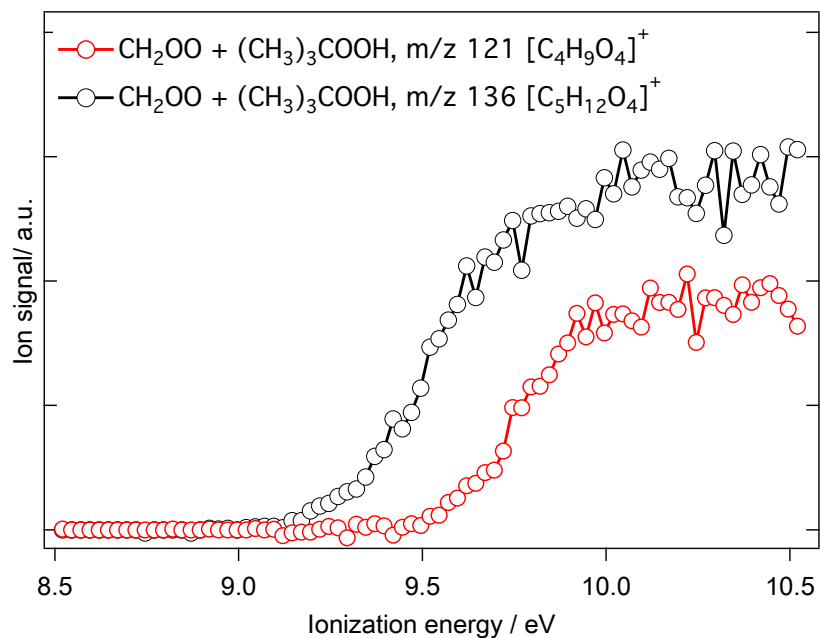


Fig. S13. Photoionization spectra of m/z 136 ($C_5H_{12}O_4^+$, black open circles) and m/z 121 ($C_4H_9O_4^+$, red open circles) from the reaction of $CH_2OO + (CH_3)_3COOH$.

Supplementary Note 4: *Ab initio* Stationary Point Calculations and Theoretical Kinetics.

4.1 Pressure dependent parameters.

We first consider DHP (from $\text{CH}_2\text{OO} + \text{H}_2\text{O}_2$) and SOZ (from $\text{CH}_2\text{OO} + \text{HPMF}$) and the two baths He and Ar. For DHP (+M), from $\text{CH}_2\text{OO} + \text{H}_2\text{O}_2$ reaction our results from 300–2500 K are well represented by $\alpha_{\text{He}} = 110 (T/300 \text{ K})^{0.55} \text{ cm}^{-1}$, $\sigma_{\text{He}} = 4.12 \text{ \AA}$, $\epsilon_{\text{He}} = 13.1 \text{ cm}^{-1}$, $\alpha_{\text{Ar}} = 175 (T/300 \text{ K})^{0.55} \text{ cm}^{-1}$, $\sigma_{\text{Ar}} = 4.24 \text{ \AA}$, and $\epsilon_{\text{Ar}} = 106 \text{ cm}^{-1}$, and for SOZ (+M) $\alpha_{\text{He}} = 139 (T/300 \text{ K})^{0.58} \text{ cm}^{-1}$, $\sigma_{\text{He}} = 4.40 \text{ \AA}$, $\epsilon_{\text{He}} = 17.3 \text{ cm}^{-1}$, $\alpha_{\text{Ar}} = 178 (T/300 \text{ K})^{0.48} \text{ cm}^{-1}$, $\sigma_{\text{Ar}} = 4.48 \text{ \AA}$, and $\epsilon_{\text{Ar}} = 157 \text{ cm}^{-1}$. These values are in line with results previously obtained for hydroperoxide systems featuring several heavy atoms.²⁴ For systems larger than SOZ, we extrapolate σ and ϵ using the empirical observation that these parameters are well described by a power law in N ,²⁴ where N is the number of heavy (non-hydrogen) atoms, and we adopt the SOZ values of α , which only slowly varies with size for large systems. For the $\text{CH}_2\text{OO} + (\text{CH}_3)_3\text{COOH}$ system, we employ the related parameters from the $\text{CH}_2\text{OO} + \text{HPMF}$ system. The calculations for Ar provide a reasonable surrogate for the bath gas dependence of collisions in air.

Next, we consider pressure dependence for the van der Waals (vdW) complexes. We again adopt the *a priori* exponential down model. It is unknown how collision parameters for weakly bound complexes relate to those for strongly bound chemical adducts, which have been more widely studied. The internal energies of vdW complexes are much smaller than those for molecular adducts, which would suggest relatively lower collision strengths, while the presence of multiple low-frequency modes in vdW complexes likely enables relatively more efficient, stronger collisions.

To address these uncertainties, we computed collisional energy transfer for the vdW complex $\text{CH}_2\text{OO} \cdots \text{H}_2\text{O}_2$ (+He), which required some modifications to our usual approaches. First, we could not rely on molecular mechanics descriptions of the $\text{CH}_2\text{OO} \cdots \text{H}_2\text{O}_2$ vdW interaction, and so we sampled and generated a new fit for this interaction potential as part of this work. Second, additional steps were taken to prepare $\text{CH}_2\text{OO} \cdots \text{H}_2\text{O}_2$ complexes with realistic energy distributions prior to the bath gas collisions. Specifically, CH_2OO and H_2O_2 were equilibrated to the temperature of interest (300 K), and the two species were collided using the usual thermal bimolecular sampling strategies. Many such trajectories resulted in “misses” or otherwise short-lived complexes. Roughly half of trajectories led to long-lived complexes, and these complexes were used to provide initial conditions for subsequent bath gas collisions.

We found that the collisional energy transfer rates were 2 times larger for the vdW complex $\text{CH}_2\text{OO} \cdots \text{H}_2\text{O}_2$ than for DHP. Low impact parameter (head-on) collisions showed similar collision strengths for the two systems, while energy transfer was significant out to much larger impact parameters for the weakly bound $\text{CH}_2\text{OO} \cdots \text{H}_2\text{O}_2$ complex than for DHP. We therefore chose to represent this energy transfer enhancement for the vdW species of interest here by multiplying the Lennard–Jones diameter σ by $\sqrt{2}$, which has the effect of doubling the collisional energy transfer rate.

4.2 $\text{CH}_2\text{OO} + \text{H}_2\text{O}_2$.

4.2.1 Potential energy surface.

A recent study of Vereecken *et al.* provides a detailed theoretical analysis of the reaction of CH_2OO with H_2O_2 .³⁶ Their CCSD(T)/aug-cc-pVTZ//M062X/aug-cc-pVTZ based exploration of the reactive potential energy surface (PES) indicates the presence of two distinct insertion channels leading to either a dihydroperoxide (DHP) or an ether oxide. The barriers for these two

insertions are submerged below the reactant energy by 2 kcal/mol. The DHP species is quite stable (at -50 kcal/mol), but the barrier for its OO fission lies well below (-10 kcal/mol) the reactant energy. Meanwhile, the ether oxide is less stable (-6 kcal/mol) than the van der Waals complex formed from the reactants (-9 kcal/mol). A 1,2 H transfer connects the dihydroperoxide and ether oxide products via a 3 kcal/mol barrier (relative to reactants).

Given the limited basis set in the CCSD(T) analysis of Vereecken *et al.*²⁵ and the lack of any post-CCSD(T) corrections, one expects considerable uncertainties in their predicted energies; indeed errors of 2-3 kcal/mol would not be unexpected. The predicted kinetics is expected to be quite sensitive to the barrier heights for the submerged channels. The relatively small size of this reaction system permits the application of considerably higher levels of electronic structure theory. Thus, we have repeated the PES exploration at the ANL0-B2F level of theory, where 2σ uncertainties of about 0.2 to 0.3 kcal/mol are generally expected^{26,27}. This level of theory couples CCSD(T)-F12b/CBS(cc-pvTZ-F12,cc-pVQZ-F12)//B2PLYPD3/cc-pVTZ evaluations with CCSDT(Q)/cc-pVDZ corrections for higher order excitations, CCSD(T)/CBS(cc-pcVTZ,cc-pcVQZ) core-valence corrections, B2PLYP-D3/cc-pVTZ anharmonicity corrections (from second order vibrational perturbation theory), and CCSD(T)/aug-cc-pCVTZ-dk relativistic corrections. One-dimensional hindered rotor mappings were performed at the B2PLYP-D3/cc-pVTZ level. The corresponding energies are reported in Table S4, and a corresponding schematic diagram of the PES is provided in Figure S14. The structures and harmonic frequencies are provided in section 5.

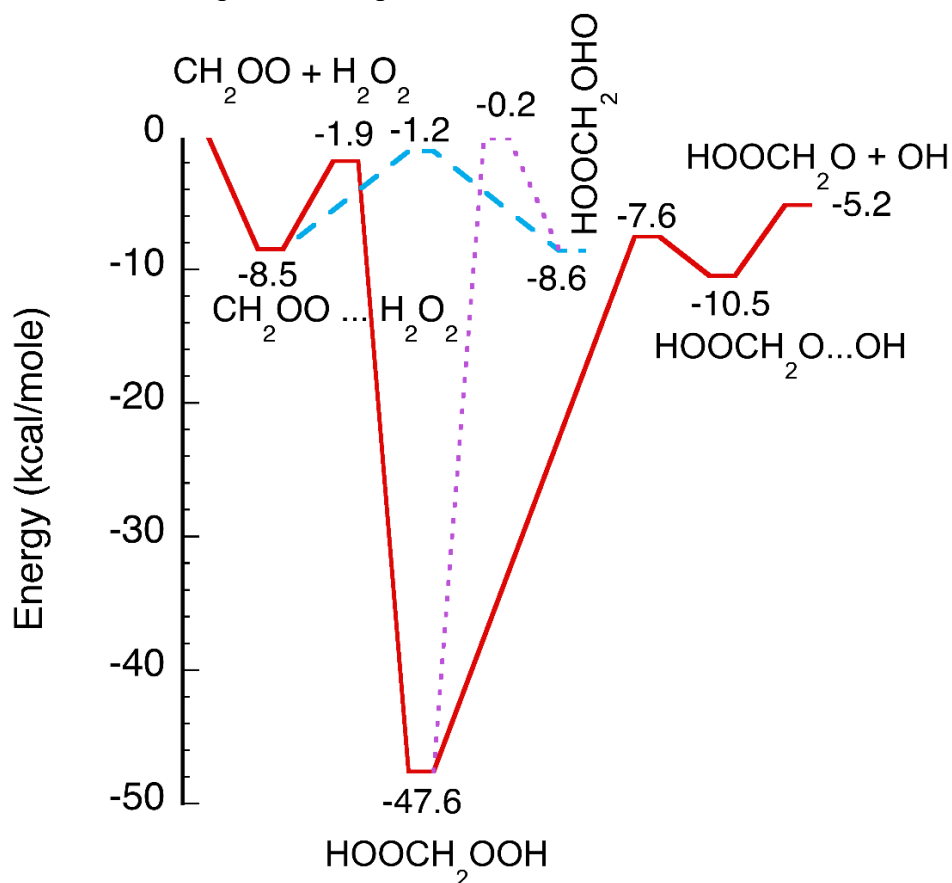


Fig. S14. Schematic diagram of the reaction path energies for the reaction of CH₂OO with H₂O₂ from the present ANL0-B2F calculations.

The barrier for OO fission from the chemical adduct occurs in a region where there are expected to be strong-multireference effects. Thus, our prediction of the energy for that barrier is based on CASPT2(2e,2o)/CBS//CASPT2/cc-pVTZ calculations. In particular, the location of the barrier on the singlet PES is first determined at the CASPT2/cc-pVTZ level (with two electrons in the two orbitals correlating with the radical orbitals of the fragments). The spin splitting between the singlet and triplet states at these barriers are then evaluated at the CASPT2/CBS//CASPT2/cc-pVTZ level, and the energy of the triplet state relative to separated OH + OCH₂OOH fragments is evaluated at the CCSD(T)-F12/cc-pVTZ-F12 level. Finally, the OH + OCH₂OOH energies are tied back to the reactant energies through ANL0-B2F estimates. These energies are also reported in Table S4.

Table S4. Stationary point energies (kcal/mol) for the reaction of CH₂OO with H₂O₂.

Stationary point	Conformer	CCSD(T)-F12			T(Q)		Core valence	Relativistic	Harmonic	Anharmonic	Total ^a	Ref. ³⁵
		DZF	TZF	QZF	CBS	DZ						
H ₂ O ₂ + CH ₂ OO		0	0	0	0	0	0	0	0	0	0	0
H ₂ O ₂ ...CH ₂ OO		-11.28	-11.39	-11.37	-11.36	1.01	0.01	0.02	1.97	-0.11	-8.48	-9.1
HOOCH ₂ OOH		-52.93	-52.97	-53.05	-53.09	1.39	0.10	0.07	3.79	0.09	-47.65	-49.7
HOOCH ₂ OHO		-13.96	-14.25	-14.36	-14.42	1.35	0.20	0.04	4.37	-0.18	-8.64	-6.2
H ₂ O ₂ ...CH ₂ OO=	a	-2.34	-2.54	-2.56	-2.58	0.51	0.23	-0.02	2.12	-0.35	-0.09	-1.8
HOOCH ₂ OOH	b	-2.20	-2.36	-2.38	-2.40	0.61	0.23	-0.01	1.10	-0.73	-1.20	-
	c	-2.73	-2.92	-2.94	-2.95	0.60	0.21	-0.01	1.06	-0.81	-1.90	-
H ₂ O ₂ ...CH ₂ OO=	a	-0.85	-1.08	-1.11	-1.13	0.86	0.28	-0.02	0.98	-0.63	0.34	-
HOOCH ₂ OHO	b	-1.70	-1.93	-1.98	-2.00	0.93	0.31	-0.02	1.40	-0.75	-0.13	-1.6
	c	-3.02	-3.23	-3.27	-3.30	0.88	0.29	-0.01	1.59	-0.61	-1.15	-
HOOCH ₂ OHO=	a	-0.98	-1.15	-1.19	-1.22	1.00	0.27	-0.02	1.56	-0.04	1.55	2.6
HOOCH ₂ OOH	b	-2.70	-2.87	-2.91	-2.94	0.97	0.26	-0.03	1.54	-0.04	-0.24	-
HOOCH ₂ OOH=		-	-	-	-	-	-	-	-	-	-7.56 ^b	-9.5
HOOCH ₂ O...OH		-	-	-	-	-	-	-	-	-	-	-
³ HOOCH ₂ O...OH		-12.90	-12.54	-12.31	-12.20	1.68	0.03	-0.01	0.25	-0.22	-10.48	-
HOOCH ₂ O+OH		-5.76	-5.34	-5.14	-5.03	1.76	0.05	-0.04	-1.83	0.01	-5.19	-

^aThe total energy is the sum of the CCSD(T)-F12/CBS energy, the CCSDT(Q)/cc-pVDZ, core-valence, relativistic, anharmonic, and harmonic ZPE corrections. For OH a spin orbit correction is also included.

^bThe energy for the OO fission transition state comes from CASPT2(2e,2o)/CBS // CASPT2/cc-pVTZ predictions of the singlet-triplet splitting of the TS energy, and a CCSD(T)-F12/CBS-F12 prediction of the triplet state energy at the TS relative to the energy of HOOCH₂O + OH.

Inspection of Table S4 indicates that the T(Q) correction for higher order excitations is quite significant, varying from 0.5 kcal/mol for the transition state for the formation of DHP all the way up to 1.8 kcal/mol for the OO fission products from the DHP. The consistent sign of this correction is due to the fact that higher-order excitations have their most significant effect on the CH₂OO reactant, where they have a stabilizing effect. Notably, the anharmonic corrections are also quite large, having a magnitude as large of 0.8 kcal/mol, but with the opposite sign of the T(Q) correction. The largest uncertainties in these calculations likely arise from the estimated harmonic zero-point energies for species such as CH₂OO, where multireference effects may have significant effects, and the anharmonic corrections, which are not always well determined with second-order vibrational perturbation theory. It is noteworthy that with the CCSD(T)-F12 method and cc-pVnZ-F12 basis sets there is very little basis set dependence beyond the cc-pVTZ-F12 basis set, and even the cc-pVDZ-F12 results are mostly converged to within 0.3 kcal/mol. This rapid convergence validates the use of the cc-pVTZ-F12 basis set in our analyses of the reaction of CH₂OO with HPMF.

The prior CCSD(T)/aug-cc-pVTZ//M062X/aug-cc-pVTZ theoretical predictions of Vereecken²⁵ are within expected accord with the present higher level analyses. In particular, the discrepancies range from -2.0 to 2.4 kcal/mol. We expect that the major source of these discrepancies is in the limitation to the aug-cc-pVTZ basis set. Notably, there is remarkably good, if somewhat accidental agreement (since the prior calculation is apparently for a higher energy geometry) for the key transition state corresponding to formation of the dihydroperoxide. Note that here we employed random sampling of all the torsional modes for both minima and transition states in order to determine the lowest energy conformers. This sampling yielded three separate first order saddlepoints for the transition state connecting H₂O₂...CH₂OO with HOOCH₂OOH as well as for that connecting it to HOOCH₂OH. For the transition state connecting HOOCH₂OOH to HOOCH₂OH eight conformers were discovered. Within the latter set, six of the conformers were higher in energy by 4 kcal/mol, and so were neglected in the kinetic analysis.

4.2.2 Theoretical kinetics.

The formation of the entrance vdW complex H₂O₂...CH₂OO and dissociation from HOOCH₂O...OH on to HOOCH₂ + OH are both barrierless processes. The overall rate coefficients and branching fractions are expected to be only weakly dependent on the rates for these processes. Instead, the tight transition state for proceeding from the vdW complex onwards, and for partial decomposition of the DHP are expected to be rate limiting. Thus, for simplicity, both these channels were treated with phase space theory normalized to a typical collision rate coefficient of $5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K.

The transition state for formation of the DHP from the H₂O₂...CH₂OO vdW complex provides the dominant bottleneck for the chemical conversions. Thus, we have included a variational treatment of this channel. This variational analysis was based on B2PLYP-D3/cc-pVTZ evaluations of the vibrational frequencies along the intrinsic reaction coordinate pathway. Higher level energies along the pathway were obtained from a combination of CCSD(T)-F12b/cc-pvQZ-F12 and CCSDT(Q)/cc-pVDZ evaluations. The latter corrections were included because a significant variation in the higher order corrections might be expected since the chemical bonding changes dramatically as the H₂O₂ inserts across the CH₂OO. However, this variation was found to be a negligible component of the reaction path energy variation near the saddle point. In the end, the overall variational effects on the rate coefficient were found to be minimal, *i.e.*, less than a few %.

The pressure and temperature dependence of the present predictions for the rate coefficient are illustrated in Extended Data Figures 4 and 5, respectively. These predictions are for He as a bath gas. The branching to the HOOCH_2OHO and exit channel wells are both very small (< 0.2 % for pressures below 1 bar in the 200 to 400 K temperature range) and so are not illustrated here. The branching to the bimolecular products $\text{HOOCH}_2 + \text{OH}$ is strongly pressure dependent. At atmospheric pressures, almost all the flux is stabilized prior to reaching those products. Interestingly, under some conditions, we even predict substantial stabilization of the van der Waals complex. For example, at room temperature and a pressure of 1 bar, 36 % of the reactive flux is predicted to stabilize in the $\text{H}_2\text{O}_2 \dots \text{CH}_2\text{OO}$ vdW complex. This vdW complex rapidly redissociates or isomerizes to other products (a total rate coefficient of $\sim 1 \times 10^7 \text{ s}^{-1}$). Thus, for comparison with experiment we calculate effective rate coefficient for the other products corresponding to the sum of their direct rate coefficients plus the contribution from the sequential process involving vdW stabilization followed by isomerization.

The predicted total effective rate coefficient, $2.9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, is in excellent agreement with the present experimentally measured value of $(2.2 \pm 0.9) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for 40 Torr He, 300 K. Nevertheless, it is still worth noting that there is considerable uncertainty in the present predictions. For example, raising the barrier from $\text{H}_2\text{O}_2 \dots \text{CH}_2\text{OO}$ to HOOCH_2OOH by 0.3 kcal/mol (its estimated uncertainty) decreases the predicted rate coefficient by a factor of 1.5, and one might expect similar uncertainties in the predicted partition function ratio. The total rate coefficient is predicted to be only weakly dependent on pressure, and so uncertainty in the energy transfer parameters are not expected to significantly affect the predicted total rate coefficient. This weak dependence on pressure stems from the fact that the barrier for chemical adduct formation is significantly submerged.

For Ar as a bath gas at 1 bar, our effective total rate coefficient for loss of CH_2OO is well represented by the expression $1.27 \times 10^{-18} T^{1.47} \exp(1236/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Notably, our predicted total rate coefficient is remarkably consistent with that estimated by Vereecken²⁵ ($1.3 \times 10^{-14} \exp(900/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which equates to $2.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, whereas we predict $3.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). However, Vereecken predicts a substantial production of ether oxide (28%) at 300 K, whereas we predict only 0.3 % for Ar bath gas at 298 K and 1 bar. This difference likely arises from the fact that Vereecken is reporting only the flux that reaches that channel, whereas our master equation analysis considers the probability that the ether oxide (HOOCH_2OHO) is stabilized. The shallowness of the HOOCH_2OHO well essentially precludes that stabilization.

4.3 CH₂OO + HPMF.

4.3.1 Potential energy surface.

The reaction of CH₂OO with hydroperoxymethylformate (HPMF) occurs through first the formation of a long-range hydrogen bonded vdW complex. From that vdW complex, there are three separate chemical transformations that can occur over saddle points that are submerged with respect to reactants. These processes involve (i) secondary ozonide formation (SOZ) through concerted formation of two CO bonds to form an OCH₂OOCH ring with an OCHOOH substituent, (ii) formation of the HOOCH₂OOCH₂OCHO keto-hydroperoxide through an OH insertion reaction across the CI (involving the OH component of the OOH group of HPMF), and (iii) formation of the ether oxide through an insertion involving the full OOH group of HPMF. The lowest energy saddle point structures for each of these species are also illustrated in Figure S15.

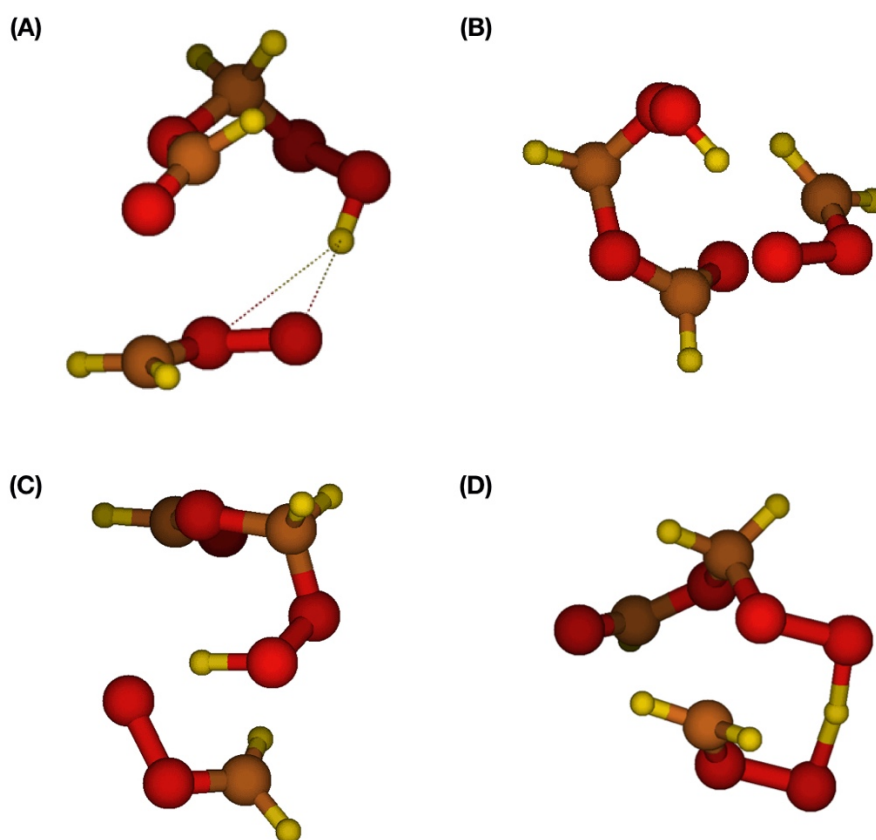


Fig. S15. Schematic depiction of the structures for: (A) the vdW complex, (B) the TS to the SOZ, (C) the TS to form the hydroperoxide adduct (HOOCH₂OOCH₂OCHO) and (D) the TS to form the ether oxide (HOOCH₂O(O)CH₂OCHO). The yellow atoms denote H atoms, the brown atoms denote C atoms, and the red atoms denote O atoms.

We explored the PES for these channels and their subsequent decay channels at the CCSD(T)-F12/cc-pVTZ-F12//B2PLYP-D3/cc-pVTZ level (*cf.* Table S5). The corresponding schematic reaction path diagram is provided in Fig. S16. The calculations reported above for the reaction of CH₂OO + H₂O₂ and related unreported calculations for the SOZ formation in H₂CO reacting with CH₂OO were used to obtain approximate corrections to the more limited *ab initio*

treatment employed for this system. In particular, the difference between the high- and low-level treatments for the smaller systems yields estimated corrections of 0.84, 0.94, 0.15, 0.44, and 1.38 kcal/mol for the entrance vdW complex, the transition states for forming the SOZ, the hydroperoxide, and the chemical adducts, respectively. Notably, each of these corrections increases the barrier height and thus decreases the predicted rate coefficient.

Table S5. Stationary point energies (kcal/mol) for the reaction of CH₂OO with HPMF.

Stationary point	B2PLYP-D3 cc-pVTZ	CCSD(T)-F12 cc-pVDZ-F12	CCSD(T)-F12 cc-pVTZ-F12	E ₀	Total ^a
HPMF + CH ₂ OO	0	0	0	0	0
HPMF...CH ₂ OO	-13.6	-12.7	-12.9	1.3	-10.6
SOZ	-40.9	-44.5	-44.8	5.0	-38.4
HOOCH ₂ OOCH ₂ OCHO	-56.0	-56.3	-56.3	3.9	-51.0
HOOCH ₂ O(O)CH ₂ OCHO	-11.7	-12.8	-13.0	4.4	-7.3
³ Diradical	-9.6	-9.5	-	1.2	-6.8
Diradical	-	-	-	-	-6.8 ^a
HOOCH ₂ OC(O)CH ₂ OH	-113.1	-115.8	-116.0	4.0	-110.6
HOOCH ₂ OCH(OH)OCHO	-105.0	-107.8	-107.9	3.5	-103.1
HPMF...CH ₂ OO = SOZ	-10.6	-9.3	-9.6	2.6	-6.0
HPMF...CH ₂ OO = HOOCH ₂ OOCH ₂ OCHO	-5.0	-3.0	-3.1	0.0	-3.0
HPMF...CH ₂ OO = HOCH ₂ O(O)CH ₂ OCHO	-4.1	-2.9	-3.1	-0.2	-2.8
SOZ = Diradical	-	-	-	-	-2.4 ^b
Diradical = HOOCH ₂ OC(O)CH ₂ OH	-	-	-	-	-3.2 ^b
Diradical = HOOCH ₂ OCH(OH)OCHO	-	-	-	-	1.3 ^b
HOOCH ₂ O + OCH ₂ OCHO	-13.3	-11.5	-11.0	-2.2	-11.8
OH + OCH ₂ OC(O)OCHO	-74.1	-75.1	-74.8	-1.5	-74.8
OH + OCH ₂ OCH(OH)OCHO	-61.3	-62.6	-62.2	-2.5	-63.4

^a The total energy is the sum of the CCSD(T)-F12/cc-pVTZ-F12/B2PLYP-D3/cc-pVTZ electronic energy, the B2PLYP-D3/cc-pVTZ ZPE correction, and the *ad hoc* correction for higher order effects. For OH a spin orbit correction is also included.

^b These states involve significant multireference character. Correspondingly the energies are from CASPT2(2e,2o)/cc-pVTZ predictions of the energies relative to the triplet diradical state, which are then added to the CCSD(T)-F12/cc-pVTZ-F12/B2PLYP-D3/cc-pVTZ based total energy for the triplet diradical state.

Monte Carlo based torsional sampling schemes were again employed in locating the torsional minima for the three key saddle points connecting the entrance vdW complex to the chemical adducts. For the connection to the SOZ, which is the lowest barrier process from the vdW complex, we found 6 separate first order saddle points, with all of them submerged relative to reactants. For the connection to the hydroperoxide adduct (HOOCH₂OOCH₂OCHO) we found 28 saddle points, with 16 of them submerged relative to reactants. Finally, for the connection to the ether oxide adduct [HOOCH₂O(O)CH₂OCHO] we found 9 saddle points, with all of them submerged relative to reactants. For simplicity, we report only the properties for the lowest

Monte Carlo torsional sampling was also employed in the determination of the lowest energy configurations for the chemical adducts. In this instance, a preliminary sampling was performed at the ω B97-XD/6-31+G(d) level and then only the lowest energy configuration was further evaluated at the B2PLYP-D3 and CCSD(T)-F12 levels. This more restricted exploration was deemed appropriate given the reduced importance of these stationary points in the kinetic evaluations. For each of these chemical adducts, one-dimensional hindered rotor mappings were performed at the ω B97-XD/6-31+G(d) level.

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4.3.2 Theoretical kinetics.

As illustrated in Figure S16, all three transformations from the entrance vdW complex have a submerged barrier and so might be expected to play an important role in the kinetics. We have formulated a master equation representation that includes all the processes illustrated in Figure S16.

For the entrance channel we performed variable reaction coordinate transition state theory (VRC-TST)^{28,29} calculations with a center-of-mass separation distance as the reaction coordinate. The interaction energies were evaluated with direct ω B97-XD/6-31+G(d) evaluations. A dynamical correction factor of 0.85 is applied to account for the typical overprediction of VRC-TST calculations. At 300 K the high-pressure recombination to the vdW complex was predicted to have a rate coefficient of $3.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In the atmospheric temperature regime, the bottlenecks from the vdW complex on to the chemical adduct are already much more rate limiting, and so there is little dependence of the overall rate predictions on this addition rate for atmospheric conditions.

We also explored the importance of variational effects for the three bottlenecks connecting the vdW complex to the chemical adducts. These VTST calculations were based on RRHO analyses along the ω B97-XD/6-31+G(d) minimum energy path. The variational corrections to the overall rate coefficient and the branching to significant channels ($> 1\%$) were predicted to be 15% or less. These corrections were deemed to be less than other expected uncertainties in the calculations. Furthermore, it is difficult to include a proper coupling of variational and torsional effects. Thus, variational corrections were ignored in the final analysis.

The bimolecular exit channels to $\text{OH} + \text{OCH}_2\text{OC}(\text{O})\text{OCHO}$ and to $\text{OH} + \text{OCH}_2\text{OCH}(\text{OH})\text{OCHO}$ are each exothermic by more than 60 kcal/mol. Thus, we simply presume that there is no stabilization of their adducts. Exploratory calculations validated that perspective. We used an ad hoc phase space theory model to treat the dissociation of the $\text{HOOCH}_2\text{OOCH}_2\text{OCHO}$ complex into $\text{HOOCH}_2\text{O} + \text{OCH}_2\text{OCHO}$. In this model, the attractive potential was adjusted to yield a high-pressure recombination rate coefficient of $4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K, which is our best estimate of what the rate for that process would be. At 300 K and 1 atm we predict less than 1% stabilization of the flux that reaches the $\text{HOOCH}_2\text{OOCH}_2\text{OCHO}$, and so our results for significant branching channels are essentially independent of the presumed rate.

The effect of the multitude of different first order saddle point conformers was incorporated through a direct sum over RRHO contributions for each of them. For the chemical adducts, we instead incorporated one-dimensional hindered rotor treatments since their available energies are sufficient to invalidate such RRHO based treatments.

As illustrated in Extended Data Figure 6, the present master equation simulations indicate that the total rate coefficient is nearly pressure independent and increases gradually with decreasing temperature. Interestingly, they again suggest significant stabilization of the pre-reactive vdW complex under atmospheric conditions. However, this vdW complex is predicted to decompose through redissociation and/or isomerization with a large rate coefficient of $\sim 1 \times 10^7 \text{ s}^{-1}$. Thus, it is best to focus on the effective rate coefficients given by the sum of the direct rate coefficients to the given products and the product of the direct rate coefficient to the vdW complex with the branching of the vdW complex decomposition to the given products.

The temperature dependence of the effective rate coefficient is illustrated in Extended Data Figure 7 for a pressure of 1 bar. The reaction is seen to be quite rapid with the SOZ as the dominant product for 330 K and lower. There is also significant branching to the $\text{HOOCH}_2\text{O} + \text{OCH}_2\text{OCHO}$ products arising from the decomposition of the hydroperoxide adduct

($\text{HOOCH}_2\text{OOCH}_2\text{OCHO}$). The increasing importance of the $\text{HOOCH}_2\text{O} + \text{OCH}_2\text{OCHO}$ product channel with increasing temperature is indicative of the low entropy/tight nature of the ring forming transition state that leads to the SOZ complex. The branching to the remaining channels not illustrated here is predicted to be less than 1% for all the conditions considered here. Although not illustrated here, it is interesting that the preliminary stabilization of the HPMF...CI vdW complex modestly enhances the production of the SOZ, because it has the lowest barrier for the vdW decomposition.

Over the 200 to 400 K temperature range, the present predictions for the effective rate coefficients at 1 bar pressure to form the SOZ and the $\text{HOOCH}_2\text{O} + \text{OCH}_2\text{OCHO}$ products are well reproduced by the modified Arrhenius expressions $6.28 \times 10^{13} \text{ T}^{-9.96} \exp(-572/\text{T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $1.28 \times 10^{-8} \text{ T}^{-1.75} \exp(219/\text{T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. At 300 K these rate coefficients are 2.0×10^{-12} and $1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively.

4.4 $\text{CH}_2\text{OO} + \text{t-BuOOH}$.

4.4.1 Potential energy surface.

The reaction of CH_2OO with $(\text{CH}_3)_3\text{COOH}$ (t-BuOOH) should be reasonably representative of the reaction of CH_2OO with larger hydroperoxides such as the SOZ arising from the reaction of CH_2OO with HPMF. Furthermore, the present experimental measurements of the rate coefficient for this reaction provide further validation of the present theoretical kinetic procedures. Thus, we have undertaken detailed theoretical explorations of this reaction. The focus of this analysis is an exploration of the potential energy surface for forming hydroperoxide, $[(\text{CH}_3)_3\text{COOCH}_2\text{OOH}; \text{tBuOOCH}_2\text{OOH}]$ and ether oxide $[(\text{CH}_3)_3\text{CO}(\text{O})\text{CH}_2\text{OOH}; \text{tBuO}(\text{O})\text{CH}_2\text{OOH}]$ complexes at the CCSD(T)-F12/cc-pVTZ-F12//B2PLYP-D3/cc-pVTZ level. Preliminary PES mappings were again performed at the $\omega\text{B97-XD/6-31+G(d)}$ level.

Higher level ANL0-B2F calculations for the related reaction of CH_3OOH with CH_2OO (performed as described for the $\text{CH}_2\text{OO} + \text{H}_2\text{O}_2$ reaction) were used to correct for the limitations in the CCSD(T)-F12/cc-pVTZ-F12//B2PLYP-D3/cc-pVTZ energy scheme. In particular, the $\text{CH}_2\text{OO} + \text{t-BuOOH}$ saddle point and van der Waals energies are corrected by the difference between the high-level energies and the CCSD(T)-F12/cc-pVTZ-F12//B2PLYP-D3/cc-pVTZ energies for the corresponding $\text{CH}_2\text{OO} + \text{CH}_3\text{OOH}$ stationary point energy. This correction amounts to 0.24, 0.03, and 0.50, and kcal/mol for the van der Waals complex, and the saddle points for forming $\text{tBuOOCH}_2\text{OOH}$ and $\text{tBuO}(\text{O})\text{CH}_2\text{OOH}$, respectively.

For the entrance van der Waals complex we optimized the geometry for about 200 randomly sampled orientations of the two reactants, but with the initial structures of the two reactants set to that of their lowest conformations. This preliminary sampling, which was performed at the $\omega\text{B97-XD/6-31+G(d)}$ level, yielded a remarkably large set of 22 unique minima for the van der Waals complex with interaction energies ranging from -12.3 to -2.6 kcal/mol at the B2PLYP-D3/cc-pVTZ// $\omega\text{B97-XD/6-31+G(d)}$ level.

For the two saddle points (for formation of either a hydroperoxide or an ether oxide), we also optimized the geometry for a set of randomly sampled torsional conformations. This sampling yielded 3 distinct saddle point confirmations for both the hydroperoxide and ether oxide forming cases, respectively. For the two chemical complexes, we simply employ the energies for the structures arising from a minimum energy path analysis beginning at the lowest energy saddle point.

The resulting energetic predictions are reported in Table S6 and a corresponding schematic reaction path diagram is provided in Fig. S17. For simplicity, for the van der Waals complex we report only the energy of the minimum energy complex, although all complexes are included in the kinetic evaluations. Notably, the saddle points for formation of the hydroperoxide and ether oxide complexes are both submerged by more than 3 kcal/mol relative to the reactant energy. Thus, one expects this reaction to be quite rapid.

Table S6. Stationary point energies (kcal/mol) for the reaction of CH₂OO with (CH₃)₃COOH (t-BuOOH).

Stationary point	B2PLYP-D3 cc-pVTZ	CCSD(T)-F12 cc-pVDZ-F12	CCSD(T)-F12 cc-pVTZ-F12	E0	Total ^a
t-BuOOH + CH ₂ OO	0	0	0	0	0
t-BuOOH...CH ₂ OO	-13.4	-12.1	-12.2	1.7	-10.2
tBuOOCH ₂ OOH	-53.9	-54.1	-54.1	3.7	-50.3
tBuO(O)CH ₂ OOH	-17.0	-17.0	-17.3	4.1	-13.2
t-BuOOH...CH ₂ OO =	-6.6	-4.3	-4.5	1.1	-3.4
tBuOOCH ₂ OOH; geom a					
t-BuOOH...CH ₂ OO =	-6.3	-4.0	-4.1	1.0	-3.1
tBuOOCH ₂ OOH; geom b					
t-BuOOH...CH ₂ OO =	-6.2	-4.0	-4.2	1.3	-2.9
tBuOOCH ₂ OOH; geom c					
t-BuOOH...CH ₂ OO =	-8.5	-6.6	-6.8	1.7	-4.6
tBuO(O)CH ₂ OOH; geom a					
t-BuOOH...CH ₂ OO =	-7.1	-5.2	-5.4	1.4	-3.4
tBuO(O)CH ₂ OOH; geom b					
t-BuOOH ...CH ₂ OO =	-6.7	-4.4	-4.6	0.9	-3.2
tBuO(O)CH ₂ OOH; geom c					

^aThe total energy is the sum of the CCSD(T)-F12/cc-pVTZ-F12//B2PLYP-D3/cc-pVTZ electronic energy, the B2PLYP-D3/cc-pVTZ ZPE correction, and the ad hoc correction for higher order effects.

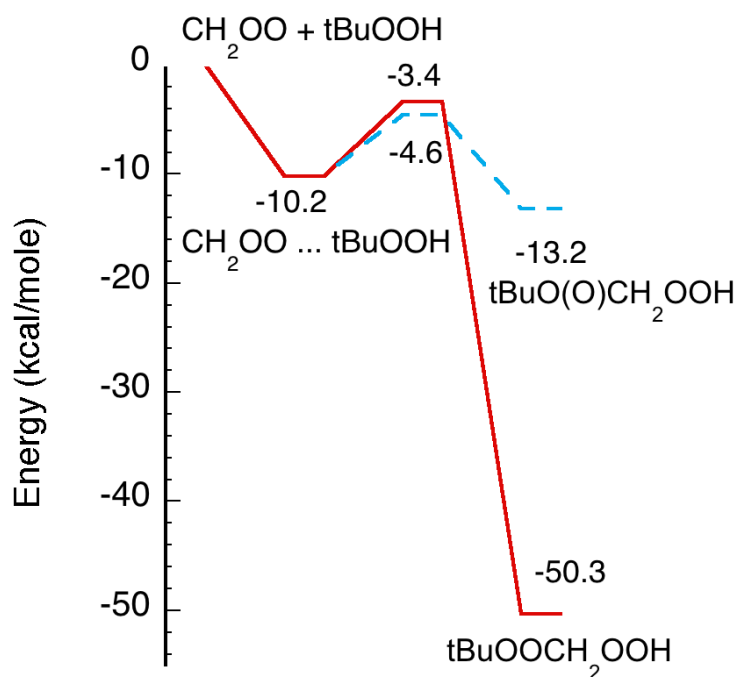


Fig. S17. Schematic diagram of the reaction path energies for the reaction of CH₂OO with t-BuOOH ((CH₃)₃COOH). The energies are from the present high-level corrected CCSD(T)-F12/cc-pVDZ-F12//B2PLYP-D3/cc-pVTZ calculations.

It is interesting to contrast the stationary point energies across the chemically similar series of insertions from H₂O₂ to CH₃OOH and finally t-BuOOH. Generally, the interactions become increasingly more attractive across this series. The van der Waals well energy decreases from -8.5 to -9.5 to -10.2 kcal/mol, the barrier to formation of the hydroperoxide decreases from -1.9 to -2.3 to -3.4 kcal/mol, while the barrier to formation of the ether oxide varies from -1.2 to -5.0 to -4.6 kcal/mol. Similarly, the well depths in the chemical complexes arising from the reaction with t-BuOOH are about 2 kcal/mol more stable than those arising from the reaction with H₂O₂. Some part of this increased attractiveness may simply be indicative of the increased dispersion interactions for larger molecules. It is perhaps worth noting that these increased well depths do not directly correlate with increased rate coefficients across the series as the steric effects are also changing, with the larger reactants having more sterically hindered transition states.

4.4.2 Theoretical kinetics.

The rate coefficients were predicted with *ab initio* transition state theory based master equation calculations incorporating the above described *ab initio* determined properties for the stationary points on the PES.

The partition functions and state densities were generally evaluated with a combination of one-dimensional hindered rotor treatments for the torsional modes and RRHO based analyses for the remaining modes. The hindered-rotor parameters are based on B2PLYP-D3/cc-pVTZ evaluations. For the vdW complex and the transition states, we included sums over each of the minima and first order saddle point structures as appropriate. For the chemical adducts, RRHO only treatments (i.e., with no consideration of hindered rotor effects) were deemed sufficient because (i) the tBuOOCH₂OOH is so strongly bound that all flux that reaches it is stabilized, and (ii) the tBuO(O)CH₂OOH adduct is so weakly bound that it is only rarely stabilized.

The formation of the entrance vdW complex t-BuOOH...CH₂OO is a barrierless process. Under atmospherically relevant conditions, the overall rate coefficient and branching fractions are only weakly dependent on the capture rate for formation of the vdW complex. Instead, the tight transition states for proceeding from the vdW complex onwards, are generally rate limiting. Thus, for simplicity, this channel was treated with phase space theory normalized to a typical collision rate coefficient of $5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K.

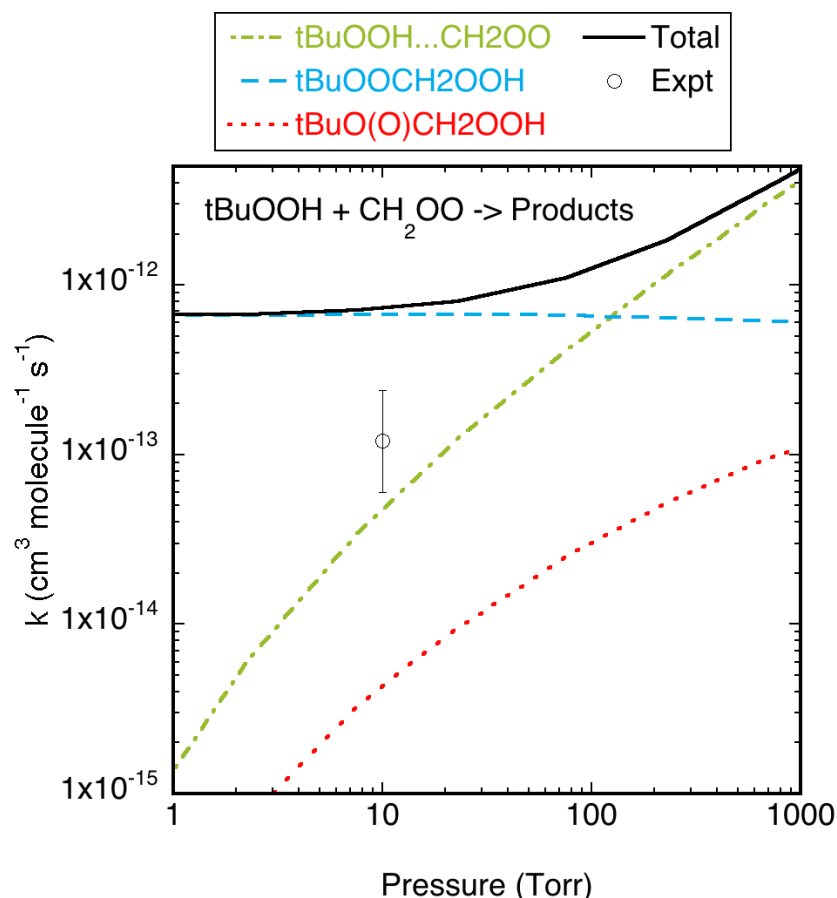


Fig. S18. Plot of the pressure dependence of the theoretically predicted rate coefficients for the reaction of CH_2OO with t-BuOOH . The rates were calculated for room temperature in He bath gas. The symbol denotes the experimental data from the present study.

The pressure and temperature dependence of the present predictions for the rate coefficients are illustrated in Figs. S18 and S19, respectively. These predictions are for He as a bath gas. Under low temperature and high pressure conditions, we again predict substantial stabilization of the van der Waals complex. This vdW complex again rapidly redissociates or isomerizes on to the chemical adducts. Thus, we also calculate effective rate coefficients for the formation of the chemical adducts corresponding to the sum of their direct rate coefficients plus the contribution from the sequential process involving vdW stabilization and then isomerization.

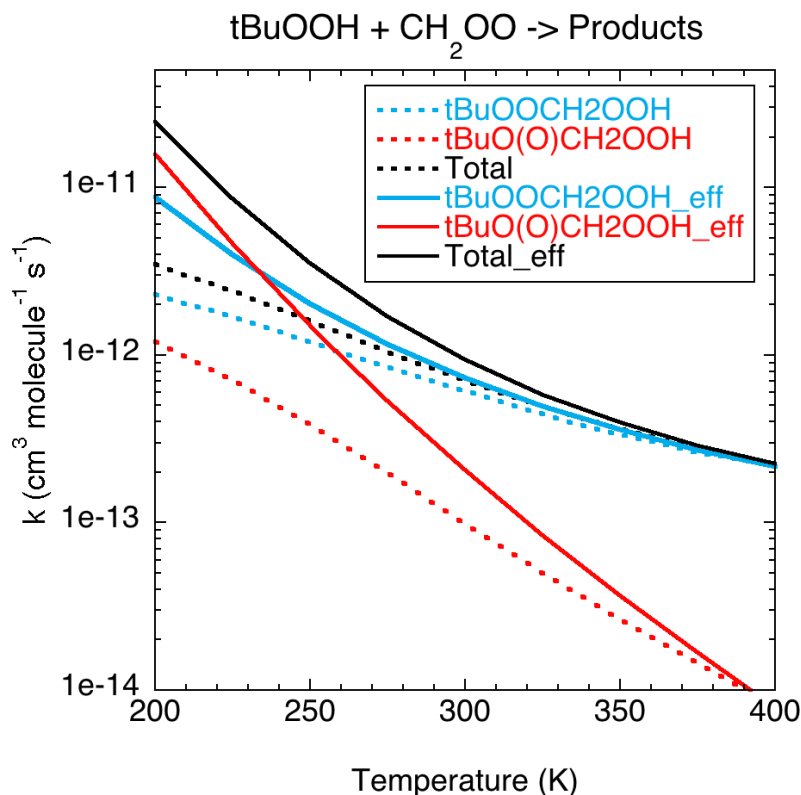


Fig. S19. Plot of the temperature dependence of the theoretically predicted rate coefficients for the reaction of CH_2OO with t-BuOOH . The rates were calculated for 1 Bar of Ar. The lines are labelled according to their products, with the eff label corresponding to the effective rate coefficient obtained by summing the direct contributions with the contributions from the rapid decay of the initially formed $\text{CH}_2\text{OO} \dots \text{t-BuOOH}$ van der Waals complex. The total rate coefficients is the sum of the rate coefficients for forming $\text{tBuOOCH}_2\text{OOH}$ and $\text{tBuO(O)CH}_2\text{OOH}$.

The predicted total effective rate coefficient is a factor of 6 greater than the present experimentally measured value of $(1.2^{+1.2}_{-0.6}) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (10 Torr of He, 300 K), and a factor of 3 greater than the estimated experimental upper limit. Raising the barrier by 0.9 kcal/mol would bring the theoretical prediction into agree with experiment. However, such an error in the barrier height is somewhat greater than the 0.5 kcal/mol that we would estimate as the uncertainty in this quantity. Of course, there are other possible shortcomings in the calculations, such as the neglect of variational effects, and inaccurate partition function evaluations, which may explain the remaining discrepancies. Notably, the total effective rate coefficients is again predicted to be only weakly dependent on pressure, and so uncertainty in the energy transfer parameters are not expected to significantly affect the comparison with the present experiment. This weak dependence on pressure again arises from the fact that the barrier for chemical adduct formation is significantly submerged.

At 1 bar of Ar, which we take as a surrogate for N_2 , the theoretically predicted effective rate coefficients for forming $\text{tBuOOCH}_2\text{OOH}$ and $\text{tBuO(O)CH}_2\text{OOH}$ are well represented over the 200 to 400 K temperature range by the expressions, $2.13 \times 10^{-14} T^{-0.212} \exp(1426/T)$ and $3.88 \times 10^{-23} T^{-14.20} \exp(-802/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively.

4.5 CH₂OO + SOZ.

4.5.1 Potential energy surface.

The reaction of CH₂OO with the SOZ arising from the reaction of HPMF with CH₂OO should be representative of the sequential insertion scheme. Unfortunately, due to the relatively large size of the SOZ, only more limited PES explorations and kinetics estimates were feasible. The primary goal of these explorations is to determine the feasibility of further CH₂OO additions. To this end we searched for low energy submerged barriers leading to the formation of chemical adducts. In particular, since this SOZ has a terminal OOH group that should react with CH₂OO in much the same way that H₂O₂ does, we have searched for analogues of the hydroperoxide and ether oxide forming channels. The reaction of CH₂OO with the t-BuOOH provides an even better analogy for these pathways. Notably, the analog of the hydroperoxide forming channel would lead to an effective oligomerization route since each new product would have a new OOH group to interact with the next CH₂OO molecule.

Of necessity, these explorations were based on much more modest electronic structure calculations. In particular, the properties of the saddle points were determined at the B2PLYP-D3/cc-pVTZ// ω B97-XD/6-31+G(d) level. The higher-level analyses for the H₂O₂ + CH₂OO and CH₃OOH + CH₂OO reactions provide a useful validation/correction scheme for these more limited calculations. In particular, high level estimates for the saddle point energies are obtained from the difference between the high-level energies and the corresponding B2PLYP-D3/cc-pVTZ energy for the smaller systems. We again employed ω B97-XD/6-31+G(d) based Monte Carlo torsional samplings in order to facilitate the search for the lowest energy saddle point conformations. The results of this analysis are reported in Table S6.

For the entrance SOZ...CH₂OO van der Waals complex we optimized the geometry for a set of 300 randomly sampled orientations of the two reactants, but with the initial structures of the two reactants set to that of their lowest conformations. This yielded a remarkably large set of 47 unique minima for the van der Waals complexes with electronic interaction energies ranging from -12.3 to -2.6 kcal/mol at the ω B97-XD/6-31+G(d) level. Perhaps there are even more vdW minima arising from different torsional conformations of the reactants since these coordinates were not varied in the initial sampling.

For the two saddle points (for formation of either a hydroperoxide or an ether oxide), we also optimized the geometry for a set of randomly sampled torsional conformations. This sampling yielded 8 and 6 distinct saddlepoint conformations that were submerged with respect to the SOZ + CH₂OO reactants for the hydroperoxide and ether oxide forming cases, respectively. For the two chemical complexes, we simply report the energies for the structures arising from a minimum energy path analysis beginning at the lowest energy saddle point.

The predicted reaction path energies are reported in Table S7 and a schematic reaction path diagram is provided in Fig. S20. Importantly, the barrier for formation of the hydroperoxide chemical complex is significantly submerged (-1.8 kcal/mol) relative to reactants. Thus, the reaction to form the insertion product is expected to be reasonably rapid, and one can expect oligomerization through repeated addition of CH₂OO units to also be effective. The 9 kcal/mol well depth for the ground vdW complex, suggests there may be significant stabilization of that complex. Meanwhile, the similar energy shallow well for the ether oxide complex, together with the relatively high barrier to its formation, suggest that the formation of the hydroperoxide complex will dominate the kinetics

Table S7. Stationary point energies (kcal/mol) for the reaction of CH₂OO with the SOZ from the reaction of CH₂OO with HPMF.

Stationary point	B2PLYP-D3 cc-pVTZ	E ₀	Total	Total ^a (H ₂ O ₂ reference)	Total ^a (CH ₃ OOH reference)
SOZ + CH ₂ OO	0	0	0	0	
SOZ...CH ₂ OO	-12.0	1.3	-10.7	-8.4	-9.0
SOZ...CH ₂ OO = hydroperoxide	-4.6	0.2	-4.4	-1.7	-1.9
SOZ...CH ₂ OO = Ether oxide	-3.5	0.6	-2.9	-0.1	-0.8
hydroperoxide	-50.4	3.2	-47.1	-45.4	
Ether oxide	-11.6	3.5	-9.7	-8.6	

^a These columns refer to the final estimated energies arising from using either the CH₂OO + H₂O₂, or the CH₂OO + CH₃OOH calculations as references to generate the ad hoc corrections.

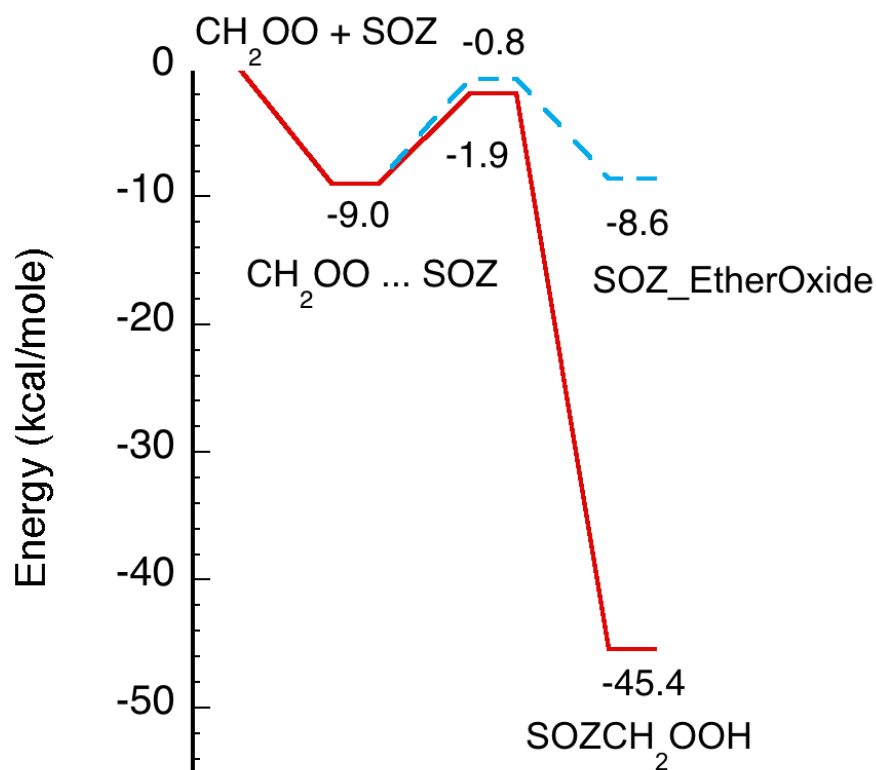


Fig. S20. Schematic diagram of the reaction path energies for the reaction of CH₂OO with the SOZ arising from the reaction of HPMF with CH₂OO. The energies are from high level corrected B2PLYP-D3/cc-pVTZ//ωB97-XD/6-31+G* calculations.

4.5.2 Theoretical kinetics.

The rate coefficients were predicted with *ab initio* transition state theory based master equation calculations incorporating the above described *ab initio* determined properties for the stationary points on the PES. The partition functions and state densities were evaluated through the sum of RRHO based energy levels. For the reactants, the vdW complex, and the saddle points each of the different conformers from the conformational sampling were included in these sums.

The formation of the entrance vdW complex $\text{SOZ}\dots\text{CH}_2\text{OO}$ is again a barrierless processes, with the chemical components of the overall rate coefficient and branching fractions only weakly dependent on the capture rate for formation of the vdW complex. Instead, the tight transition states for proceeding from the vdW complex onwards, are generally rate limiting. Thus, for simplicity, this channel was treated with phase space theory normalized to a typical collision rate coefficient of $8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K.

The rate calculations for this reaction are meant to be only qualitatively predictive due to the uncertainties in the reaction path energies, coupled with the limitation to RRHO based state counting procedures. However, multi-structural effects are adequately accounted for. Qualitatively, we expect prediction accuracies of about a factor of 5 to 10.

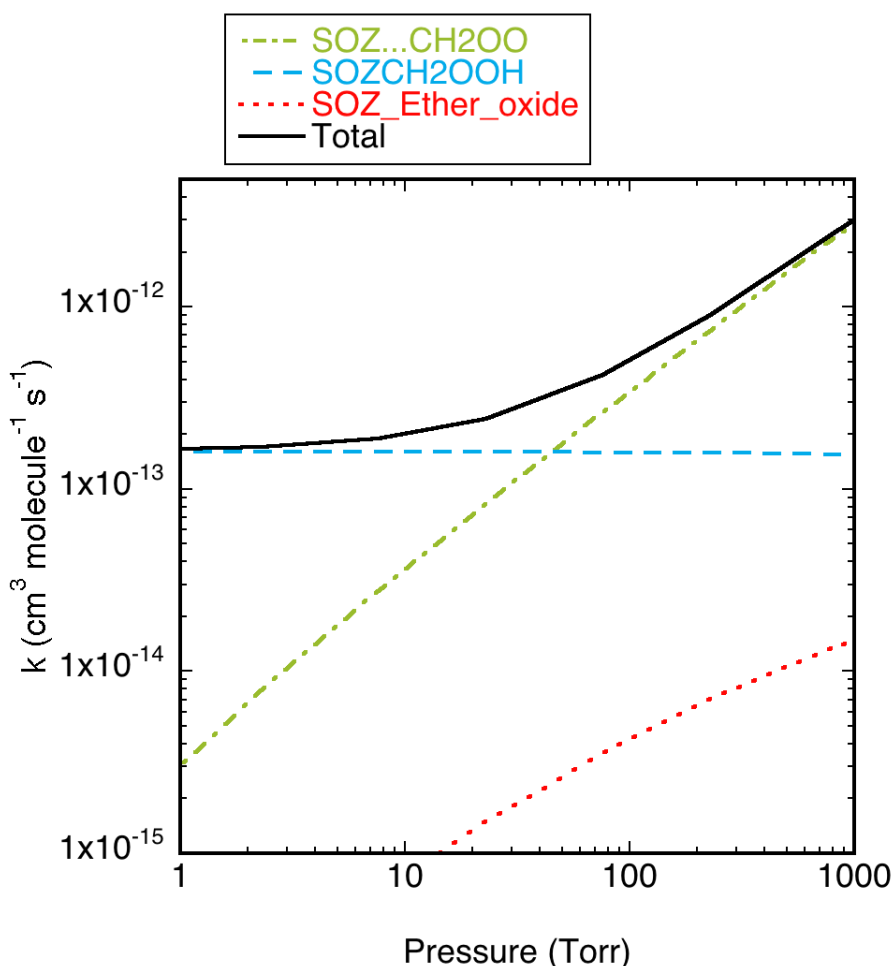


Fig. S21. Plot of the pressure dependence of the theoretically predicted rate coefficients for the reaction of CH_2OO with the SOZ arising from the reaction of HPMF with CH_2OO . The rates were calculated for room temperature in Ar as a surrogate for N_2 bath gas.

The pressure and temperature dependence of the present predictions for the rate coefficients are illustrated in Figs. S21 and S22, respectively. These predictions are for Ar as a bath gas. Notably, we predict significant stabilization of the vdW complexes, with this being the dominant channel by more than a factor of 10 at room temperature and 1 bar. The role of such vdW complexes in the aerosol formation process bears further consideration in future studies. For now, we note that this vdW complex rapidly redissociates or isomerizes on to the chemical

adducts. Thus, we also calculate effective rate coefficients for the formation of the chemical adducts corresponding to the sum of their direct rate coefficients plus the contribution from the sequential process involving vdW stabilization and then isomerization.

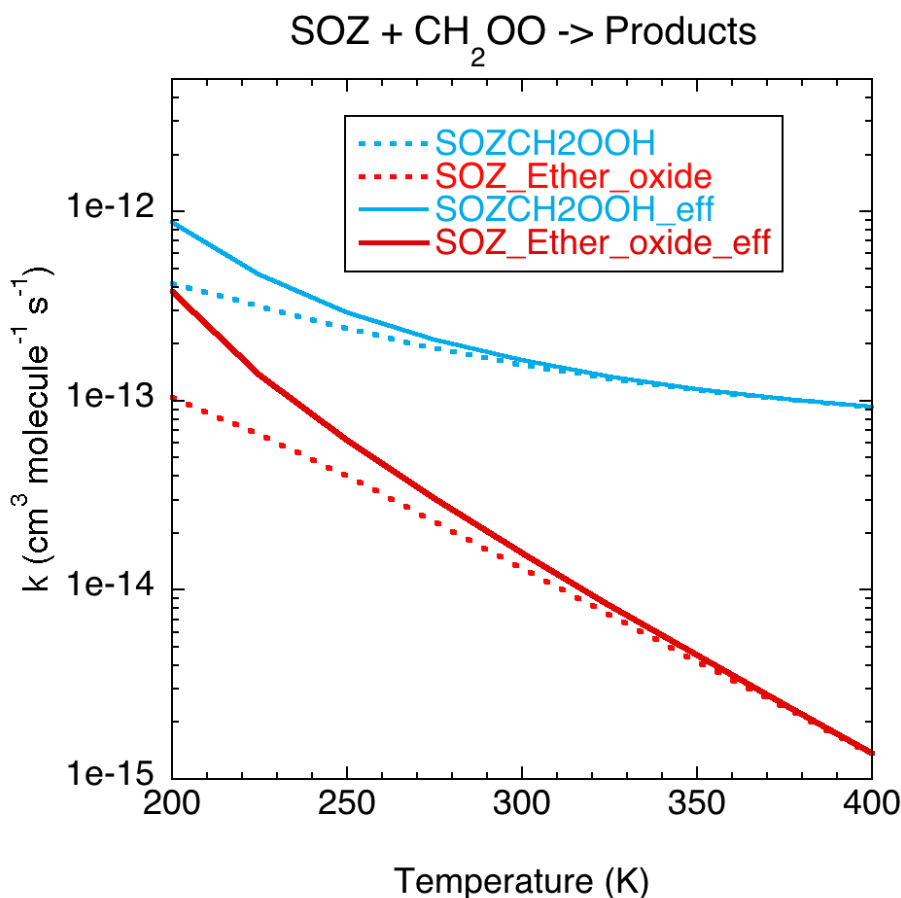


Fig. S22. Plot of the temperature dependence of the theoretically predicted rate coefficients for the reaction of CH₂OO with the SOZ arising from the reaction of HPMF with CH₂OO. The rates were calculated for 1 Bar of Ar. The lines are labelled according to their products, with the eff label corresponding to the effective rate coefficient obtained by summing the direct contributions with the contributions from the rapid decay of the initially formed CH₂OO...SOZ van der Waals complex. The total rate coefficient is the sum of the rate coefficients for forming the hydroperoxide and ether oxide complexes.

At 1 bar of Ar, which we take as a surrogate for N₂, the theoretically predicted effective rate coefficient for forming the SOZCH₂OOH hydroperoxide complex is well represented over the 200 to 400 K temperature range by the expression, $8.87 \times 10^{-25} T^{3.46} \exp(1851/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. At 300 K this equates to $2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Supplementary Note 5: Theoretical chemical structures and energies.

5.1 $\text{CH}_2\text{OO} + \text{H}_2\text{O}_2$.

All structures calculated at the B2PLYPD3/cc-pVTZ level of theory except where noted.

5.1.1 H_2O_2 .

1	8	0	0.000000	0.726449	-0.057254
2	8	0	0.000000	-0.726449	-0.057254
3	1	0	0.797838	0.892753	0.458032
4	1	0	-0.797838	-0.892753	0.458032
Frequencies --	369.4137		940.9154		1324.3449
Frequencies --	1440.1650		3795.2016		3796.2368

5.1.2 CH_2OO .

1	6	0	1.069953	-0.227482	0.000000
2	8	0	0.000000	0.456522	0.000000
3	8	0	-1.174418	-0.166744	0.000000
4	1	0	0.997707	-1.305395	0.000000
5	1	0	1.977920	0.352063	0.000000
Frequencies --	540.1900		673.2007		877.2132
Frequencies --	1006.2644		1252.7561		1349.5055
Frequencies --	1496.5409		3153.7273		3316.1734

5.1.3 $\text{H}_2\text{O}_2 \dots \text{CH}_2\text{OO}$.

1	6	0	1.137970	1.092785	0.066295
2	8	0	1.655571	-0.053362	0.116420
3	8	0	0.946967	-1.109961	-0.365794
4	1	0	0.149592	1.221364	-0.358380
5	1	0	1.758903	1.876050	0.474089
6	8	0	-1.461816	-0.472875	0.624579
7	8	0	-1.841602	0.528237	-0.356782
8	1	0	-0.635589	-0.832587	0.213162
9	1	0	-2.493689	0.042150	-0.874024
Frequencies --	76.1584		122.1091		162.3392
Frequencies --	195.2492		269.1973		274.8162
Frequencies --	542.4166		702.6280		891.5519
Frequencies --	916.4393		940.8564		1028.5626
Frequencies --	1270.4543		1350.2560		1401.5470
Frequencies --	1521.8508		1540.6635		3120.7083
Frequencies --	3284.6776		3295.9958		3798.0899

5.1.4 $H_2O_2 \dots CH_2OO = HOOCH_2OOH$.

Geometry a

1	6	0	-0.849900	1.050525	-0.014355
2	8	0	-1.109831	-0.053423	-0.572414
3	8	0	-0.934423	-1.118180	0.376681
4	1	0	-1.017893	1.172542	1.045804
5	1	0	-0.728636	1.894495	-0.680651
6	8	0	1.047562	0.391056	0.642945
7	8	0	1.671740	-0.227567	-0.507508
8	1	0	0.398842	-0.355454	0.902544
9	1	0	1.046710	-0.949826	-0.699199
Frequencies --	-269.8487		137.2042		192.8257
Frequencies --	289.8508		393.8461		436.9041
Frequencies --	539.8606		793.2157		834.9483
Frequencies --	929.1246		1065.0741		1128.1156
Frequencies --	1216.0098		1401.9443		1473.2170
Frequencies --	1558.0144		1604.9283		2756.5585
Frequencies --	3140.6219		3275.5724		3644.9910

Geometry b

1	6	0	-0.431111	1.047335	0.331606
2	8	0	-1.221049	0.338256	-0.370150
3	8	0	-1.159904	-1.046526	0.107131
4	1	0	-0.247339	0.740274	1.353881
5	1	0	-0.389763	2.090301	0.040941
6	8	0	1.247472	0.523131	-0.262573
7	8	0	1.273913	-0.920096	0.053645
8	1	0	1.941589	0.841189	0.335709
9	1	0	0.158729	-1.113897	0.055406
Frequencies --	-454.9737		83.2951		158.1917
Frequencies --	170.1933		364.2199		459.8037
Frequencies --	545.2504		809.1385		844.8436
Frequencies --	918.1356		1119.7824		1211.5834
Frequencies --	1286.7639		1363.3152		1415.0596
Frequencies --	1534.4517		1570.3632		2040.9141
Frequencies --	3138.5972		3272.3018		3795.1954

Geometry c

1	6	0	-0.080644	0.979920	0.328875
2	8	0	-1.120681	0.470150	-0.380741
3	8	0	-1.419288	-0.857620	0.137211
4	8	0	1.199337	0.516384	-0.241503
5	1	0	-0.107232	0.689353	1.376120
6	1	0	-0.056051	2.054752	0.161557
7	8	0	1.262772	-1.054957	-0.010779
8	1	0	1.820985	0.073325	0.479445
9	1	0	-0.550957	-1.288603	-0.023870
Frequencies --	-473.9415		116.1168		168.5038
Frequencies --	187.5297		359.6149		436.4622

Frequencies --	518.3566	818.3146	847.5301
Frequencies --	932.2582	1111.2363	1201.2485
Frequencies --	1235.5102	1364.2295	1415.7549
Frequencies --	1531.0280	1597.6042	2019.2658
Frequencies --	3133.6474	3269.9868	3808.8683

5.1.5 HOOCH_2OOH .

1	6	0	0.000000	0.000000	0.866250
2	8	0	0.000000	1.168437	0.091566
3	8	0	0.000000	-1.168437	0.091566
4	1	0	0.906152	0.064211	1.465432
5	1	0	-0.906152	-0.064211	1.465432
6	8	0	-1.338893	1.329420	-0.443822
7	8	0	1.338893	-1.329420	-0.443822
8	1	0	-1.289384	0.792638	-1.246134
9	1	0	1.289384	-0.792638	-1.246134
Frequencies --	107.1118		175.9806		203.8520
Frequencies --	266.3350		345.8548		521.9366
Frequencies --	659.6462		869.0593		878.2646
Frequencies --	1031.8771		1042.6147		1166.4609
Frequencies --	1313.5959		1375.1162		1390.6797
Frequencies --	1403.3640		1459.5066		3083.5154
Frequencies --	3158.2248		3763.8403		3766.8385

5.1.6 $\text{H}_2\text{O}_2 \dots \text{CH}_2\text{OO} = \text{HOOCH}_2\text{OHO}$.

Geometry a

1	6	0	-0.431111	1.047335	0.331606
2	8	0	-1.221049	0.338256	-0.370150
3	8	0	-1.159904	-1.046526	0.107131
4	1	0	-0.247339	0.740274	1.353881
5	1	0	-0.389763	2.090301	0.040941
6	8	0	1.247472	0.523131	-0.262573
7	8	0	1.273913	-0.920096	0.053645
8	1	0	1.941589	0.841189	0.335709
9	1	0	0.158729	-1.113897	0.055406
Frequencies --	-510.6457		50.6605		322.6876
Frequencies --	410.1794		476.4472		542.1277
Frequencies --	723.5130		820.6359		835.9811
Frequencies --	975.6375		1042.1889		1139.5512
Frequencies --	1227.9647		1244.4407		1275.2793
Frequencies --	1397.6821		1555.7603		1898.3967
Frequencies --	3117.7257		3241.3937		3721.2965

Geometry b

1	6	0	-0.514686	1.097659	0.084905
2	8	0	-1.137009	0.144763	-0.496904
3	8	0	-1.047964	-1.019088	0.405170

4	1	0	-0.605300	1.175446	1.162004
5	1	0	-0.416728	1.993984	-0.515188
6	8	0	1.231310	0.567851	0.111303
7	8	0	1.254417	-0.834882	-0.301871
8	1	0	1.480961	0.500293	1.045358
9	1	0	0.223153	-1.124824	0.056809
Frequencies --			-460.5833	105.7730	340.0923
Frequencies --			430.4705	500.9778	550.9116
Frequencies --			741.3030	815.7838	854.0933
Frequencies --			999.6367	1075.9065	1219.2579
Frequencies --			1247.5665	1284.8377	1309.4773
Frequencies --			1389.7465	1547.9105	1818.4265
Frequencies --			3115.0038	3233.9260	3728.3000

Geometry c

1	6	0	-0.466161	1.006682	0.387016
2	8	0	-1.246143	0.304699	-0.338771
3	8	0	-1.089787	-1.107079	0.029600
4	1	0	-0.231737	0.657488	1.384362
5	1	0	-0.482038	2.067969	0.166353
6	8	0	1.236692	0.600903	-0.176179
7	8	0	1.352756	-0.830410	0.134808
8	1	0	1.197923	0.588673	-1.146928
9	1	0	0.284681	-1.099125	0.078449
Frequencies --			-381.0517	105.6656	318.9024
Frequencies --			394.8533	477.2437	539.4754
Frequencies --			742.8612	814.2673	855.3586
Frequencies --			1011.4664	1128.5715	1201.0379
Frequencies --			1244.2219	1258.9987	1355.2750
Frequencies --			1458.4106	1579.7409	1895.9725
Frequencies --			3122.6601	3243.6479	3698.9048

5.1.7 $\text{HOOCCH}_2\text{OHO}$.

1	6	0	0.077929	0.982935	0.363536
2	8	0	1.101084	0.489548	-0.369822
3	8	0	-1.231351	0.437520	-0.113062
4	1	0	0.088839	0.683762	1.405758
5	1	0	0.015448	2.055435	0.192786
6	8	0	1.374030	-0.869086	0.090065
7	8	0	-1.213586	-1.048848	0.052262
8	1	0	0.436775	-1.228075	0.026220
9	1	0	-1.250057	0.518195	-1.081523
Frequencies --			152.6692	292.4647	357.9195
Frequencies --			440.3555	578.3570	711.4878
Frequencies --			813.9659	844.5859	877.6524
Frequencies --			927.9081	1103.6748	1156.9534
Frequencies --			1262.9943	1311.2403	1395.5444

Frequencies --	1473.8337	1642.8248	3048.0642
Frequencies --	3103.2130	3197.1339	3696.0084

5.1.8 $\text{HOOCH}_2\text{OHO} = \text{HOOCH}_2\text{OOH}$.

Geometry a

1	6	0	-0.080644	0.979920	0.328875
2	8	0	-1.120681	0.470150	-0.380741
3	8	0	-1.419288	-0.857620	0.137211
4	8	0	1.199337	0.516384	-0.241503
5	1	0	-0.107232	0.689353	1.376120
6	1	0	-0.056051	2.054752	0.161557
7	8	0	1.262772	-1.054957	-0.010779
8	1	0	1.820985	0.073325	0.479445
9	1	0	-0.550957	-1.288603	-0.023870
Frequencies --	-1311.1832	129.5209	253.3408		
Frequencies --	326.9796	447.5618	589.9637		
Frequencies --	633.0208	716.2869	854.4412		
Frequencies --	873.6412	975.2686	1126.6536		
Frequencies --	1191.1071	1303.4828	1405.7593		
Frequencies --	1468.8591	1541.4749	2861.7337		
Frequencies --	3085.7480	3168.2683	3473.3412		

Geometry b

1	6	0	0.057457	1.006436	0.310070
2	8	0	1.054885	0.459371	-0.442857
3	8	0	1.441223	-0.805905	0.163539
4	8	0	-1.266274	0.494486	-0.054678
5	1	0	-0.002203	2.066650	0.070411
6	1	0	0.168047	0.798777	1.370177
7	8	0	-1.210707	-1.086405	0.023554
8	1	0	-1.237835	-0.125355	-0.915200
9	1	0	0.574225	-1.271068	0.097727
Frequencies --	-1380.1657	162.8906	263.5237		
Frequencies --	332.2305	450.4723	577.9924		
Frequencies --	696.3939	723.9774	874.0148		
Frequencies --	880.0931	967.9237	1120.1405		
Frequencies --	1191.3634	1298.4840	1397.9400		
Frequencies --	1471.2976	1540.8219	2782.3759		
Frequencies --	3092.7281	3176.3236	3407.1404		

5.1.9 $\text{HOOCH}_2\text{OOH} = \text{HOOCH}_2\text{O...OH}$.

(CASPT2/cc-pVTZ structure and frequencies)

O	-0.2952249913	-0.0915031795	-2.2578353346
O	0.7217235750	-0.2240167155	-1.2403970319
C	0.2681631009	0.5228342382	-0.1480636515
O	-0.8077795043	0.0147832134	0.4959160777
O	0.1965090241	-0.1817177576	3.0754652003

H	-0.8147729930	-0.8869799648	-2.0782787209		
H	1.1168024144	0.5679344597	0.5421525947		
H	-0.0119815531	1.5382688246	-0.4592686933		
H	-0.5526304863	0.2086588164	2.5986587261		
Wavenumbers [cm-1]	62.92	73.45	157.56	249.69	288.36
Wavenumbers [cm-1]	320.81	407.16	630.38	836.66	898.44
Wavenumbers [cm-1]	1046.27	1096.90	1239.97	1373.51	1389.27
Wavenumbers [cm-1]	1393.00	3013.95	3095.13	3781.68	3790.92
Wavenumbers [cm-1]	128.70				

5.1.10 ³HOOCH₂O...OH.

1	8	0	-0.468741	-1.429232	-0.235809
2	6	0	-1.282840	-0.379338	0.005447
3	8	0	-0.694874	0.746246	0.587804
4	8	0	0.074644	1.407361	-0.449577
5	1	0	-1.757694	-0.122537	-0.955554
6	1	0	-2.071889	-0.691693	0.705128
7	1	0	0.963197	1.054031	-0.253992
8	8	0	2.226357	-0.349554	0.145307
9	1	0	1.464346	-0.962343	0.089934
Frequencies --	91.2494		148.4693		165.3592
Frequencies --	222.5950		348.8410		407.2295
Frequencies --	477.0707		606.2964		695.4122
Frequencies --	829.5191		889.1952		1021.6694
Frequencies --	1072.8779		1218.4688		1341.4098
Frequencies --	1362.4210		1466.2836		2941.5025
Frequencies --	2996.1221		3577.4540		3626.7255

5.1.11 HOOCH₂O.

1	8	0	1.370949	-0.646357	-0.144762
2	6	0	0.707313	0.454384	0.232549
3	8	0	-0.568672	0.634676	-0.335957
4	8	0	-1.411865	-0.412375	0.202047
5	1	0	0.635746	0.417764	1.332755
6	1	0	1.263014	1.359894	-0.049066
7	1	0	-1.265937	-1.111519	-0.449605
Frequencies --	158.7462		295.3539		387.0900
Frequencies --	624.0159		824.9089		881.7353
Frequencies --	1023.9340		1084.7758		1214.9852
Frequencies --	1347.9142		1367.5078		1387.1741
Frequencies --	2933.2577		3003.4012		3764.1084

5.1.12 OH.

1	8	0	0.000000	0.000000	0.107864
2	1	0	0.000000	0.000000	-0.862910
Frequencies --	3750.3682				

5.2 CH₂OO + HPMF.

All structures calculated at the B2PLYPD3/cc-pVTZ level of theory except where noted. The lowest energy conformers only are reported herein.

5.2.1 HPMF.

1	8	0	1.599683	-0.957059	0.107337
2	8	0	1.321601	0.341212	-0.473965
3	1	0	0.719080	-1.376065	0.034663
4	6	0	0.471282	1.045171	0.350670
5	1	0	0.536404	0.684720	1.373500
6	1	0	0.720520	2.096772	0.258103
7	8	0	-0.926253	1.014569	-0.074920
8	6	0	-1.564268	-0.151958	-0.111733
9	8	0	-1.095848	-1.245997	0.100935
10	1	0	-2.611553	0.013494	-0.374987
Frequencies --	107.8164		202.0553		254.4911
Frequencies --	303.6306		445.5943		546.8596
Frequencies --	605.8846		783.3262		854.5777
Frequencies --	896.9378		1056.0037		1094.1592
Frequencies --	1161.8712		1211.0170		1319.2065
Frequencies --	1412.9430		1430.1372		1486.2489
Frequencies --	1503.3832		1761.3734		3095.8241
Frequencies --	3104.4567		3183.6330		3561.4537

5.2.2 HPMF...CH₂OO.

1	6	0	-2.429127	-0.134521	-0.554691
2	8	0	-1.503496	-0.972783	-0.611301
3	8	0	-1.129401	-1.548276	0.585006
4	1	0	-2.901632	0.070164	0.393814
5	1	0	-2.699061	0.318450	-1.496265
6	8	0	1.502729	-1.220974	0.835021
7	8	0	1.908523	-0.823982	-0.500098
8	1	0	0.544790	-1.444965	0.678556
9	6	0	1.943137	0.551346	-0.504533
10	1	0	2.456921	0.939900	0.374726
11	1	0	2.436689	0.837612	-1.427867
12	8	0	0.622989	1.120512	-0.574187
13	6	0	0.029190	1.442421	0.583410
14	8	0	-1.123551	1.789853	0.624530
15	1	0	0.680748	1.368570	1.460150
Frequencies --	36.6256		68.1886		106.8202
Frequencies --	110.5088		136.3561		185.8866
Frequencies --	218.3875		245.5313		273.1751
Frequencies --	342.2424		446.5301		528.1360
Frequencies --	539.5195		695.0475		696.5871
Frequencies --	806.3809		870.6328		888.4179
Frequencies --	1001.7432		1027.8182		1039.8087

Frequencies --	1076.0131	1142.9729	1210.7994
Frequencies --	1240.6068	1334.4090	1408.5984
Frequencies --	1417.2033	1435.6724	1499.1104
Frequencies --	1560.2091	1587.9709	1780.3269
Frequencies --	3062.5867	3073.3269	3162.2004
Frequencies --	3167.8699	3204.4611	3315.4671

5.2.3 HPMF...CH₂OO = SOZ.

1	6	0	1.635923	-0.466999	0.991388
2	8	0	2.061144	-0.668234	-0.192552
3	8	0	1.001793	-0.618266	-1.108331
4	1	0	0.641050	-0.773058	1.272788
5	1	0	2.421003	-0.288268	1.713119
6	8	0	0.840407	1.334863	0.628037
7	6	0	0.313367	1.277220	-0.500138
8	8	0	-1.000088	1.081687	-0.713902
9	1	0	0.772738	1.702531	-1.385792
10	6	0	-1.788569	0.575400	0.360316
11	8	0	-1.380633	-0.682270	0.800041
12	8	0	-1.485024	-1.604995	-0.311592
13	1	0	-1.700675	1.209806	1.240475
14	1	0	-2.796411	0.548996	-0.041475
15	1	0	-0.602825	-1.456009	-0.722118
Frequencies --	-339.6489		115.2494		150.4444
Frequencies --	171.2103		200.3792		244.9088
Frequencies --	279.7850		339.2655		403.5096
Frequencies --	445.5086		524.6367		560.6170
Frequencies --	585.5319		747.4285		780.5406
Frequencies --	846.0834		881.9407		912.6748
Frequencies --	949.9797		997.5575		1057.5828
Frequencies --	1119.8081		1156.7306		1191.7030
Frequencies --	1247.5529		1319.9910		1390.7570
Frequencies --	1398.1824		1431.8918		1487.4764
Frequencies --	1511.8310		1547.1626		1578.4052
Frequencies --	3093.6085		3149.6889		3167.5088
Frequencies --	3169.0123		3291.4986		3434.7603

5.2.4 SOZ.

1	6	0	1.630996	-0.337188	0.960079
2	8	0	1.892263	-0.970810	-0.271464
3	8	0	0.720878	-0.550674	-1.018228
4	1	0	0.855330	-0.862405	1.514427
5	1	0	2.571152	-0.267453	1.498944
6	8	0	1.187112	0.962392	0.601844
7	6	0	0.584226	0.842677	-0.655846
8	8	0	-0.748665	1.166508	-0.712518
9	1	0	1.095585	1.471050	-1.380130

10	6	0	-1.564798	0.846051	0.407797
11	8	0	-1.484695	-0.480970	0.825329
12	8	0	-1.995101	-1.316135	-0.240619
13	1	0	-1.252790	1.410643	1.284785
14	1	0	-2.568870	1.102971	0.084308
15	1	0	-1.177275	-1.446533	-0.749269
Frequencies --	88.7740		107.8259		158.0773
Frequencies --	217.8968		226.8682		357.8687
Frequencies --	394.5151		430.4062		508.3976
Frequencies --	531.2386		670.6025		721.8399
Frequencies --	778.9157		881.1018		889.7686
Frequencies --	929.0945		952.4738		1006.9203
Frequencies --	1046.6531		1057.5888		1106.2288
Frequencies --	1155.8811		1175.9640		1184.8196
Frequencies --	1251.3820		1321.0087		1330.9501
Frequencies --	1416.1719		1427.5833		1436.0083
Frequencies --	1449.3552		1495.8311		1535.7022
Frequencies --	3085.7281		3091.0883		3128.5570
Frequencies --	3162.8314		3166.6873		3680.3745

5.2.5 HPMF...CH₂OO = HOOCH₂OOCH₂OCHO.

1	6	0	-2.212493	0.066223	0.862896
2	8	0	-2.548049	-0.714225	-0.076190
3	8	0	-1.339311	-1.185457	-0.701695
4	1	0	-1.284969	-0.080904	1.396985
5	1	0	-3.013716	0.680805	1.254409
6	8	0	-0.925038	1.181396	-0.389105
7	1	0	-0.897518	0.106021	-0.710521
8	8	0	0.216230	1.283545	0.503814
9	6	0	1.367905	1.222549	-0.275103
10	8	0	1.530640	-0.056284	-0.890000
11	1	0	1.326657	1.927448	-1.099063
12	1	0	2.177910	1.422836	0.421454
13	6	0	1.927313	-1.058124	-0.069643
14	8	0	2.222006	-0.940070	1.086330
15	1	0	1.943472	-1.991334	-0.637398
Frequencies --	-663.4759		36.0430		73.7998
Frequencies --	94.9059		153.3725		184.5942
Frequencies --	253.3215		295.9025		360.2118
Frequencies --	420.2389		436.7364		525.9141
Frequencies --	604.0943		781.0492		817.7337
Frequencies --	840.4301		876.4963		936.2952
Frequencies --	985.1732		1045.0917		1082.9813
Frequencies --	1133.1480		1185.6994		1186.3526
Frequencies --	1238.1950		1325.8469		1405.3700
Frequencies --	1417.0667		1432.4157		1481.3263
Frequencies --	1485.6293		1576.6826		1793.0362

Frequencies --	1817.6083	3095.5170	3105.6635
Frequencies --	3134.8980	3179.2325	3273.7561

5.2.6 $\text{HOCH}_2\text{OOCH}_2\text{OCHO}$.

1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.392990
3	8	0	1.385196	0.000000	1.824173
4	1	0	0.743307	0.693249	-0.390716
5	1	0	-1.016686	0.261251	-0.287808
6	8	0	0.368575	-1.237254	-0.569798
7	1	0	1.586032	-0.954074	1.831552
8	8	0	-0.766108	-2.142771	-0.432801
9	6	0	-0.524204	-2.991784	0.640713
10	8	0	0.533635	-3.918180	0.349544
11	1	0	-0.298909	-2.453188	1.553148
12	1	0	-1.430124	-3.585282	0.720228
13	6	0	1.738377	-3.670285	0.879726
14	8	0	2.037729	-2.762925	1.614239
15	1	0	2.435539	-4.446294	0.556231
Frequencies --	75.5607	112.0362	129.3482		
Frequencies --	145.0475	216.6969	260.6659		
Frequencies --	300.8276	327.9766	405.4054		
Frequencies --	501.0166	577.4695	613.6541		
Frequencies --	665.5803	760.4738	817.5320		
Frequencies --	878.5113	923.4763	997.1026		
Frequencies --	1052.8688	1059.6253	1065.1359		
Frequencies --	1159.5436	1174.8127	1198.8601		
Frequencies --	1316.9995	1328.9321	1397.3559		
Frequencies --	1417.9949	1432.5217	1457.7220		
Frequencies --	1474.7016	1506.2385	1773.2738		
Frequencies --	3078.6934	3099.4587	3121.5134		
Frequencies --	3151.7559	3197.9849	3619.7696		

5.2.7 $\text{HPMF} \dots \text{CH}_2\text{OO} = \text{HOCH}_2\text{O}(\text{O})\text{CH}_2\text{OCHO}$.

1	6	0	0.885773	-0.764138	1.066794
2	8	0	0.938988	-1.348635	-0.066386
3	8	0	2.095542	-0.848596	-0.813318
4	1	0	1.811158	-0.423914	1.510495
5	1	0	0.032026	-1.047361	1.668672
6	8	0	0.429496	1.008975	0.728427
7	8	0	1.414927	1.416004	-0.284732
8	1	0	1.804353	0.352376	-0.651262
9	6	0	-0.856016	1.359320	0.254886
10	8	0	-1.274907	0.595824	-0.863642
11	1	0	-1.530845	1.213937	1.093567
12	1	0	-0.795746	2.385462	-0.084165
13	6	0	-1.895943	-0.571893	-0.593654

14	8	0	-2.095646	-1.020733	0.503054
15	1	0	-2.191035	-1.042951	-1.532685
Frequencies --	-770.7487		56.5156		85.2797
Frequencies --	126.8914		155.3050		216.9506
Frequencies --	297.7048		322.1512		374.1556
Frequencies --	445.5680		510.4324		514.8889
Frequencies --	612.3166		691.4738		767.1727
Frequencies --	827.8025		846.8388		939.4439
Frequencies --	966.2792		1028.0641		1051.8870
Frequencies --	1141.7242		1159.9692		1190.1366
Frequencies --	1240.4259		1261.4541		1341.7622
Frequencies --	1383.1683		1405.0753		1436.4817
Frequencies --	1476.8451		1535.9721		1784.3844
Frequencies --	1905.2266		3113.1059		3119.0707
Frequencies --	3140.2513		3206.1013		3267.3472

5.2.8 $\text{HOOCH}_2\text{O}(\text{O})\text{CH}_2\text{OCHO}$.

1	6	0	1.122146	-0.650176	0.829094
2	8	0	1.949677	-0.994537	-0.181189
3	8	0	3.018988	-0.003264	-0.256927
4	1	0	1.623483	-0.223957	1.690474
5	1	0	0.465970	-1.488979	1.041140
6	8	0	0.193999	0.470017	0.430915
7	8	0	1.024954	1.623913	0.023624
8	1	0	2.437809	0.814459	-0.296801
9	6	0	-0.609600	0.180069	-0.751780
10	8	0	-1.495448	-0.858148	-0.429193
11	1	0	-1.104506	1.116402	-0.963775
12	1	0	0.053798	-0.162445	-1.534542
13	6	0	-2.709685	-0.481189	0.083468
14	8	0	-3.067808	0.641667	0.264481
15	1	0	-3.288613	-1.384885	0.285122
Frequencies --	49.4847		60.5513		96.3882
Frequencies --	182.7217		242.7954		284.8807
Frequencies --	325.8984		356.0646		390.1585
Frequencies --	476.5564		505.2625		607.6607
Frequencies --	719.4684		754.7376		829.1653
Frequencies --	844.6271		875.6200		928.8035
Frequencies --	993.7791		1044.5334		1131.8165
Frequencies --	1137.0124		1173.1154		1199.8654
Frequencies --	1289.7889		1307.5230		1382.4313
Frequencies --	1401.3256		1415.0474		1471.3601
Frequencies --	1501.6618		1623.8748		1820.0710
Frequencies --	3077.9289		3103.5111		3118.8408
Frequencies --	3162.6208		3207.6570		3252.5496

5.2.9 SOZ = OCH₂OCH(O)OCH₂OOH; Diradical.

PT2(2,2)/cc-pVTZ

C	-0.7915869917	-0.0623737618	-2.1897457012		
O	0.1195687963	0.8000376156	-2.6912957400		
O	0.4494155303	1.0431845014	-0.3488300775		
H	-1.6210314598	0.4954911209	-1.7462229512		
H	-1.1675990328	-0.6516263701	-3.0331966855		
O	-0.2480576783	-0.9647713893	-1.2402851931		
C	0.7414688644	-0.3039663773	-0.4932007562		
O	0.8915771503	-0.9070590323	0.7432338599		
H	1.7097297238	-0.3641347014	-0.9923370978		
C	-0.3000626136	-0.9940226072	1.5013607995		
O	-0.8685279859	0.2507101172	1.7659495669		
O	0.0189331832	0.9334175558	2.6804383763		
H	-1.0751937964	-1.5267726017	0.9555379278		
H	-0.0067583256	-1.4978551685	2.4166060596		
H	0.5731539094	1.4135212148	2.0476058682		
Wavenumbers [cm-1]	48.04				
Wavenumbers [cm-1]	80.94	107.68	202.92	224.38	278.37
Wavenumbers [cm-1]	316.92	411.83	451.08	500.32	607.26
Wavenumbers [cm-1]	682.10	719.96	888.29	897.28	923.64
Wavenumbers [cm-1]	1001.03	1023.61	1074.42	1078.51	1104.44
Wavenumbers [cm-1]	1153.28	1189.74	1230.62	1323.03	1332.43
Wavenumbers [cm-1]	1369.94	1401.10	1410.91	1431.66	1443.88
Wavenumbers [cm-1]	1497.88	3041.47	3093.22	3099.63	3128.58
Wavenumbers [cm-1]	3208.85	3765.58			
Wavenumbers [cm-1]	-356.94				

5.2.10 ³OCH₂OCH(O)OCH₂OOH; Diradical.

1	6	0	2.347484	-0.005990	-0.699728
2	8	0	3.246512	0.218140	0.263799
3	8	0	0.056223	1.318690	0.198909
4	1	0	2.127350	0.978026	-1.149728
5	1	0	2.771950	-0.640419	-1.486923
6	8	0	1.154622	-0.651539	-0.295305
7	6	0	0.385486	0.071603	0.632237
8	8	0	-0.690649	-0.708836	1.019779
9	1	0	0.963814	0.288902	1.549146
10	6	0	-1.528628	-1.107452	-0.055016
11	8	0	-1.911968	-0.038312	-0.865863
12	8	0	-2.798350	0.807435	-0.091104
13	1	0	-1.005709	-1.776239	-0.735959
14	1	0	-2.385220	-1.577410	0.417986
15	1	0	-2.149356	1.413552	0.298811
Frequencies --	50.1489		69.5354		113.5791
Frequencies --	135.9252		198.0902		209.3727
Frequencies --	272.2402		395.4037		428.7432

Frequencies --	475.0336	518.7467	559.3766
Frequencies --	641.3120	754.6562	794.1577
Frequencies --	875.1341	878.7250	982.7529
Frequencies --	1013.1742	1043.4304	1063.6176
Frequencies --	1086.6916	1135.1284	1174.4990
Frequencies --	1212.8656	1280.6074	1310.4068
Frequencies --	1315.5682	1356.4923	1392.9872
Frequencies --	1419.3666	1426.9431	1495.5260
Frequencies --	2915.2532	2924.3243	3015.6016
Frequencies --	3095.0786	3167.7085	3715.8946

5.2.11 ³OCH₂OCH(O)OCH₂OOH; Diradical.

PT2(2,2)/cc-pVTZ

C	0.0386886448	-0.7482882754	2.3120116674		
O	0.1768025247	0.2175999897	3.2367746923		
O	1.3264015854	0.2557535132	0.0633726423		
H	1.0545953806	-1.1101221912	2.0992344361		
H	-0.5474590107	-1.5761852542	2.7182213445		
O	-0.6226890565	-0.3618216131	1.1242986082		
C	0.0531897356	0.6286521715	0.4018234479		
O	-0.7321367040	1.0121962903	-0.6687314239		
H	0.2317026668	1.5306080132	1.0080565490		
C	-1.1241718401	-0.0667864717	-1.4997207545		
O	-0.0479144305	-0.8575072781	-1.8992930403		
O	0.7564683149	-0.0535515611	-2.7909183078		
H	-1.7737846351	-0.7584074423	-0.9681451895		
H	-1.6133063872	0.3990771264	-2.3490004724		
H	1.3470586179	0.3607345535	-2.1426097967		
Wavenumbers [cm-1]	49.48				
Wavenumbers [cm-1]	72.11	117.21	144.23	206.29	215.74
Wavenumbers [cm-1]	283.61	392.23	429.64	485.34	520.02
Wavenumbers [cm-1]	561.58	643.21	760.10	803.15	889.61
Wavenumbers [cm-1]	897.96	1005.04	1033.42	1077.95	1094.49
Wavenumbers [cm-1]	1111.52	1161.36	1190.82	1234.83	1305.39
Wavenumbers [cm-1]	1319.83	1345.71	1387.57	1413.09	1422.91
Wavenumbers [cm-1]	1437.40	1503.82	3002.20	3012.07	3099.06
Wavenumbers [cm-1]	3126.83	3206.68	3742.44		

5.2.12 ¹OCH₂OCH(O)OCH₂OOH; Diradical.

PT2(2,2)/cc-pVTZ

C	0.0792259366	-0.7263842154	2.3408002229		
O	0.0927916970	0.2508349518	3.2637869839		
O	1.3545937835	0.2220326122	0.0213891335		
H	1.1297626337	-1.0013338792	2.1692531678		
H	-0.4475357152	-1.6001768413	2.7324892130		
O	-0.5653791256	-0.4030315390	1.1260631775		
C	0.0940018723	0.5973111581	0.4015689270		

O	-0.7160969939	1.0049645610	-0.6408088965		
H	0.2931920104	1.4863790741	1.0209476269		
C	-1.1372207939	-0.0570244794	-1.4798593027		
O	-0.0766610863	-0.8435556504	-1.9258753160		
O	0.7058138704	-0.0242121572	-2.8233995659		
H	-1.7734560762	-0.7560153643	-0.9415387157		
H	-1.6498576551	0.4267358213	-2.3050093774		
H	1.3148932921	0.3757139229	-2.1831377111		
Wavenumbers [cm-1]	50.22	71.86	116.61	143.45	205.20
Wavenumbers [cm-1]	215.78	280.62	392.48	430.90	487.88
Wavenumbers [cm-1]	522.53	555.24	641.60	760.03	797.99
Wavenumbers [cm-1]	889.16	902.18	1001.93	1036.41	1076.38
Wavenumbers [cm-1]	1090.56	1109.44	1160.72	1190.87	1234.89
Wavenumbers [cm-1]	1304.94	1319.92	1345.86	1385.08	1410.88
Wavenumbers [cm-1]	1423.07	1437.43	1504.07	2997.37	3011.00
Wavenumbers [cm-1]	3097.69	3125.96	3206.00	3741.67	

5.2.13 ¹OCH₂OCH(O)OCH₂OOH; Diradical = HOOCH₂OC(O)OCH₂OH.

PT2(2,2)/cc-pVTZ

C	-0.1262006779	0.4727094166	0.4405218669		
O	0.9046205757	-0.1260563743	1.1890773415		
C	0.2518966279	-0.6629723412	2.3218355180		
O	-0.5315770261	0.2792261695	2.9070494222		
H	-0.8446703137	0.9181853019	1.2289679270		
O	0.2219091158	1.5565349275	-0.1869290867		
H	1.0111094403	-0.9296053885	3.0650780789		
H	-0.3265811668	-1.5500293819	2.0462878797		
O	-0.8871418501	-0.4610475365	-0.2655481787		
C	-0.1178356026	-1.1827334552	-1.2182155800		
O	0.6354880338	-0.3548006727	-2.0424362009		
O	-0.2985089035	0.3869439123	-2.8577683552		
H	0.6295734128	-1.8067714882	-0.7297882840		
H	-0.8450824265	-1.7602082052	-1.7804787321		
H	-0.4289830394	1.1589678691	-2.2848957554		
Wavenumbers [cm-1]	67.04	86.45	127.52	202.08	218.56
Wavenumbers [cm-1]	281.86	395.57	424.12	497.46	521.94
Wavenumbers [cm-1]	585.02	677.98	773.66	799.35	891.98
Wavenumbers [cm-1]	917.82	990.47	1028.49	1048.59	1079.27
Wavenumbers [cm-1]	1097.86	1110.40	1174.76	1206.12	1238.61
Wavenumbers [cm-1]	1284.47	1319.95	1396.97	1424.05	1432.02
Wavenumbers [cm-1]	1457.29	1497.74	2232.20	3038.52	3096.71
Wavenumbers [cm-1]	3112.17	3196.44	3739.80		
Wavenumbers [cm-1]	656.02				

5.2.14 $\text{HOCH}_2\text{OC(O)OCH}_2\text{OH}$.

1	8	0	-2.753624	-0.756615	-0.005325
2	6	0	-1.793620	0.277031	-0.002574
3	8	0	-0.576993	-0.453117	0.016615
4	6	0	0.517338	0.321326	0.009157
5	8	0	1.587386	-0.469336	0.034902
6	6	0	2.853517	0.243906	0.003662
7	8	0	3.865006	-0.686428	0.072930
8	8	0	0.519831	1.528939	-0.015410
9	1	0	-1.869991	0.881812	-0.904203
10	1	0	-1.882640	0.900628	0.886643
11	1	0	2.869743	0.844988	-0.904641
12	1	0	2.919237	0.880145	0.879689
13	1	0	3.886141	-1.188152	-0.747075
14	8	0	-4.014173	-0.049618	-0.105888
15	1	0	-4.405366	-0.283600	0.745524
Frequencies --	34.9649		52.1396		80.0396
Frequencies --	101.5472		125.3881		178.8637
Frequencies --	226.9810		241.1079		321.6632
Frequencies --	368.1867		375.6106		469.6891
Frequencies --	605.0495		755.2990		798.0261
Frequencies --	948.4348		959.5501		1023.5589
Frequencies --	1065.1645		1140.0247		1152.3412
Frequencies --	1162.0896		1167.3628		1234.2844
Frequencies --	1272.8005		1322.8149		1388.3505
Frequencies --	1411.4491		1440.0728		1468.9880
Frequencies --	1544.5819		1557.8479		1790.3229
Frequencies --	3062.7259		3075.7989		3129.1548
Frequencies --	3164.9436		3781.6445		3834.4818

5.2.15 ${}^1\text{OCH}_2\text{OCH(O)OCH}_2\text{OOH}$; Diradical = $\text{HOCH}_2\text{OCH(OH)OCHO}$.

PT2(2,2)/cc-pVDZ

C	-0.5304250483	-0.1259831277	-2.4904488004
O	0.1812855402	-0.5904266411	-1.3519457523
C	-0.1166057259	0.2857749923	-0.3016399267
O	0.0648603889	1.6056268635	-0.7061703118
H	-0.5896780309	1.0122503642	-2.4121311220
O	0.0619396963	-0.3529047488	-3.6426902256
H	-1.5847750662	-0.4870247033	-2.4831368082
H	-1.1571638688	0.1254627529	0.0539958803
O	0.7970597056	0.1220246745	0.7294401703
C	0.4214377996	-0.9278313927	1.6142839373
O	-0.6551279289	-0.5685809054	2.4276344608
O	-0.1484610185	0.4291800620	3.3524027135
H	0.0699238711	-1.8115923768	1.0569515022
H	1.3206721942	-1.1386065117	2.2077457832
H	-0.1574412957	1.2147245240	2.7754176071

Wavenumbers [cm-1]	20.90				
Wavenumbers [cm-1]	57.39	95.00	138.79	168.67	227.17
Wavenumbers [cm-1]	292.13	411.70	481.54	486.51	565.54
Wavenumbers [cm-1]	623.95	710.92	788.69	868.53	1004.75
Wavenumbers [cm-1]	1037.52	1053.74	1085.07	1117.75	1125.88
Wavenumbers [cm-1]	1146.95	1206.97	1247.49	1311.73	1319.82
Wavenumbers [cm-1]	1364.76	1398.65	1400.67	1415.22	1444.77
Wavenumbers [cm-1]	1490.80	2552.66	3000.19	3021.11	3123.30
Wavenumbers [cm-1]	3220.91	3756.17			
Wavenumbers [cm-1]	-484.58				

5.2.16 $\text{HOOCH}_2\text{OCH}(\text{OH})\text{OCHO}$

1	8	0	-2.302752	-0.440535	-0.515293
2	6	0	-1.537247	-0.362335	0.687327
3	8	0	-0.207008	-0.571775	0.321678
4	6	0	0.386196	0.469093	-0.391870
5	8	0	1.672346	0.045583	-0.772653
6	6	0	2.520868	-0.316390	0.237169
7	8	0	3.641574	-0.656708	0.008405
8	8	0	0.420581	1.590435	0.437308
9	1	0	-1.688699	0.610309	1.153036
10	1	0	-1.809174	-1.171290	1.359972
11	1	0	-0.137242	0.668653	-1.324423
12	1	0	2.068179	-0.257201	1.229235
13	1	0	0.686678	2.350420	-0.089747
14	8	0	-3.664811	-0.168849	-0.101071
15	1	0	-3.818086	0.671687	-0.550829
Frequencies --	32.5492		64.6759		96.7293
Frequencies --	116.1238		159.7212		214.1978
Frequencies --	226.0528		291.4735		319.2536
Frequencies --	340.5387		421.5096		485.5582
Frequencies --	582.2848		614.5477		796.0047
Frequencies --	945.5869		966.3449		1037.3095
Frequencies --	1042.6231		1050.1935		1101.4798
Frequencies --	1131.0784		1155.9480		1190.5903
Frequencies --	1270.0406		1294.0466		1378.6488
Frequencies --	1412.3411		1423.6920		1439.4031
Frequencies --	1456.7644		1548.7764		1832.1925
Frequencies --	3077.0985		3094.2815		3113.9534
Frequencies --	3146.7650		3781.8494		3833.1882

5.2.17 HOOCH_2O .

1	6	0	0.707116	0.454775	0.232649
2	8	0	-0.568628	0.634587	-0.336076
3	8	0	-1.411810	-0.412428	0.202103
4	1	0	0.635246	0.418023	1.332602
5	1	0	1.263541	1.359686	-0.049411

6	8	0	1.370971	-0.646539	-0.144677
7	1	0	-1.265745	-1.111314	-0.449895
Frequencies --	158.9577		296.6339		387.2210
Frequencies --	623.9770		824.8484		881.7393
Frequencies --	1024.2060		1083.1635		1215.0561
Frequencies --	1348.0460		1367.4729		1387.4858
Frequencies --	2935.2054		3003.9523		3763.2392

5.2.18 OCH_2OCHO .

1	8	0	1.683703	-0.559256	-0.448699
2	6	0	1.013453	0.152921	0.450761
3	8	0	-0.078140	0.928452	-0.086130
4	1	0	0.633089	-0.529860	1.222686
5	1	0	1.679858	0.885667	0.920336
6	6	0	-1.254753	0.276709	-0.191084
7	8	0	-1.464134	-0.854505	0.151062
8	1	0	-1.996577	0.948884	-0.630944
Frequencies --	59.7432		253.6697		306.4699
Frequencies --	566.7389		710.9445		846.8069
Frequencies --	908.9809		1049.8026		1111.9369
Frequencies --	1151.7401		1230.5407		1365.6355
Frequencies --	1384.1510		1408.8799		1792.0384
Frequencies --	2977.2197		3028.2200		3082.9283

5.2.19 OH .

1	8	0	0.000000	0.000000	0.107864
2	1	0	0.000000	0.000000	-0.862910
Frequencies --	3750.3682				

5.2.20 $OCH_2OC(O)OCHO$.

1	8	0	2.960284	-0.000252	0.856753
2	6	0	2.429997	-0.234155	-0.339068
3	8	0	1.098253	-0.774527	-0.314343
4	6	0	0.125203	0.145331	-0.184444
5	8	0	-1.038890	-0.492161	-0.092405
6	6	0	-2.187207	0.384631	0.066973
7	8	0	-3.313574	-0.402743	0.143165
8	8	0	0.284034	1.342195	-0.167355
9	1	0	2.436792	0.703276	-0.911626
10	1	0	3.027556	-0.982921	-0.871856
11	1	0	-2.014956	0.994175	0.952900
12	1	0	-2.273562	1.012262	-0.813567
13	1	0	-3.304647	-0.881720	0.976866
Frequencies --	47.2283		65.5149		92.4202
Frequencies --	155.5622		171.3985		321.4753
Frequencies --	361.8259		398.5920		507.5432
Frequencies --	622.5791		704.2828		800.0313

Frequencies --	831.2707	927.6575	973.4725
Frequencies --	1063.6894	1094.9383	1113.4367
Frequencies --	1164.0735	1232.7948	1272.4937
Frequencies --	1300.0038	1364.7039	1398.0376
Frequencies --	1411.8853	1464.3368	1544.3874
Frequencies --	1792.3436	2977.5732	3029.3366
Frequencies --	3078.1123	3164.4186	3834.5311

5.2.21 $OCH_2OCH(OH)OCHO$.

1	8	0	2.949454	-1.096464	-0.147891
2	6	0	2.173990	-0.037225	0.004061
3	8	0	0.793475	-0.381335	0.115762
4	6	0	-0.019604	0.679927	0.455771
5	8	0	-1.316370	0.197379	0.710396
6	6	0	-1.912927	-0.510677	-0.299047
7	8	0	-3.027705	-0.920096	-0.186308
8	8	0	0.002950	1.596734	-0.602078
9	1	0	2.489558	0.528506	0.900409
10	1	0	2.326577	0.629885	-0.861858
11	1	0	0.292462	1.150366	1.392494
12	1	0	-1.271612	-0.646316	-1.172309
13	1	0	-0.500180	2.375669	-0.342491
Frequencies --	61.2244		84.3120		100.9713
Frequencies --	155.2038		180.9980		279.2164
Frequencies --	340.6765		409.7484		468.7301
Frequencies --	547.1208		651.1927		766.0999
Frequencies --	788.3068		996.9325		1031.5904
Frequencies --	1040.0714		1086.0219		1105.5273
Frequencies --	1128.5990		1160.5129		1182.9867
Frequencies --	1289.3225		1352.3667		1385.4107
Frequencies --	1415.8544		1429.1680		1467.3037
Frequencies --	1833.2009		2898.5728		2932.1597
Frequencies --	3041.7050		3097.8983		3824.7409

5.3 CH₂OO + t-BuOOH.

All structures calculated at the B2PLYPD3/cc-pVTZ level of theory except where noted. The lowest energy conformers only are reported herein.

5.3.1 *t*-BuOOH.

1	8	0	-1.965844	0.101766	-0.144043
2	8	0	-0.725601	-0.055774	-0.889035
3	1	0	-2.339250	-0.780360	-0.258691
4	6	0	0.385576	0.000114	0.033762
5	6	0	0.321952	-1.163315	1.015040
6	6	0	1.575549	-0.137323	-0.907177
7	6	0	0.400440	1.342832	0.751860
8	1	0	0.282683	-2.110410	0.478001
9	1	0	-0.555100	-1.081389	1.652722
10	1	0	1.205109	-1.166978	1.652320
11	1	0	1.580361	0.671305	-1.635142
12	1	0	1.537954	-1.086128	-1.439139
13	1	0	2.500591	-0.096051	-0.334795
14	1	0	-0.492577	1.460183	1.360093
15	1	0	0.437359	2.155248	0.028425
16	1	0	1.273332	1.412790	1.399922
Frequencies --	135.9211		192.5256		235.1284
Frequencies --	247.1953		256.7389		270.2138
Frequencies --	340.8045		358.7219		405.7140
Frequencies --	464.0249		530.0351		756.3445
Frequencies --	871.4923		925.1179		928.5971
Frequencies --	944.0240		968.7091		1049.2212
Frequencies --	1058.6561		1233.0456		1276.5929
Frequencies --	1293.7447		1361.3542		1403.1293
Frequencies --	1406.1626		1428.9794		1483.0430
Frequencies --	1500.7753		1502.2521		1509.9613
Frequencies --	1512.0663		1535.5059		3055.6946
Frequencies --	3059.1733		3064.3828		3126.2718
Frequencies --	3131.2265		3138.8241		3140.8916
Frequencies --	3142.6944		3151.2201		3788.4017

5.3.2 *t*BuOOH...CH₂OO.

1	6	0	2.585651	1.114740	-0.239633
2	8	0	3.091661	0.030048	0.149853
3	8	0	2.262506	-0.949934	0.605467
4	1	0	1.510316	1.254088	-0.207032
5	1	0	3.309227	1.835146	-0.590952
6	8	0	0.263449	-0.685138	-1.175204
7	8	0	-0.367466	0.475095	-0.574295
8	1	0	0.933429	-0.909895	-0.481149
9	6	0	-1.574716	0.076913	0.121684
10	6	0	-1.246939	-0.904283	1.239283
11	6	0	-2.070131	1.403909	0.680919
12	6	0	-2.564519	-0.510729	-0.873911
13	1	0	-0.474702	-0.497900	1.890123
14	1	0	-0.894288	-1.849591	0.834400
15	1	0	-2.138318	-1.100679	1.833821
16	1	0	-2.221340	2.122998	-0.122133
17	1	0	-1.354556	1.815014	1.391372
18	1	0	-3.017992	1.254980	1.195033
19	1	0	-2.145551	-1.398782	-1.339183
20	1	0	-2.793349	0.215097	-1.652430
21	1	0	-3.490141	-0.784347	-0.368484
Frequencies --	38.1807		54.2814		62.5714
Frequencies --	123.1294		156.8830		188.9909
Frequencies --	199.5053		245.7786		250.8879
Frequencies --	264.5885		288.7242		345.2258
Frequencies --	360.2140		410.4217		469.1945
Frequencies --	529.0993		542.9878		705.8258
Frequencies --	758.4127		867.0883		886.0990
Frequencies --	907.2254		930.1359		930.6964
Frequencies --	951.7725		969.3379		1036.5702
Frequencies --	1049.8441		1059.9220		1228.5809
Frequencies --	1273.6454		1278.0705		1296.4068
Frequencies --	1403.2005		1404.4595		1406.8656
Frequencies --	1429.3535		1482.3096		1497.4042
Frequencies --	1501.4659		1506.3325		1509.1616
Frequencies --	1513.4284		1534.6382		1538.5969
Frequencies --	3056.3023		3057.8515		3063.8040
Frequencies --	3101.8748		3127.6867		3130.1963
Frequencies --	3134.1356		3139.3041		3146.0688
Frequencies --	3153.6072		3278.3959		3291.8177

5.3.3 *t*ButylOOCH₂OOH.

1	6	0	1.789467	-1.049020	-0.140702
2	8	0	2.231807	0.154230	-0.702845
3	8	0	2.671636	1.003596	0.387718
4	1	0	2.498165	-1.411357	0.602615
5	1	0	1.698846	-1.721191	-0.993453
6	8	0	0.581007	-0.960784	0.554409
7	8	0	-0.454190	-0.825202	-0.475243
8	1	0	1.875986	1.533959	0.527722
9	6	0	-1.431032	0.128735	-0.014003
10	6	0	-0.786398	1.488802	0.228628
11	6	0	-2.389949	0.182291	-1.197256
12	6	0	-2.121871	-0.396003	1.238299
13	1	0	-0.199858	1.784583	-0.639951
14	1	0	-0.147898	1.454210	1.109694
15	1	0	-1.554122	2.240972	0.403577
16	1	0	-2.785244	-0.808639	-1.410876
17	1	0	-1.883793	0.556355	-2.084928
18	1	0	-3.221351	0.844652	-0.962917
19	1	0	-1.406282	-0.512836	2.048492
20	1	0	-2.580319	-1.362550	1.038086
21	1	0	-2.897506	0.298293	1.559826
Frequencies --	58.4252		74.6044		114.7559
Frequencies --	176.4022		192.3439		217.4864
Frequencies --	245.4307		253.2434		303.5977
Frequencies --	313.1933		347.3873		350.3609
Frequencies --	409.6029		462.3615		490.3450
Frequencies --	521.6041		651.0878		770.7864
Frequencies --	861.5562		875.4832		912.5525
Frequencies --	929.3587		941.3223		976.0280
Frequencies --	1035.8272		1046.0681		1050.0579
Frequencies --	1063.8339		1163.5547		1233.2891
Frequencies --	1274.9375		1297.5482		1326.1289
Frequencies --	1380.6305		1400.2369		1405.6492
Frequencies --	1409.6422		1428.6186		1459.6202
Frequencies --	1482.9042		1500.7206		1505.6570
Frequencies --	1508.6497		1514.7797		1542.0268
Frequencies --	3053.4977		3059.2444		3064.1746
Frequencies --	3072.5830		3128.1937		3132.0476
Frequencies --	3134.4421		3141.9735		3142.0748
Frequencies --	3142.7238		3147.9622		3766.9559

5.3.4 *t*ButylO(O)CH₂OOH.

1	6	0	1.114736	0.702311	-0.892020
2	8	0	1.785459	0.867169	0.276389
3	8	0	2.593227	-0.327780	0.513388
4	1	0	1.709021	0.232651	-1.668944
5	1	0	0.694749	1.661117	-1.175662
6	8	0	-0.028426	-0.235570	-0.781574
7	8	0	0.543173	-1.556975	-0.466382
8	1	0	1.895405	-1.019695	0.286820
9	6	0	-1.202712	0.082230	0.144942
10	6	0	-0.796230	-0.110309	1.591488
11	6	0	-1.623023	1.506677	-0.166204
12	6	0	-2.248094	-0.922400	-0.298078
13	1	0	-0.056169	0.619851	1.902549
14	1	0	-0.394308	-1.107962	1.732187
15	1	0	-1.686802	0.004622	2.208484
16	1	0	-1.757054	1.656216	-1.236545
17	1	0	-0.920348	2.239510	0.223539
18	1	0	-2.582799	1.683088	0.316001
19	1	0	-1.853573	-1.928225	-0.199402
20	1	0	-2.532956	-0.752060	-1.334409
21	1	0	-3.130701	-0.814916	0.330055
Frequencies --	53.6694		90.8599		189.7147
Frequencies --	215.4525		240.0439		276.1027
Frequencies --	291.4396		301.6290		326.2795
Frequencies --	353.7006		367.4669		408.9070
Frequencies --	430.4841		461.7886		515.3978
Frequencies --	607.5622		681.0987		794.2887
Frequencies --	803.3071		844.1733		871.4941
Frequencies --	886.0923		939.4933		946.8023
Frequencies --	981.8108		1054.6237		1067.4035
Frequencies --	1136.9916		1171.8023		1197.2369
Frequencies --	1294.7597		1301.1923		1309.7801
Frequencies --	1392.5299		1408.6780		1410.4464
Frequencies --	1434.2071		1470.9059		1479.3913
Frequencies --	1504.3203		1506.0983		1509.3596
Frequencies --	1519.1327		1541.9116		1658.4491
Frequencies --	2988.1410		3061.0820		3068.3685
Frequencies --	3075.9030		3119.4771		3134.5991
Frequencies --	3141.1575		3144.0608		3153.1177
Frequencies --	3175.0047		3183.8858		3199.8640

5.3.5 *t*BuOOH...CH₂OO = *t*ButylOOCH₂OOH.

1	6	0	2.354506	-0.945413	0.394328
2	8	0	3.001204	0.024433	-0.102453
3	8	0	2.209370	1.215478	0.090414
4	1	0	1.708492	-0.791430	1.246643
5	1	0	2.710260	-1.928687	0.112123
6	8	0	0.629795	-0.505717	-0.657773
7	8	0	-0.361205	-0.671576	0.391193
8	1	0	1.091714	0.435760	-0.405154
9	6	0	-1.571418	0.041982	0.029155
10	6	0	-2.155489	-0.545772	-1.247176
11	6	0	-2.461659	-0.240002	1.232286
12	6	0	-1.285241	1.531973	-0.107081
13	1	0	-2.347924	-1.609595	-1.119719
14	1	0	-1.466572	-0.413894	-2.077399
15	1	0	-3.093292	-0.048892	-1.492627
16	1	0	-2.023567	0.170690	2.139847
17	1	0	-2.600532	-1.311519	1.362066
18	1	0	-3.436174	0.219787	1.078305
19	1	0	-0.654815	1.737411	-0.969723
20	1	0	-0.786210	1.906043	0.784947
21	1	0	-2.218887	2.076781	-0.239432
Frequencies --	-429.2806		37.8362		66.3487
Frequencies --	111.2135		168.2626		200.8633
Frequencies --	247.4073		253.4492		266.6039
Frequencies --	318.8855		345.4354		373.6391
Frequencies --	406.0921		443.1891		468.2675
Frequencies --	500.4108		560.3987		760.1102
Frequencies --	822.7163		850.7368		880.4189
Frequencies --	922.2162		930.7544		942.0455
Frequencies --	971.2076		1051.0660		1059.7763
Frequencies --	1135.7841		1213.1950		1224.2397
Frequencies --	1272.0801		1288.8566		1297.2555
Frequencies --	1406.0406		1409.5301		1414.7295
Frequencies --	1432.5176		1483.6332		1498.6954
Frequencies --	1500.9659		1505.8559		1509.0682
Frequencies --	1515.7327		1533.6940		1587.5432
Frequencies --	2007.1218		3058.8271		3059.5632
Frequencies --	3065.2043		3130.4729		3133.0206
Frequencies --	3133.4194		3139.3678		3141.4131
Frequencies --	3143.0925		3150.7366		3269.7468

5.3.6 *t*BuOOH...CH₂OO = *t*ButylO(O)CH₂OOH.

1	6	0	1.430978	0.861760	-0.818337
2	8	0	1.944058	0.787246	0.347843
3	8	0	2.402585	-0.584493	0.583934
4	1	0	1.830776	0.229479	-1.600470
5	1	0	1.023607	1.833855	-1.064850
6	8	0	-0.096397	-0.153766	-0.824383
7	8	0	0.447220	-1.495865	-0.639148
8	1	0	1.315453	-1.239780	-0.048745
9	6	0	-1.212997	0.092050	0.134623
10	6	0	-0.777511	-0.161154	1.567040
11	6	0	-1.584612	1.546090	-0.107759
12	6	0	-2.324804	-0.848707	-0.297779
13	1	0	0.027739	0.502237	1.866540
14	1	0	-0.444943	-1.186691	1.691073
15	1	0	-1.633286	0.008086	2.219500
16	1	0	-1.739130	1.736845	-1.168728
17	1	0	-0.827122	2.225233	0.278223
18	1	0	-2.516199	1.760226	0.412440
19	1	0	-1.991085	-1.879549	-0.227986
20	1	0	-2.625155	-0.643381	-1.323451
21	1	0	-3.186708	-0.711773	0.353756
Frequencies --	-268.9030		46.0105		95.4723
Frequencies --	181.6209		195.5030		243.1511
Frequencies --	257.5555		289.8313		300.4086
Frequencies --	341.1206		354.9256		397.7669
Frequencies --	416.1867		442.1464		502.6679
Frequencies --	525.7408		576.4124		704.5053
Frequencies --	810.1381		819.2894		881.5562
Frequencies --	937.8437		943.1068		976.8885
Frequencies --	1009.1948		1053.9316		1063.1152
Frequencies --	1109.5536		1194.2858		1223.1198
Frequencies --	1256.3213		1289.8002		1296.6740
Frequencies --	1374.7784		1408.5735		1413.7786
Frequencies --	1437.1595		1482.7311		1499.9377
Frequencies --	1502.7579		1510.1299		1513.3157
Frequencies --	1520.9556		1535.6602		1699.5940
Frequencies --	1924.5341		3059.9335		3065.3190
Frequencies --	3075.9042		3129.8153		3134.1629
Frequencies --	3139.4587		3139.9923		3151.7701
Frequencies --	3164.8293		3178.6641		3247.9271

5.4 CH₂OO + SOZ.

All structures calculated at the ωB97XD/6-31+G* level of theory.

5.4.1 SOZ...CH₂OO.

1	6	0	-0.281981	1.979645	1.203302
2	8	0	-0.321957	2.534925	0.088734
3	8	0	-1.066738	1.958203	-0.908749
4	1	0	-0.842349	1.065719	1.388234
5	1	0	0.340565	2.478505	1.938442
6	6	0	1.398898	-0.135760	-1.316554
7	8	0	2.213967	0.564606	-0.404609
8	8	0	1.640464	0.172811	0.848405
9	1	0	0.419938	0.344844	-1.428504
10	1	0	1.950514	-0.227514	-2.251139
11	8	0	1.284624	-1.410182	-0.711193
12	6	0	1.130298	-1.152151	0.633900
13	8	0	-0.184860	-1.108962	1.096608
14	1	0	1.709309	-1.878064	1.210650
15	6	0	-1.153304	-1.895846	0.420026
16	8	0	-1.690243	-1.263607	-0.690015
17	8	0	-2.555553	-0.226604	-0.218236
18	1	0	-0.714879	-2.818089	0.029488
19	1	0	-1.927974	-2.092621	1.163011
20	1	0	-2.056215	0.582371	-0.501765
Frequencies --	51.2219		72.7880		85.4889
Frequencies --	101.2428		117.1371		126.7805
Frequencies --	140.1465		168.7132		201.6318
Frequencies --	247.0062		253.9151		347.4882
Frequencies --	409.9345		484.5874		556.1462
Frequencies --	559.4035		652.8793		695.9920
Frequencies --	755.7737		809.1498		853.6123
Frequencies --	903.2451		930.1572		938.4629
Frequencies --	971.3929		980.0018		1031.3839
Frequencies --	1047.2622		1082.9046		1103.2164
Frequencies --	1133.9863		1167.4462		1195.5764
Frequencies --	1208.8734		1261.1334		1277.7829
Frequencies --	1335.1225		1357.2504		1413.0717
Frequencies --	1437.0344		1449.1087		1468.8460
Frequencies --	1501.4385		1548.5940		1562.6226
Frequencies --	1648.4344		3096.1709		3115.1945
Frequencies --	3137.9132		3175.4453		3188.5607
Frequencies --	3211.6831		3326.8253		3374.1317

5.4.2 SOZ...CH₂OO = hydroperoxide.

1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.269180
3	8	0	1.357106	0.000000	1.709780

4	1	0	0.785825	0.528498	-0.533957
5	1	0	-0.939069	-0.280345	-0.469252
6	8	0	1.308628	-1.572253	-0.141647
7	8	0	0.733348	-2.737273	0.448326
8	1	0	1.616587	-1.024400	0.757004
9	6	0	0.604475	-3.701378	-0.547013
10	1	0	1.505674	-3.749180	-1.159056
11	1	0	0.432926	-4.624061	0.012511
12	8	0	-0.442083	-3.477897	-1.468167
13	6	0	-1.742191	-3.494613	-1.011581
14	8	0	-2.119139	-2.143541	-0.700059
15	8	0	-3.016449	-2.279496	0.402805
16	6	0	-2.349161	-3.270390	1.143106
17	8	0	-1.962366	-4.214484	0.160201
18	1	0	-2.362791	-3.887563	-1.819055
19	1	0	-3.069803	-3.724229	1.823034
20	1	0	-1.470596	-2.858131	1.649880
Frequencies --			-591.3555	31.1930	43.6934
Frequencies --			80.0525	124.5676	128.5824
Frequencies --			153.4177	207.6011	235.2186
Frequencies --			328.2795	367.2147	411.2713
Frequencies --			436.9544	471.8631	526.4273
Frequencies --			599.2117	672.5848	743.3983
Frequencies --			800.5116	819.6862	882.5286
Frequencies --			921.6178	944.1776	973.7466
Frequencies --			991.0802	1043.2038	1061.2449
Frequencies --			1096.3276	1107.3298	1145.3236
Frequencies --			1165.9512	1190.7927	1205.9040
Frequencies --			1214.0070	1250.0661	1266.6985
Frequencies --			1341.3226	1358.2047	1423.7225
Frequencies --			1430.3497	1442.9654	1462.0621
Frequencies --			1506.5098	1550.5504	1555.6651
Frequencies --			1598.4177	1907.3260	3107.2982
Frequencies --			3126.0946	3156.8930	3168.8321
Frequencies --			3200.5535	3205.0114	3310.9128

5.4.3 SOZ...CH₂OO = ether oxide.

1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.288195
3	8	0	1.363612	0.000000	1.781656
4	1	0	0.776850	0.564137	-0.513825
5	1	0	-0.994351	-0.067246	-0.432201
6	8	0	0.701233	-1.550588	-0.481251
7	8	0	2.088207	-1.401129	-0.133527
8	1	0	1.960854	-0.816735	0.771227
9	6	0	0.234140	-2.715564	0.263844
10	1	0	1.013064	-3.456531	0.101569

11	1	0	0.138277	-2.442268	1.316608
12	8	0	-0.943726	-3.164546	-0.304848
13	6	0	-2.145019	-2.970250	0.362600
14	8	0	-2.541373	-1.612408	0.201022
15	8	0	-3.290402	-1.341702	1.385931
16	6	0	-2.469675	-1.957358	2.350070
17	8	0	-2.090354	-3.179020	1.736023
18	1	0	-2.852109	-3.654415	-0.108306
19	1	0	-3.083222	-2.158869	3.228004
20	1	0	-1.590947	-1.342273	2.568513
Frequencies --			-330.8476	31.7662	62.1823
Frequencies --			94.3753	103.3235	162.2381
Frequencies --			191.7712	281.9024	309.0899
Frequencies --			357.8103	373.2745	386.3160
Frequencies --			441.6450	489.0291	506.1841
Frequencies --			599.0067	626.5979	743.9467
Frequencies --			796.5290	853.6091	933.3612
Frequencies --			943.6177	952.5466	1002.7823
Frequencies --			1019.2040	1053.5310	1062.4701
Frequencies --			1094.8945	1103.0178	1133.4662
Frequencies --			1180.8257	1191.8770	1221.3176
Frequencies --			1242.1171	1262.4831	1276.4972
Frequencies --			1323.2387	1351.3131	1364.2281
Frequencies --			1433.3939	1439.0484	1455.5500
Frequencies --			1508.1905	1534.5575	1559.3896
Frequencies --			1642.4335	2005.2203	3104.3793
Frequencies --			3150.2789	3172.1082	3174.3107
Frequencies --			3204.1917	3236.5105	3297.9108

5.4.4 SOZ_Hydroperoxide.

1	6	0	1.884893	-0.273102	0.782083
2	8	0	2.562616	-1.070922	-0.138920
3	8	0	3.877816	-0.541488	-0.301493
4	1	0	2.499979	-0.080057	1.666228
5	1	0	0.967577	-0.820559	1.007823
6	8	0	1.600075	1.013346	0.297428
7	8	0	0.600779	0.881417	-0.729295
8	1	0	3.746690	0.091093	-1.026302
9	6	0	-0.395044	1.821424	-0.463993
10	1	0	0.043653	2.786206	-0.206187
11	1	0	-0.959186	1.863989	-1.399240
12	8	0	-1.243581	1.514108	0.618004
13	6	0	-2.056612	0.404927	0.528537
14	8	0	-1.340778	-0.717848	1.059487
15	8	0	-1.825684	-1.822714	0.294762
16	6	0	-1.849454	-1.246144	-0.985004
17	8	0	-2.419233	0.031341	-0.766411

18	1	0	-2.947156	0.613302	1.124421
19	1	0	-2.512943	-1.842607	-1.611186
20	1	0	-0.837395	-1.151934	-1.393788
Frequencies --	27.8135		42.8195		77.5589
Frequencies --	83.3029		129.7814		146.6498
Frequencies --	167.7540		247.8419		287.4015
Frequencies --	346.3498		370.3294		407.5620
Frequencies --	435.4753		516.1405		536.6926
Frequencies --	660.5214		698.4549		744.1704
Frequencies --	799.3127		871.4136		937.5492
Frequencies --	947.7603		978.3908		994.8972
Frequencies --	1045.5248		1053.3368		1089.8575
Frequencies --	1096.0050		1101.6021		1136.9200
Frequencies --	1163.9600		1190.2921		1198.8710
Frequencies --	1217.0889		1266.2975		1331.5996
Frequencies --	1341.7103		1361.9458		1418.3360
Frequencies --	1431.1185		1436.9637		1443.3015
Frequencies --	1464.5393		1478.1745		1507.2079
Frequencies --	1550.5797		3097.2677		3108.2137
Frequencies --	3122.5978		3156.2447		3195.1176
Frequencies --	3195.5425		3198.1221		3771.4909

5.45 SOZ_Ether oxide.

1	6	0	1.427780	-0.368989	1.054947
2	8	0	1.190480	-1.354480	0.148056
3	8	0	2.421731	-1.741232	-0.481760
4	1	0	2.374658	-0.478245	1.582419
5	1	0	0.551908	-0.281825	1.694761
6	8	0	1.579025	0.946142	0.389873
7	8	0	2.742429	0.872485	-0.494705
8	1	0	2.745378	-0.840644	-0.770881
9	6	0	0.489228	1.379416	-0.496681
10	1	0	0.912151	2.273980	-0.942545
11	1	0	0.319660	0.589925	-1.227763
12	8	0	-0.631113	1.714265	0.240953
13	6	0	-1.769619	0.915182	0.177671
14	8	0	-1.611082	-0.172508	1.082574
15	8	0	-2.375515	-1.217935	0.482337
16	6	0	-1.986750	-1.070582	-0.860209
17	8	0	-2.009228	0.335327	-1.061707
18	1	0	-2.595944	1.563757	0.471574
19	1	0	-2.745268	-1.544139	-1.483002
20	1	0	-0.980190	-1.469480	-1.023903
Frequencies --	40.3375		72.1259		99.7963
Frequencies --	111.0094		162.1136		202.6401
Frequencies --	272.4579		305.3512		314.8856
Frequencies --	364.0967		384.1186		434.3837

Frequencies --	470.6508	513.6918	621.5730
Frequencies --	648.2056	743.0171	751.6109
Frequencies --	783.8117	795.9436	856.3752
Frequencies --	928.5820	946.0076	951.4096
Frequencies --	999.3441	1016.7725	1059.4132
Frequencies --	1103.7842	1123.9275	1166.8762
Frequencies --	1180.7146	1191.9589	1204.3801
Frequencies --	1221.8471	1264.4871	1314.7926
Frequencies --	1330.7383	1348.2838	1408.0832
Frequencies --	1432.4636	1436.5902	1454.0762
Frequencies --	1480.5880	1529.6433	1559.2091
Frequencies --	1617.5236	3108.1862	3161.6673
Frequencies --	3170.5031	3176.0559	3206.5426
Frequencies --	3242.5289	3253.1306	3265.0259

Supplementary Note 6: Global chemical modelling.

6.1. Biogenic volatile organic compound (BVOC) precursors for CH₂OO.

To accurately account for the formation of the stabilized CH₂OO, it is required to have a more complete inventory of organic emissions than is present in the base model. The MEGAN model^{30,31} provides a comprehensive estimate of BVOCs based on a land-surface vegetation model. Guenther *et al.*³⁰ estimate that the uncertainties associated with global emissions of VOCs are a factor of 2 or 3, therefore for emissions of α -pinene, β -pinene, myrcene, sabinene, limonene, 3-carene, t- β -ocimene, camphene, ethene, propene, butene, methyl salicylate, and 2-methyl-3-buten-2-ol, we estimate a factor of 3 uncertainty.

As stated, the only monoterpene in the STOCHEM-base model that can produce CH₂OO is β -pinene (33% of total), whereas many of the monoterpenes and indeed sesquiterpenes in the MEGAN model are CH₂OO precursors on ozonolysis. In Table S8 (monoterpenes) and Table S9 (sesquiterpenes) we gather together data on the estimated emission total, the fraction of the total emission for that compound class, the estimated yield of CH₂OO on ozonolysis and the rate coefficient for ozonolysis at 300 K. These data are then used to estimate the additional production of CH₂OO relative to β -pinene.

Table S8. Monoterpene emission data and rate coefficients for their reactions with ozone at 300 K.

Compound	Tg/Year	Fraction	Yield of CH ₂ OO	$k_{(O_3)} / 10^{16} \text{ cm}^3 \text{ s}^{-1}$
α -pinene	66.1	0.407	0	0.870
β -pinene	18.9	0.116	0.05	0.148
t- β -ocimene	19.4	0.120	0.05	3.85
limonene	11.4	0.070	0.05	2.09
sabinene	9.0	0.055	0.05	0.880
myrcene	8.7	0.054	0.05	4.85
3-carene	7.1	0.043	0.05	0.37
camphene	4.0	0.025	0.05	0.009
β -phellandrene	1.5	0.009	0.05	30.0
32 other MTs	16.2	0.010	0.05	1.00

If we redistribute the monoterpene emission from a split of 66% α -pinene to 33% β -pinene (as in STOCHEM-base) to that given by MEGAN and calculate the increase in the production rate of CH₂OO, there is an increase by a factor of approximately 25.

Table S9. Sesquiterpene emission data and rate coefficients for their reactions with ozone at 300 K.

Compound	Tg/Year	Fraction	Yield of CH ₂ OO	$k_{(O_3)} / 10^{16} \text{ cm}^3 \text{ s}^{-1}$
α -farnesene	7.1	0.245	0	4.00
β -caryophyllene	7.4	0.255	0.05	110
β -farnesene	4.0	0.138	0.05	4.00
29 other MTs	10.5	0.362	0.05	1.00

Emissions of sesquiterpenes are a significant source of CH₂OO that is neglected in STOCHEM-base integration. The estimated additional flux of CH₂OO from sesquiterpenes is a

factor of ~100 greater than from β -pinene. Inclusion of alkenes that are neglected in the MEGAN model in future modelling efforts is anticipated to lead to a significant increase in modelled CH_2OO . The modelled CH_2OO and total sCI concentrations after including the MEGAN inventory as an update to the STOCHEM-base model are presented in Fig. 4(A) in the main text, and in Extended Data Figure 8, respectively.

6.2. Reactivity of OH.

In the STOCHEM-base case scenario, the OH reactivity (total loss rate, s^{-1}) is significantly underestimated in the tropical forest area: over the Amazon in the dry season, the model predicts an OH reactivity rate of 24.4 s^{-1} vs. the measured value of 49.6 s^{-1} ³². This is anticipated to be due to insufficient representation of reactive VOCs in the model, especially monoterpenes and sesquiterpenes. Using the total emission for the wider suite of monoterpenes and sesquiterpenes considered in the MEGAN suite of models and the rate coefficients for their reactions with OH at 300 K (Tables S10 and S11), we calculated an increase in the annual OH reactivity (see Figure S23) of 20% over the Amazon. Whilst the updated model yields an OH reactivity rate closer to measurements (in the dry season: 32.6 s^{-1} vs. 49.6 s^{-1} ³²), underestimation of OH reactivity signals that VOCs, and potential sources of CH_2OO , are still underrepresented in the model.

Table S10. Monoterpene emission data and rate coefficients for their reactions with OH at 300 K.

Compound	Tg/Year	Fraction	$k_{(\text{OH})} / 10^{11} \text{ cm}^3 \text{ s}^{-1}$
α -pinene	66.1	0.407	5.1
β -pinene	18.9	0.116	6.4
t- β -ocimene	19.4	0.120	30.3
limonene	11.4	0.070	16.3
sabinene	9.0	0.055	11.7
myrcene	8.7	0.054	33.5
3-carene	7.1	0.043	8.0
camphene	4.0	0.025	5.3
β -phellandrene	1.5	0.009	16.8
32 other MTs	16.2	0.010	10

Table S11. Sesquiterpene emission data and rate coefficients for their reactions with OH at 300 K.

Compound	Tg/Year	Fraction	$k_{(\text{OH})} / 10^{11} \text{ cm}^3 \text{ s}^{-1}$
α -farnesene	7.1	0.245	21.9
β -caryophyllene	7.4	0.255	20
β -farnesene	4.0	0.138	28.8
29 other MTs	10.5	0.362	23.5

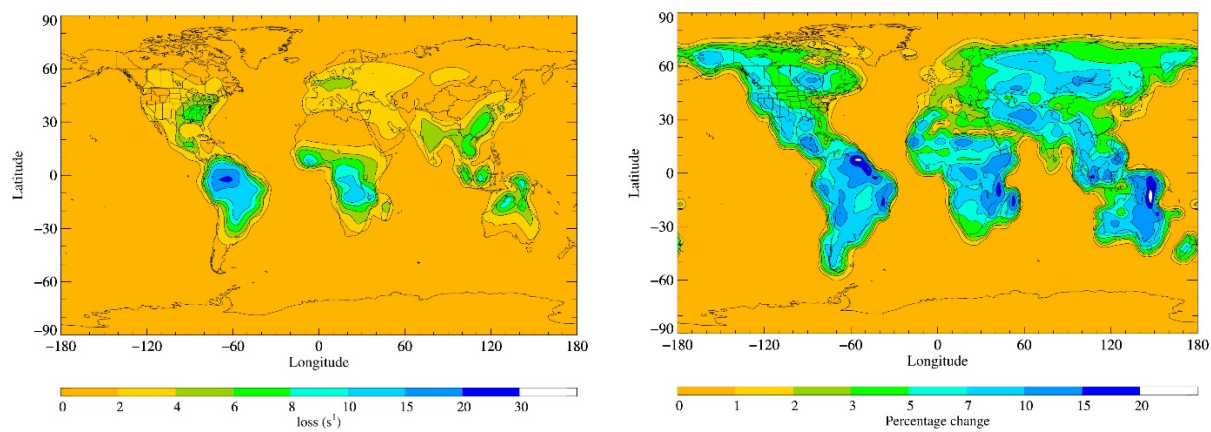


Figure S23. (*left*) The annual OH loss for STOCHEM-base case scenario and (*right*) the percent increase of OH reactivity after modifying the emission inventory of alkenes.

6.3 Impact of increased Alkenes on NO_x , SO_x and HO_x concentrations

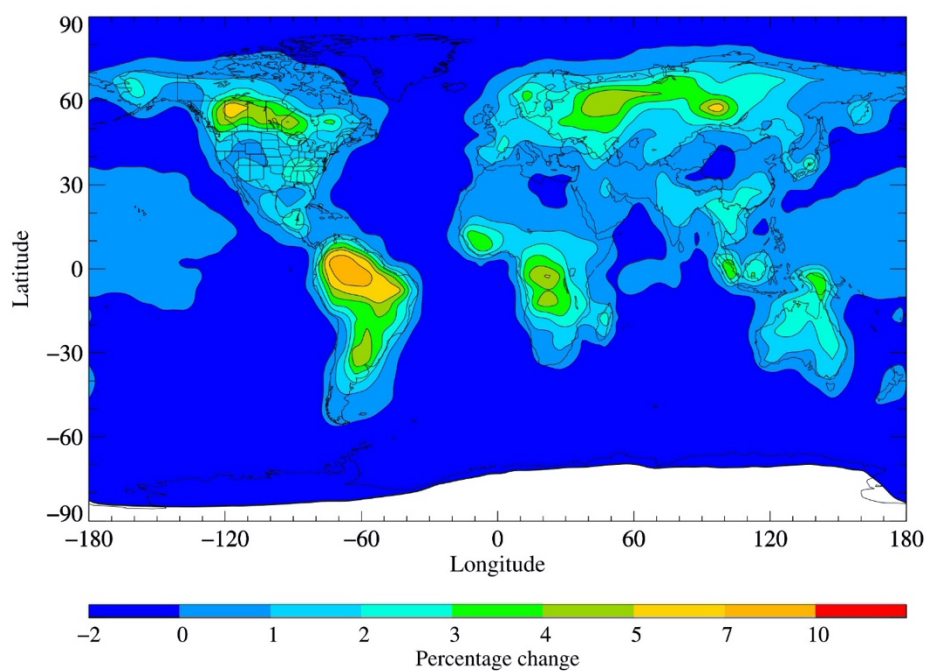


Fig. S24. Change in modelled OH concentrations after the incorporation of additional alkenes.

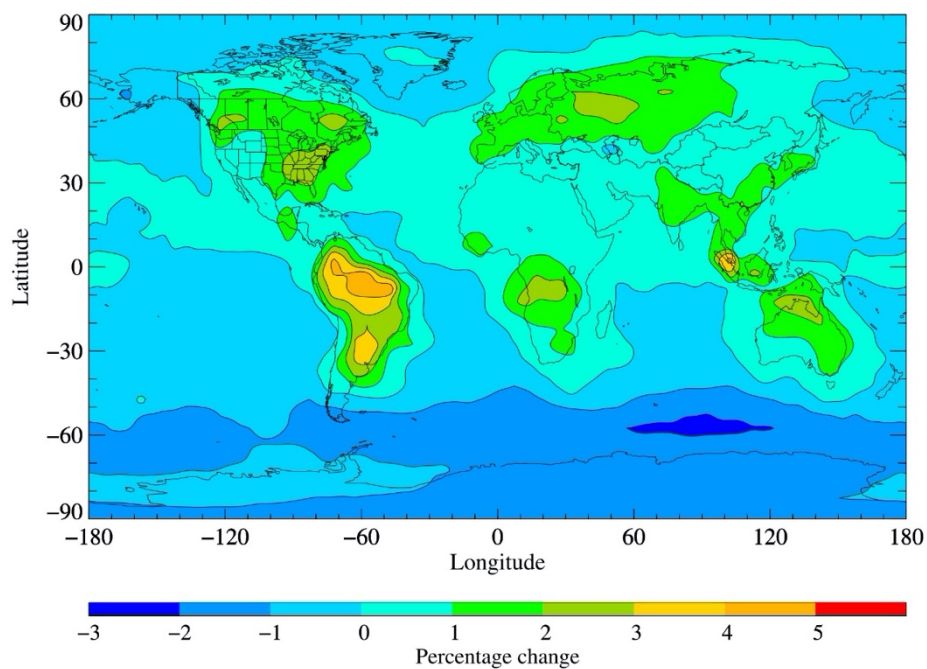


Fig. S25. Change in modelled H_2SO_4 after the incorporation of additional alkenes.

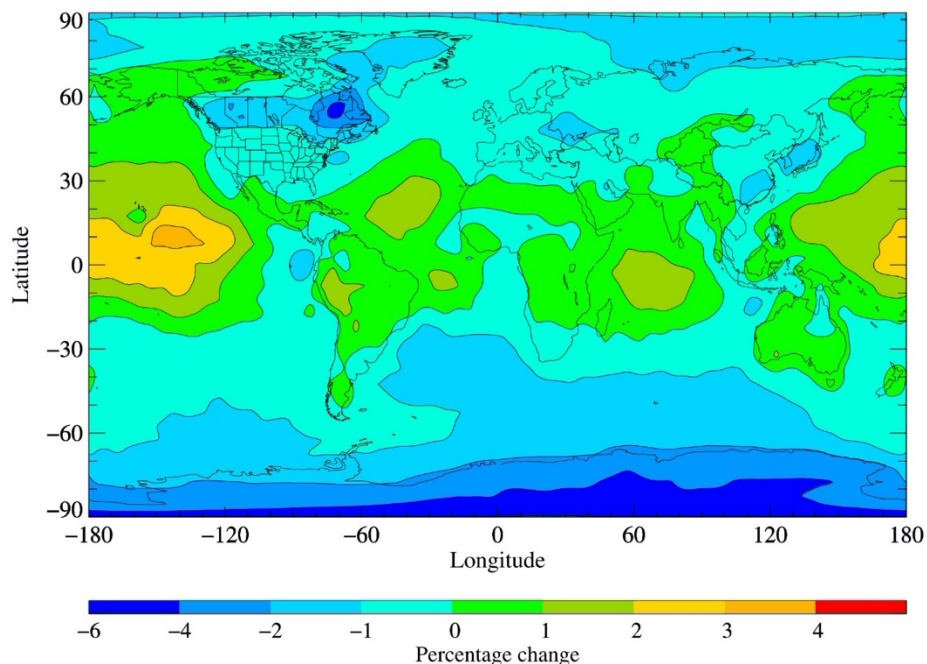


Fig. S26. Change in modelled NO_x after the incorporation of additional alkenes.

The first reports of elevated levels of OH radicals in the daytime terrestrial tropical rainforest regions were unexpected³³, and suggested that efficient OH recycling was occurring. Further measurements confirmed that elevated OH was widespread in the vegetated regions of the tropics³⁴⁻³⁹, and mechanisms were proposed to account for this recycling^{40,41}. These mechanisms centered on the isomerization of second and third generation alkoxy radicals derived from isoprene-like species. Various modelling studies have subsequently shown that high [OH] can be maintained in the presence of highly reactive [VOC] through these recycling mechanisms⁴², with a recent evaluation showing that the recycling is very efficient⁴³.

Therefore, in the current model, OH recycling mechanisms are in operation. On increasing the alkene flux, we observe a small increase in OH levels (increased production through recycling but increased loss through increased reactive VOC and their products) and minimal impact on H_2SO_4 and HNO_3 levels through OH production pathways. These results are in agreement with the study of Weber et al.,⁴⁴ who have shown that increasing BVOC emissions does not collapse the HOx budget, as a result of OH recycling.

6.4. Organic hydroperoxide species in the model.

Table S12. Summary of the organic hydroperoxides (ROOH) included in the model, and the volatile organic compounds (VOCs) which the ROOH originate from.

STOCHEM-CRI species name	Example MCM v3.3.1 analogue(s) ^a	Typical precursor
CH3OOH	CH3OOH	Many VOCs
C2H5OOH	C2H5OOH	Many VOCs
IC3H7OOH	IC3H7OOH	Many VOCs
HOC2H4OOH	HOC2H4OOH	Many VOCs
CH3CO3H	CH3CO3H	Many VOCs
C2H5CO3H	C2H5CO3H	Many VOCs
HOCH2CO3H	HOCH2CO3H	Many VOCs
RN19OOH	HEXCOOH, M2PEDOOH, M3PECOOH	≥ C ₆ VOCs
RN18OOH	C65OH4OOH, C6OH5OOH, HO2C6OOH	≥ C ₆ VOCs
RN17OOH	HEX3ONAOOH, EIPKAOOH, M2BKAOOH	≥ C ₆ VOCs
RN16OOH	PEAOOH, PEBOOH, PECOOH	≥ C ₅ VOCs
RN15OOH	C51OH2OOH, C52OH3OOH, HO2C5OOH	≥ C ₅ VOCs
RN14OOH	MPRKBOOH, DIEKAOOH, MIPKAOOH	≥ C ₅ VOCs
RN13OOH	NC4H9OOH, SC4H9OOH	≥ C ₄ VOCs
RN12OOH	HO1C4OOH, BUT2OLOOH	≥ C ₄ VOCs
RN11OOH	MEKAOOH, MEKBOOH, BUTALO2H	≥ C ₄ VOCs
RN10OOH	NC3H7OOH	≥ C ₃ VOCs
RN9OOH	HYPPO2H, IPROPOLO2H	≥ C ₃ VOCs
RN8OOH	HYPERACET, PROPALOOH, CHOC2H4OOH	≥ C ₃ VOCs
NRN12OOH	C42NO33OOH	≥ C ₄ VOCs
NRN9OOH	PR1O2HNO3, PR2O2HNO3	≥ C ₃ VOCs
NRN6OOH	ETHO2HNO3	≥ C ₂ VOCs
RU14OOH	ISOPAOOH, ISOPBOOH, ISOPCOOH, ISOPDOOH	isoprene
RU12OOH	C57OOH, C58OOH, C59OOH, HC4ACO3H, HC4CCO3H	isoprene
RU10OOH	MACROOH, MACROHOOH, MACO3H, HMKVKAOOH, HMKVKBBOOH,	isoprene
NRU14OOH	NISOPOOH	isoprene
NRU12OOH	C510OOH, NC4CO3H	isoprene
RTN28OOH	APINAOOH, APINBOOH, APINCOOH	α-pinene
RTN26OOH	PINALOOH, PERPINONIC	α-pinene
RTN25OOH	C96OOH	α-pinene
RTN24OOH	C97OOH	α-pinene

STOCHEM-CRI species name	Example MCM v3.3.1 analogue(s) ^a	Typical precursor
RTN23OOH	C98OOH	α -pinene
RTN14OOH	C614OOH	α -pinene
RTN10OOH	CO23C4CO3H	α -pinene
NRTN28OOH	NAPINAOOH, NAPINBOOH	α -pinene
RTX28OOH	BPINAOOH, BPINBOOH, BPINCOOH	β -pinene
RTX24OOH	NOPINAOOH, NOPINBOOH, NOPINCOOH, NOPIDOOH	β -pinene
RTX22OOH	C915OOH, C917OOH, C918OOH, C89CO3H	β -pinene
NRTX28OOH	NBPINAOOH, NBPINBOOH	β -pinene
RA13OOH	BZBIPEROOH	benzene
RA16OOH	TLBIPEROOH	Toluene
RA19OOH	OXYBIPEROOH	o-xylene

a: Structures can be obtained using species name and search facility on MCM website (<https://mcm.york.ac.uk/MCM/>).

6.5 Seasonal dependence of modelled sCI + ROOH oligomerization reactions

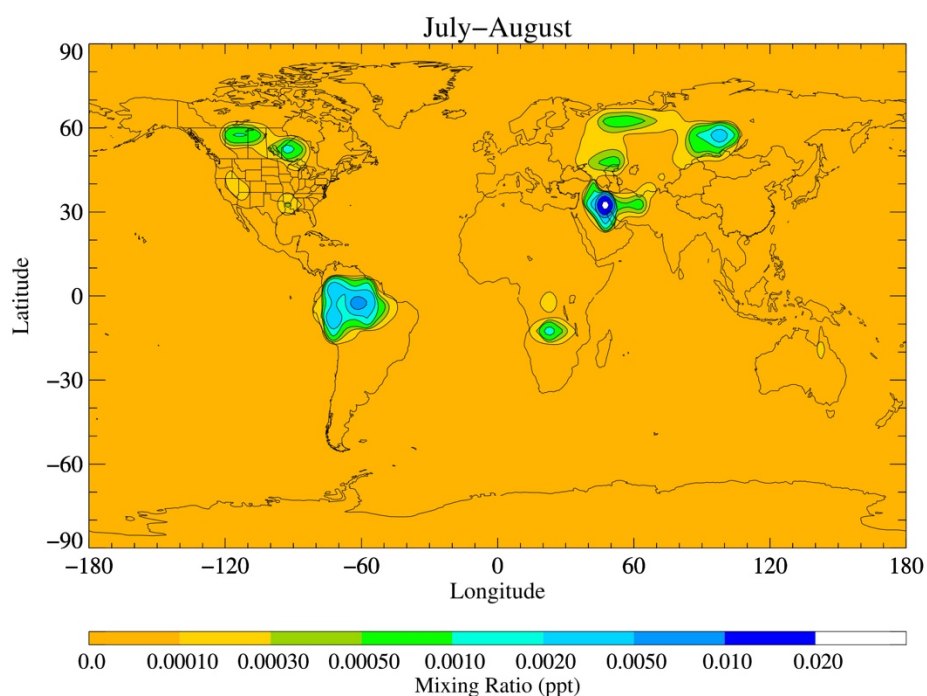


Fig. S27. Modelled mixing ratios of SOZ in July–August, resulting from $n=2$ insertions of CH_2OO into formic acid after including the modified alkene emission inventory.

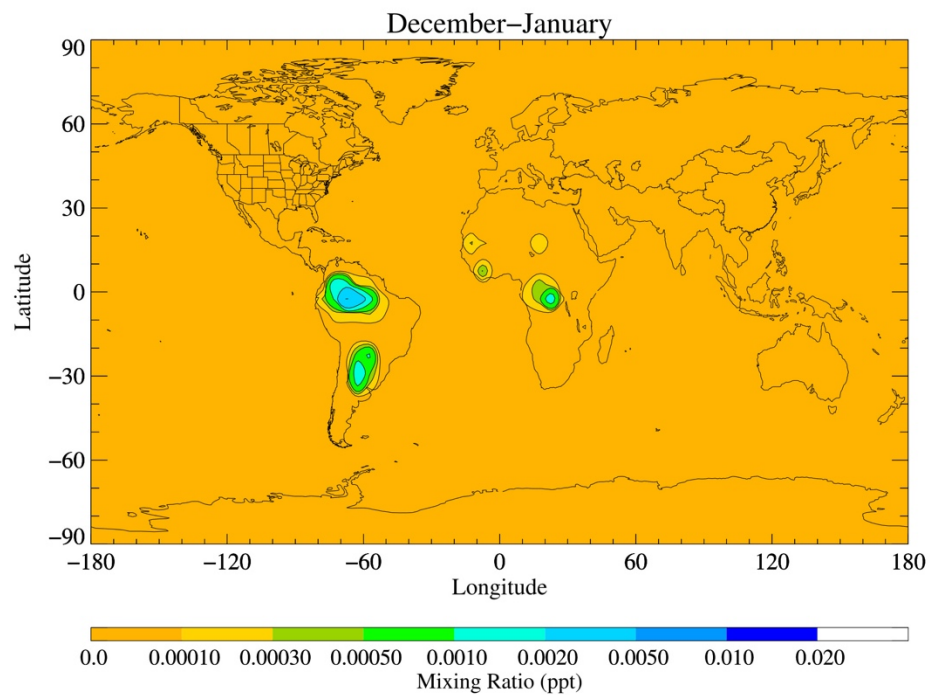


Fig S28. Modelled mixing ratios of SOZ in December–January, resulting from $n=2$ insertions of CH_2OO into formic acid after including the modified alkene emission inventory.

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