# A kinetic study of the CH<sub>2</sub>OO Criegee intermediate selfreaction, reaction with SO<sub>2</sub> and unimolecular reaction using cavity ring-down spectroscopy: Supplementary Information

Rabi Chhantyal-Pun<sup>1</sup>, Anthony Davey<sup>1</sup>, Dudley E. Shallcross<sup>1</sup>, Carl J. Percival<sup>2</sup> and Andrew J. Orr-Ewing<sup>1</sup>

## **CRDS spectrometer**

A 106-cm long, nearly confocal cavity with high reflectivity mirrors (R >99.9% at 355 nm, r = 100 cm) was used for the cavity ring down spectrometer. Probe laser radiation was passed through one of the mirrors into the cavity. The probe radiation was generated by spatially filtering the frequency doubled fundamental output from a dye laser. Spatial filtering used a pinhole and lens assembly. A New Focus 1801 photodiode detector measured the decay profile of the light transmitted from the cavity. Signal from the photodiode was digitized using a LeCroy Waverunner 6030 oscilloscope (8 bit, 350 MHz, 2.5 GSamples/s). A BNC 555 digital delay-pulse generator was used to change the delay between probe and photolysis lasers.

A LabView virtual instrument (VI) was created to acquire data from the oscilloscope and control the pulse generator. The VI also performed single exponential fits to the ring down traces and background subtraction (for the ring-down events obtained with and without photolysis laser on) at different time delays. Three successive ring-down times were averaged for both the photolysis laser on and off at each time delay. Ring-down times were weighted and averaged based on the mean square errors of the exponential fits. Ring-down times of ~5.6 microseconds with <0.5% fluctuations were obtained for empty cavity conditions at 355 nm. Temporal instrumental resolution of  $\leq$ 10 microseconds was

<sup>&</sup>lt;sup>1</sup> School of Chemistry, University of Bristol, Cantock's Close, BS8 1TS, United Kingdom

<sup>&</sup>lt;sup>2</sup> Centre for Atmospheric Science, School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Simon Building, Oxford Road, Manchester, M13 9PL, United Kingdom

expected for kinetic decay traces. Time steps of 20 and 200  $\mu$ s were used to obtain kinetic decay traces for CH<sub>2</sub>OO signals with and without added SO<sub>2</sub>, respectively.

#### Path length determination for the reactive intermediates in the cavity

Absorption of the probe 355 nm radiation by  $CH_2I_2$  ( $\sigma_{355nm} = 1.92 \times 10^{-19} \text{ cm}^2$  molecule<sup>-1</sup>) can give rise to a strong background absorption signal which results in short ring-down times and thus low sensitivity for the spectrometer. To overcome this issue, the incoming and outgoing ports were placed close to the central region of the flow tube, where the overlap of the photolysis and probe beams was maximal, to minimize the column length of  $CH_2I_2$ . Figure S1 shows the geometry of the flow tube used. As the precursor does not flow along the whole length of the flow tube, experiments were performed to calibrate the length of the region of the flow tube occupied by the  $CH_2I_2$ .



Figure S1. Schematic diagram of the layout of the flow tube and cavity ring down spectrometer, showing the overlap geometry of the photolysis and probe beams. The inset shows the overlap in detail. Geometric arguments indicate an overlap length d = 5.74 cm.

The precursor column length ( $\Box$ ) in the flow tube was measured using calibrated mixtures of  $CH_2I_2/N_2$ and  $NO_2/N_2$ . Absorption cross sections for both of these molecules are well known at 355 nm. Concentrations were calculated using the dilution ratio used to make the calibration mixture and the pressure readings taken at the centre of the flow tube. The sample distribution was approximated to be homogenous along the path length of the probe laser through the sample gas column. From measurements of the ring-down time of the cavity, the sample column lengths at 7 Torr total pressure were calculated to be  $\Box = 39 \pm 2$  and  $40 \pm 2$  cm for  $CH_2I_2/N_2$  and  $NO_2/N_2$  mixtures respectively. In both cases, uncertainties in absorption cross sections determine the precision of the measurements. These column lengths are significantly less than the full cavity length because of the confining effects of the purge gas flows and the chosen arrangement of inlet and outlet ports. Table S1 presents values of  $\Box$  for different total pressures used in the current work.

Table S1 Total precursor column lengths determined for different pressure conditions in the flow tube.

Total pressure / Torr	7	10	15	20	25	30
Sample column length / cm	39	39	36	34	38	32

The photolysis beam was introduced at a 5° angle with respect to the cavity ring down detection axis as shown in the inset in Figure S1. Geometric arguments indicate that the unfocused 5 mm diameter flat-top beam (laser manufacturer's beam profile specification in the far field) will have an overlap length, d = 5.74 cm with the probe beam around the middle section of the cavity. The probe laser beam waist at the centre of the nearly confocal cavity is 0.024 cm which is more than two orders of magnitude smaller than the overlap length and an order of magnitude smaller than the photolysis beam radius. Therefore, any effects of a Gaussian probe beam profile on the overlap are negligible.

The distribution of precursor molecules was expected to be homogenous around the centre of the flow tube (within the radical production region), as the precursor column length is nearly an order of magnitude larger than the region where the reaction kinetics are initiated and probed under all the pressure conditions we employ. Thus, the effective path length for absorption measurements of the intermediate produced in the flow tube should be determined by the overlap between the photolysis

and probe laser beams. The overall effective path length (corresponding to one ring-down time,  $\tau$ ) for the probe light through the volume in which CH<sub>2</sub>OO intermediates form and react was 90 m.

The photolysis beam has a significantly larger diameter than the probe beam, so there will be diffusion both out of and into the probe volume. Our photolysis beam has a top-hat intensity profile and a diameter of 5 mm. The probe beam diameter is 0.48 mm, and thus there will be only a very low CH<sub>2</sub>OO concentration gradient across the probe region. The radial diffusion in two concentric cylinders is expected to be a first order process, and this model is taken to be a good description of our experimental arrangement because the angle between the two cylinders is small (5°). The diffusion distance can be estimated for CH<sub>2</sub>OO based on the diffusion coefficient calculated using Chapman-Enskog theory. Using a collision integral value for diffusion of H<sub>2</sub>O in air as a lower limit for the CH<sub>2</sub>OO collision integral, diffusion coefficient values of approximately 11 and 2.6 cm<sup>2</sup> s<sup>-1</sup> were calculated for 7 and 30 Total pressures. These diffusion coefficient values translate to root mean square diffusion distance of 4.7 and 2.3 mm in 10 ms (our longest measurement times) which are within the diameter of the photolysis beam. Thus, we would not expect significant effects from diffusion in our measurements, consistent with the pure second order decay profile for CH<sub>2</sub>OO loss in the absence of SO<sub>2</sub> at total pressures from 7 to 30 Torr.

## **Flow characterization**

The Reynolds number, *Re*, for the gas flow was calculated using the following equation

$$Re = \frac{4Q}{\pi v b}$$
(S1)

where Q is the volumetric flow rate, v is the kinematic viscosity of the gas and b is the diameter of the tube. A kinematic viscosity value for nitrogen at 1 bar and 20 °C of ~1.5x10<sup>-5</sup> m<sup>2</sup>/s was used. This value is expected to increase at lower pressure and thus the calculated Re value is taken as an upper limit. The gas samples flow through tubes with diameters 0.635 cm (mass flow controller opening) and 2 cm before entering the main flow tube, which has a diameter of 6 cm. The Q value, determined by the

settings of the mass flow controllers, was expected to be constant in different diameter tubes. Table S2 shows the Re values calculated for the two tubes at the limiting values of the total volumetric flow rates used for different experiments in this work. The geometry of the main flow tube does not have a constant cross-sectional area orthogonal to the flow, making the calculation of Re value along the detection axis of the spectrometer non-trivial and beyond the scope of this work. Nevertheless, the Re value along the detection axis is expected to be smaller than the calculated values as the gases expand along the detection axis as well as orthogonal to it. At the Re values shown in Table S2, the flow should be laminar. Thus, over the different pressure conditions used for different experiments in this work, flow in the detection region of the flow tube should also be laminar. However, the arrangement of mass flow controllers connected to a 0.635 cm diameter manifold prior to the 2.0 cm tubing should ensure complete mixing of precursor gases.

Table S2 Reynolds numbers, *Re*, for the flow system calculated using Equation (S1).

Tube diameter (cm)	Re (50 sccm)	Re (500 sccm)	
0.635	10.9	109	
2	3.47	34.7	

The Knudsen number, *Kn*, for the gas flow was calculated using

$$Kn = \frac{\lambda}{L}$$
(S2)

where  $\lambda$  is the mean free path of the gas molecules and L is a representative physical length. A mean free path < 5 µm is expected for nitrogen at pressures > 7 Torr and a temperature of 20 °C. The diameter of the flow tube (6 cm) is taken as the physical length of relevance because the column length of the gases in the flow tube (~40 cm, from the previous section) should have a minimal effect. *Kn* values <0.0001 are calculated for various pressures used for the experiments in this work. At such *Kn* values, gas-gas collisions are expected to dominate over gas-wall collisions. Thus, the flow in the detection region of the flow tube is expected to be in the viscous laminar regime, dominated by gasgas collisions, over the different pressure conditions used for the experiments. Time-dependent decay signals corresponding to  $CH_2OO$  loss in the presence and in the absence of  $SO_2$  for various total pressure conditions were obtained at a 2 Hz repetition rate. No direct measurement of the dynamic flow rate of reaction species along the detection axis of the flow tube was performed in this work. However, for a range of pressure conditions, the effective  $CH_2OO$  second order decay rate coefficients (scaled by absorption cross section, see main text), k', were verified to agree (within the error of the fitted values) at measurement repetition rates of 2 and 1 Hz, as shown in Figure S2 for the case of 30 Torr total pressure. This agreement indicated that the sample refresh rate was fast enough not to affect our measurements of chemical reactivity.



Figure S2.  $CH_2OO$  signal decay traces in the absence of  $SO_2$ . Both traces were taken for the same  $CH_2I_2$ ,  $O_2$  and total (30 Torr) pressures, but at different repetition rates of the photolysis and probe lasers as indicated in the inset. The black data are the differences between the 2 Hz and 1 Hz measurements.

Total volumetric flow rates of 50 to 500 sccm were used for experiments conducted at different pressures. The cross section of the flow in the middle of the flow tube should be the product of the tube diameter (6 cm) and the sample length (< 40 cm, as measured at different total pressures). The linear flow velocity in the middle of the flow tube can be calculated by dividing the total flow rate by the flow cross section in the middle of the flow tube. Linear flow velocities of 12.5 and 125 cm s<sup>-1</sup> are

obtained for 50 and 500 sccm volumetric flow rates respectively. The flow of gas follows a path at an approximately 45 degree angle to the probe axis. Thus, the components of the linear flow velocities normal to the detection axis are 8.8 and 88 cm s<sup>-1</sup> based on geometric arguments. To cross the 5-mm photolysis beam requires 56 and 5.6 ms at 50 and 500 sccm volumetric flow rates respectively. Both time durations are much larger than the interrogation time interval for our  $CH_2OO + SO_2$  experiments, and thus mass flow should not have any effect on the pseudo rates obtained. For the  $CH_2OO + CH_2OO$  experiments, decay traces were obtained over 10 ms time intervals and they could be affected by fast flow rates at higher pressure. However, no first order contribution was observed in the  $CH_2OO$  decay traces. Thus, we conclude that mass flow should not have any significant effect on the removal of  $CH_2OO$  in our experiments.

### Effects of initial CH<sub>2</sub>OO concentration on measured rate coefficients

Figure S3 shows the k values, obtained from fits of CH<sub>2</sub>OO decay traces to equation (18), as a function of initial CH<sub>2</sub>OO concentration. The change in ring-down rate,  $\Delta \kappa$ , is directly proportional to absorbance and hence to concentration. The initial concentration of CH<sub>2</sub>OO was varied by changing the partial pressure of CH<sub>2</sub>I<sub>2</sub> in the flow tube. At low initial concentration ( $\Delta \kappa$  <25000 s<sup>-1</sup>), the R<sup>2</sup> values of second order decay fits to the time-dependent CH<sub>2</sub>OO absorbance were <0.97. We expect physical loss mechanisms like diffusion and mass flow to contribute significantly to the overall CH<sub>2</sub>OO loss in this concentration regime, which results in high effective k values and poor fit quality. At high initial concentrations ( $\Delta \kappa$  >75000 s<sup>-1</sup>), the R<sup>2</sup> values are > 0.99 and k is constant as a function of initial concentration. Second order loss processes like CH<sub>2</sub>OO self-reaction are the dominant removal mechanism under such conditions. At these higher initial concentrations, >90% of the signal decayed by a time delay of 10 ms. Effects of diffusion and mass flow are expected to be minimal over such time scales in the experiments (see above), and two pieces of evidence support this expectation under these experimental conditions: (i) plots of CH<sub>2</sub>OO concentrations against time show pure second-order decay behaviour with negligible first order contributions; (ii) the rate coefficients derived from analysis of these time-dependent concentrations do not change with value of the initial concentration. For different total pressure conditions, the CH<sub>2</sub>OO concentrations were varied such that an R<sup>2</sup> value > 0.99 was obtained for all the reported second order decay fits to the observed decay traces. The high initial absorbance limit k' value of 8.8 x 10<sup>6</sup> cm/s is greater than the value (8.24 ± 0.1) x 10<sup>6</sup> cm/s presented in the main text for the same total pressure conditions because no background interference correction (explained in detail in the next section) was performed for this value. Background correction (particularly for the depletion of CH<sub>2</sub>I<sub>2</sub> absorption by photolysis) becomes important with higher CH<sub>2</sub>I<sub>2</sub> concentrations to obtain absolute k' values, but the qualitative relative trend shown in Figure S3 is not expected to change significantly as shown by the three k' values at the highest initial absorbances.



Figure S3. k' dependence on initial  $\Delta \kappa$ , which is directly proportional to CH<sub>2</sub>OO concentration. k' values were obtained from second order fits to the CH<sub>2</sub>OO decay traces and the error bars are 1 $\sigma$  values from the fits. All decay traces were obtained at same O<sub>2</sub> and total (7 Torr) pressures, no SO<sub>2</sub> and various CH<sub>2</sub>I<sub>2</sub> pressures. 8.8 x 10<sup>6</sup> cm s<sup>-1</sup> is the weighted average k' value at the three highest initial  $\Delta \kappa$  values. The inset shows an expanded view of the last three data points.

#### Spectral interferences and background subtraction

Various molecules other than  $CH_2OO$  can absorb the 355 nm probe wavelength, and most relevant to the current study are likely to be IO, HCHO,  $CH_2I_2$  and  $ICH_2OO$ . Background absorption of the 355 nm light by the precursor  $CH_2I_2$  (absorption cross section 1.92 x  $10^{-19}$  cm<sup>2</sup> molecule<sup>-1</sup>) <sup>1</sup> was subtracted in the current measurements by taking the difference between data sets obtained with and without the photolysis laser. This method is referred to here as photolysis laser on – off. This method should also subtract out baseline losses from the cavity mirrors and the scattering of the probe light by the gas molecules inside the cavity.

HCHO is a possible product of  $CH_2OO + I$  reaction and  $CH_2OO$  self-reaction, and its concentration could be around a factor of 2 larger than the  $CH_2OO$  concentration. The HCHO cross section at 355 nm, 9.61 x 10<sup>-21</sup> cm<sup>2</sup> molecule<sup>-1</sup>, is more than 3 orders of magnitudes smaller than the  $CH_2OO$  cross section, which is on the order of 10<sup>-17</sup> cm<sup>2</sup> molecule<sup>-1</sup>.<sup>2-5</sup> Thus, we do not expect significant interference from HCHO.

The ICH<sub>2</sub>OO absorption cross-section is not well known at 355 nm because of possible interference from CH<sub>2</sub>OO in previous work. The yield of ICH<sub>2</sub>OO is expected to rise with increasing pressure, with a maximum value of  $\sim 0.25$  compared to CH<sub>2</sub>OO production at 30 Torr, and thus could interfere in absorption measurements at 355 nm.<sup>6</sup> ICH<sub>2</sub>OO interference is expected to be largest at short time delays and then decay due to reaction with CH<sub>2</sub>OO or with itself.

Figure S4 shows photolysis laser on – off traces with and without SO<sub>2</sub> ( $1.6 \times 10^{16}$  molecule cm<sup>-3</sup>). At such a high SO<sub>2</sub> concentration, a pseudo first order half-life for CH<sub>2</sub>OO of around 1 µs is expected based on previously reported CH<sub>2</sub>OO + SO<sub>2</sub> bimolecular reaction rate coefficients.<sup>2</sup> This half-life is much smaller than the time steps (200 µs) used to obtain the decay traces. ICH<sub>2</sub>OO is not expected to react quickly with SO<sub>2</sub>. Thus, the signal depletion between the two traces shown in Figure S4 should be mostly from consumption of CH<sub>2</sub>OO. However, the photolysis laser on – off trace in the presence of high SO<sub>2</sub> concentration shows a small negative signal. Within the signal-to-noise ratio of the trace, this depletion signal does not show any time dependence. Thus, it should be mainly from the depletion

of the  $CH_2I_2$  background absorption due to photo-dissociation. Photolysis laser on – off traces taken without  $SO_2$  or with low  $SO_2$  concentration were subtracted from photolysis laser on – off traces taken in the presence of a high  $SO_2$  concentration for all the  $CH_2OO$  decay traces (for  $CH_2OO + CH_2OO$  and  $CH_2OO + SO_2$  rate determination) before fitting. This approach should remove any possible spectral interference from  $ICH_2OO$  absorption and  $CH_2I_2$  depletion by photolysis.



Figure S4. Laser photolysis on - off traces obtained with and without addition of SO<sub>2</sub>. Both traces were taken at the same  $CH_2I_2$ ,  $O_2$  and total (20 Torr) pressures.

This background correction procedure does not eliminate interference from IO which is a product of  $CH_2OO + I$  reaction. The IO absorption cross section at 355 nm, 1.85 x  $10^{-18}$  cm<sup>2</sup> molecule<sup>-17</sup>, is 5-10 times smaller than that for  $CH_2OO$  and could interfere in absorption measurements at longer time delays when the  $CH_2OO$  concentration is low. To test for IO interference, we examined the  $CH_2OO$  decay traces for signs of a growing absorption at later time delays. The k' decay rate coefficient values obtained from the fits performed for background corrected decay traces with fitting windows spanning from 200 µs to 5 ms ( $k' = (12.04 \pm 0.21) \times 10^6$  cm s<sup>-1</sup>) and 200 µs to 10 ms ( $k' = (12.20 \pm 0.16) \times 10^6$  cm s<sup>-1</sup>) are within the error of the fits. This good agreement suggests that the spectral interference from IO is insignificant on a 10 ms timescale under our experimental conditions. Similar analysis performed for decay traces obtained at different total pressures also showed no significant

IO contribution. This absence of IO interference is because of the lower absorption cross section for IO compared to  $CH_2OO$  at 355 nm, as well as the slower rate of formation of IO.

#### Pressure dependence of k' for the CH<sub>2</sub>OO self-reaction

Figure 2 of the main manuscript shows an observed dependence of k' on the pressure of N<sub>2</sub> in the flow tube. We attribute this pressure dependence to changes in the yield of ICH<sub>2</sub>O<sub>2</sub> radicals following photolysis of CH<sub>2</sub>I<sub>2</sub> in the presence of O<sub>2</sub>. Higher pressures of bath gas promote branching to ICH<sub>2</sub>O<sub>2</sub> which is in competition with I-atom elimination to form CH<sub>2</sub>OO.

We have modelled the pressure dependence of the bimolecular reaction rate coefficient for the selfreaction, as plotted in figure 2, using the following scheme:

$$CH_2OO + CH_2OO \rightarrow Product 1$$
  $k_8$   
 $CH_2OO + ICH_2O_2 \rightarrow Product 2$   $k_{12}$ 

$$CH_2OO \rightarrow Product 3$$
  $k_e$ 

In the model, we fixed the values of  $k_8$  and  $k_6$  to the self-reaction (7.35 x 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) and unimolecular reaction (11.6 s<sup>-1</sup>) rate coefficients determined in this study. We used (pressure dependent) ICH<sub>2</sub>OO yields from the recent paper by Huang *et al.*<sup>8</sup> Table S3 reports the values of  $k_{12}$ we obtain to account for the pressure-dependent self-reaction rates.

Total Pressure / Torr	$k_{12}$ / 10 <sup>-10</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>		
7	2.90		
10	2.95		
15	2.88		
20	2.91		
25	3.15		
30	3.72		

Table S3 Rate coefficients for the  $CH_2OO + ICH_2O_2$  reaction estimated from the pressure-dependence of k' (figure 2).

The  $k_{12}$  values are larger than those suggested by Vereecken *et al.*<sup>9</sup> for peroxy radical + Criegee intermediate reactions by analogy with other barrierless association reactions. However, they agree well with the  $k = 2.23 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> value computed for the analogous HO<sub>2</sub> + CH<sub>2</sub>OO reaction by Long *et al.*<sup>10</sup> using transition state theory with *ab initio* calculated potential energies and structures. We estimate a limiting capture rate coefficient for the ICH<sub>2</sub>O<sub>2</sub> + CH<sub>2</sub>OO reaction of 8 x  $10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> because of long-range attractive dipole-dipole interactions between the polar ICH<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>OO. In this calculation, we used dipole moments of 2.7 D for ICH<sub>2</sub>O<sub>2</sub> and 4.5 D for CH<sub>2</sub>OO. The capture rate coefficient provides an expected upper limit for this barrierless reaction, and is a factor of at least two larger than our derived  $k_{12}$  values.

The apparent increase in  $k_{12}$  with pressure (Table S3) may simply be a consequence of Product 2 being a peroxy radical that can further react with CH<sub>2</sub>OO, with higher pressures promoting ICH<sub>2</sub>O<sub>2</sub> and hence Product 2 formation. To test this hypothesis, we extended the model above to include further reaction of Product 2 with CH<sub>2</sub>OO, and assumed a rate coefficient for this peroxy radical + Criegee intermediate reaction similar to that for the ICH<sub>2</sub>O<sub>2</sub> + CH<sub>2</sub>OO reaction. With this assumption, we obtain satisfactory fits to our observed pressure dependent rate coefficients plotted in figure 2, and an average rate coefficient for peroxy + CH<sub>2</sub>OO somewhere in the range 0.7 – 2.6 x 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, with a best-estimate average of 1.5 x 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

#### CH<sub>2</sub>OO + SO<sub>2</sub> reaction rate fitting procedures

The reaction rate of CH<sub>2</sub>OO with SO<sub>2</sub> was obtained for SO<sub>2</sub> concentrations ranging from 4 x 10<sup>13</sup> to 2 x 10<sup>14</sup> molecule cm<sup>-3</sup>. A reaction rate is desirable that is high enough to obtain pseudo first order reaction rate coefficients with the effects of processes like diffusion minimized. The temporal resolution of the current CRDS experiment ( $\leq 10 \ \mu$ s, as determined by the ring-down time) limits the observation of reaction rates to half-lives  $\geq 100 \ \mu$ s. A maximum value of the pseudo first order rate coefficient of around 8000 s<sup>-1</sup> was obtained at the highest SO<sub>2</sub> concentration, which corresponds to a minimum half-life of around 90  $\mu$ s. The reaction rate at the lowest SO<sub>2</sub> concentrations used

corresponds to a pseudo first order rate coefficient of around 2000 s<sup>-1</sup>. Under low reaction rate conditions, contributions from side reactions like the  $CH_2OO$  self-reaction can be important.

Figure S5 shows the  $k_4$  values corresponding to the CH<sub>2</sub>OO + SO<sub>2</sub> bimolecular reaction rate coefficient, obtained from linear fits to pseudo first order rate coefficients derived with and without inclusion of the self-reaction in the kinetic model. These two sets of values agree within the error of the fits due to the robustness of the pseudo first order approximation in the SO<sub>2</sub> concentration range used. However, the  $k_4$  value obtained with inclusion of the second order contribution in the analysis is slightly larger and the correction is expected to increase at lower SO<sub>2</sub> concentration values used in previously published studies of the CH<sub>2</sub>OO + SO<sub>2</sub> reaction. Inclusion of a second-order contribution is also important to obtain the intercept value in the fit which is related to the unimolecular loss of CH<sub>2</sub>OO. The intercept value obtained from a model including second-order loss is smaller by an amount outside the bounds of uncertainties of the two measurements. The contribution from the second-order mechanism is expected to increase under higher pressure conditions because the  $k^{'}$  value increases with pressure. All the  $k_4$  values reported in this work take the second-order contribution to the loss of CH<sub>2</sub>OO into account in the analysis of experimental data.



Figure S5.  $CH_2OO + SO_2$  bimolecular reaction rate coefficients,  $k_4$ , obtained using pseudo first order rates derived from either first-order (red) or simultaneous first and second-order (black) fits to  $CH_2OO$  decay trace. Error bars are 1 $\sigma$  value of the individual fits to obtain pseudo first-order rates. The slope of the fitted line gives the bimolecular reaction rate coefficient whereas the intercept value is related to the unimolecular loss of  $CH_2OO$ . The decay traces used for the rate analysis were taken at 10 Torr total pressure. Plot (I) is for the higher end of our  $SO_2$  concentration range, where bimolecular reactions with  $CH_2OO$  dominate, and plot (II) is for the lower part of the  $SO_2$  concentration range

At low  $SO_2$  concentration, an effective increase in the  $CH_2OO$  +  $SO_2$  reaction rate coefficient was observed. To analyse these observations, we propose a mechanism in which collision with  $SO_2$  can reversibly catalyse CH<sub>2</sub>OO isomerization. The calculations of Vereecken et al. suggest that singlet bisoxy (SBO) radical might be the isomerization path in question, although the reverse reaction to CH<sub>2</sub>00 is calculated to be significantly endothermic. One alternative candidate for the isomeric form (denoted *Isomer* in our generalized scheme) is a triplet state biradical (of  $CH_2OO$ , bisoxy, or perhaps another structurally distinct species). The calculations of Vereecken et al. identify that in the vicinity of the OCH<sub>2</sub>OS(0)O biradical intermediate, singlet-triplet splittings are as small as 0.4 kJ mol<sup>-1</sup>; this, or another region of near-degeneracy could favour promotion of efficient biradical intersystem crossing (ISC) in the presence of  $SO_2$ . The [SO<sub>2</sub>] dependence of the pseudo first-order reaction rate coefficients can then be explained by the set of reactions below. Reactions S3 and S4 show the reversibly catalysed isomerization or ISC of CH<sub>2</sub>00 by SO<sub>2</sub>. We note that the calculations of Vereecken et al. suggest the reverse step from singlet isomers such as SBO will be substantially endothermic and therefore unlikely, but also that the single-reference methods of calculation employed in that study are inferior to multireference methods for biradical species such as  $CH_2OO$  and SBO (as discussed by the authors of ref [9]). ISC is plausibly reversible via the initially encountered, or another region of near-degeneracy of singlet and triplet states. In the absence of an alternative mechanism to account for our observations, we are therefore forced to propose the reversibility of this isomerization/ISC process, and therefore to question the accuracy of the published electronic structure calculations, or encourage calculation of triplet biradical reaction pathways. Reaction S5 shows the unimolecular dissociation of the isomer, for example to formic acid. Reaction S6 shows the  $CH_2OO$  +  $SO_2$  bimolecular reaction leading to products such as  $SO_3$  + HCHO. Reaction S7 shows the unimolecular dissociation of  $CH_2OO$  in the absence of  $SO_2$ . Reactions S6 and S7 are labelled as reaction 4 and 6, respectively in the main text.

$$CH_200 + SO_2 \rightarrow Isomer + SO_2 \tag{S3}$$

$$Isomer + SO_2 \rightarrow CH_2OO + SO_2 \tag{S4}$$

$$Isomer \rightarrow Product$$
 (S5)

 $CH_2OO + SO_2 \rightarrow HCHO + SO_3 \tag{S6}$ 

$$CH_2OO \rightarrow Product$$
 (S7)

$$CH_2OO + CH_2OO \rightarrow Products$$
 (S8)

The change in  $[CH_2OO]$  is given by

$$\frac{d[CH_2OO]}{dt} = -(k_{S3} + k_{S6})[CH_2OO][SO_2] + k_{S4}[Isomer][SO_2] - k_{S7}[CH_2OO] -$$
(S9)

Using the steady state approximation (valid for *Isomer* as an intermediate when  $k_{S3}[CH_2OO][SO_2] \approx k_{S4}[Isomer][SO_2] + k_{S5}[Isomer]_{j,} [Isomer]$  is obtained as

$$[Isomer] = \frac{k_{S3}[CH_2OO][SO_2]}{k_{S4}[SO_2] + k_{S5}}$$
(S10)

Combining Equations (S9) and (S10) gives an equation analogous to equation (20) of the main text:

$$\frac{d[CH_2OO]}{dt} = -2k_{S8}[CH_2OO]^2 - k_{eff}[CH_2OO]$$
(S11)

with

$$k_{eff} = \frac{\left(k_{S5}(k_{S3} + k_{S6}) + k_{S6}k_{S4}[SO_2]\right)[SO_2]}{k_{S4}[SO_2] + k_{S5}} + k_{S7}$$
(S12)

Here,  $k_{eff}$  is identified as being equivalent to  $k_{pseudo}$  in the main text.

At large [SO<sub>2</sub>],  $k_{S4}$  [SO<sub>2</sub>] >>  $k_{S5}$  so  $k_{S6}$   $k_{S4}$  [SO<sub>2</sub>] >>  $k_{S6}$   $k_{S5}$ 

$$k_{eff} = k_{S6}[SO_2] + \frac{k_{S5}k_{S3}}{k_{S4}} + k_{S7}$$
(S13)

 $[SO_2]$  is not expected to change significantly during the course of the reaction and thus the pseudo first order approximation should be valid.  $k_{S5}k_{S3}/k_{S4}$  is the high pressure limiting value for the collisionally activated rate coefficient.

For small [SO<sub>2</sub>],  $k_{S4}$  [SO<sub>2</sub>] <<  $k_{S5}$ 

$$k_{eff} = (k_{S3} + k_{S6})[SO_2] + k_{S7}$$
(S14)

Thus, both SO<sub>2</sub>-catalysed isomerization/ISC and bimolecular reaction contribute to the  $k_{eff}$  value at low [SO<sub>2</sub>]. The CH<sub>2</sub>OO isomerization/ISC pathway does not destroy SO<sub>2</sub> and the change in [SO<sub>2</sub>] during the course of overall reaction depends on the relative values of  $k_{S3}$  and  $k_{S6}$ . For  $k_{S3} \gtrsim k_{S6}$  change in [SO<sub>2</sub>] should be relatively small and thus a pseudo first order approximation could still be valid for the overall reaction. Our numerical modelling confirms this to be the case.

This model can be further extended to allow the  $Isomer + SO_2$  reaction to produce  $HCHO + SO_3$  (if *Isomer* remains a singlet species, or there is further ISC back to the singlet PES):

$$Isomer + SO_2 \rightarrow HCHO + SO_3 \tag{S15}$$

If this reaction pathway is open, a steady-state analysis gives

$$k_{eff} = \frac{\left(k_{S5}(k_{S3} + k_{S6}) + \left(k_{S6}k_{S4} + k_{S6}k_{S15} + k_{S3}k_{S15}\right)\left[SO_2\right]\right)\left[SO_2\right]}{\left(k_{S4} + k_{S15}\right)\left[SO_2\right] + k_{S5}} + k_{S7}$$
(S16)

At large  $[SO_2]$ , equation (S16) reduces to:

$$k_{eff} = \frac{\left(k_{S6}k_{S4} + k_{S6}k_{S15} + k_{S3}k_{S15}\right)\left[SO_2\right]}{\left(k_{S4} + k_{S15}\right)} + \frac{k_{S5}\left(k_{S3} + k_{S6}\right)}{\left(k_{S4} + k_{S15}\right)} + k_{S7}$$
(S17)

suggesting that in the high [SO<sub>2</sub>] regime, the gradient of the pseudo first-order plot is not simply  $k_{S6}$ unless  $k_{S15} \ll k_{S4}$ .

At small [SO<sub>2</sub>], equation (S16) becomes

$$k_{eff} = (k_{S3} + k_{S6})[SO_2] + k_{S7}$$
(S18)

To test the validity of our analytical solutions to the above kinetic model, which invoke the steadystate approximation, we also carried out numerical fits for the low  $SO_2$  concentration data using a  $k_4$ value obtained from the high  $SO_2$  concentration fits, as described by the model shown below:

CH<sub>2</sub>OO + CH<sub>2</sub>OO → Product 1 
$$k_{obs}$$
 (fixed at 1.06 x 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>)  
CH<sub>2</sub>OO + SO<sub>2</sub> → Product 2  $k_4$  (fixed at 3.93 x 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>)

$$CH_2OO \rightarrow Product 3$$
  $k_{uni}$  (floated)

The  $k_{obs}$  value was fixed to the effective CH<sub>2</sub>OO second order loss rate coefficient value at 10 Torr total pressure. The  $k_4$  value was fixed to the slope value of the linear fit obtained for the pseudo first order rate values at the four highest SO<sub>2</sub> concentrations at 10 Torr total pressure. The values of  $k_{uni}$  obtained by this numerical analysis are plotted in Figure S6 as a function of SO<sub>2</sub> concentration, and the low- SO<sub>2</sub> concentration regime is fitted to a straight line. Comparison with equation (S18) shows that the gradient of this line should be equal to  $k_{s3}$  because  $k_{s6}$  has already been included in the numerical fits, and we observe excellent agreement in the  $k_{s3}$  values obtained by the two analysis methods {(3.53 ± 0.32) × 10<sup>-11</sup> and (3.87 ± 0.31) × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>}.

There is a contribution from the CH<sub>2</sub>OO unimolecular loss process on top of the CH<sub>2</sub>OO + SO<sub>2</sub> reaction that depends on [SO<sub>2</sub>]. This observation and our numerical modelling of reaction rates at low [SO<sub>2</sub>] (see later) indicate that the curvature is not simply attributable to transition from a first to second order process (in part because the self-reaction rate of CH<sub>2</sub>OO exceeds that of CH<sub>2</sub>OO + SO<sub>2</sub>). Moreover, we suggest that there is evidence of similar curvature in the data of Sheps,<sup>2</sup> as shown in figure S7. Comparison with the analytical kinetic model suggests that in the high [SO<sub>2</sub>] limit,  $k_{uni} =$ 

 $\frac{k_{S5}k_{S3}}{k_{S4}} + k_{S7}$  (see equation (S13)) whereas as  $[SO_2] \rightarrow 0$ ,  $k_{uni} \rightarrow k_{S7}$  (or, more precisely, an upper limit for  $k_{S7}$  because of small contributions from diffusion and mass flow to the unimolecular loss of

CH<sub>2</sub>OO). The intercept value obtained from the linear fit of the low SO<sub>2</sub> concentration  $k_{uni}$  values is 16 ± 9 s<sup>-1</sup> which agrees with the values obtained by analytical fitting (e.g. see figure S5). The  $k_{uni}$  values obtained from numerical fits using the FACSIMILE program are listed in Table S5.



Figure S6. Dependence of the unimolecular decomposition rate coefficient for  $CH_2OO$  on  $[SO_2]$  as derived from numerical fits to  $CH_2OO + SO_2$  kinetic data.



Figure S7. Comparison of pseudo first order rate coefficients for the CH<sub>2</sub>OO + SO<sub>2</sub> reaction from the current work (black circles), and from the study by Sheps [Ref. 2] (blue triangles).

In support of our interpretation of behaviour special to  $SO_2$ , we note that our very recent studies of reactions of  $CH_2OO$  with organic acids (under the same flow and pressure conditions as we used for the  $CH_2OO + SO_2$  study) do not show curvature of the pseudo first order plots at the lower end of the organic acid concentration range. Moreover, the intercepts of these plots give a unimolecular loss that is  $\leq 11.6 \text{ s}^{-1}$ , not the 700 s<sup>-1</sup> we would obtain from the  $CH_2OO + SO_2$  data without our more complete kinetic analysis. These experimental data will be published elsewhere. The chemistry of

 $CH_2OO + SO_2$  is much more complex than the published pseudo first-order kinetic studies have so far recognized and we propose a plausible hypothesis here that brings the unimolecular decay rate coefficients into much better agreement with theory.

# Reaction rate coefficients as a function of total pressure

Table S4.  $CH_2OO + CH_2OO$  reaction rate coefficient scaled by  $CH_2OO$  absorption cross section,  $k' = k_{obs}/\sigma_{355nm}$ ,  $CH_2OO + SO_2$  reaction rate coefficient,  $k_4$ , and the intercept from the linear fit 1 as shown in figure 8 as a function of total pressure (balance N<sub>2</sub>).

Total Pressure (Torr)	k' (10 <sup>6</sup> cm s-1)	<i>k</i> <sub>4</sub> (10 <sup>-11</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	Intercept from linear fit 1 (s <sup>-1</sup> )
7	8.24±0.09		
10	9.37±0.13	3.93±0.13	629±147
15	10.6±0.09	3.99±0.12	695±125
20	12.20±0.16	3.73±0.05	736±58
25	13.31±0.16	3.92±0.15	581±186
30	14.31±0.23	4.06±0.24	549±281

Table S5. First-order  $CH_2OO$  loss rates used to generate Figure S5 and Figure S6.  $k_{pseudo1}$ ,  $k_{pseudo2}$  and  $k_{uni}$  were obtained from first order, simultaneous first + second order and FACSIMILE fits respectively.

[SO <sub>2</sub> ] (10 <sup>12</sup> molecule cm <sup>-3</sup> )	k <sub>pseduo1</sub> (s <sup>-1</sup> )	k <sub>pseduo2</sub> (s <sup>-1</sup> )	<i>k<sub>uni</sub></i> (s⁻¹)
1.08	436 ± 21	92 ± 6	56 ± 5
2.16	564 ± 25	171 ± 7	100 ± 6
4.32	775 ± 26	349 ± 12	199 ± 10
6.48	929 ± 29	482 ± 16	252 ± 13
8.64	1054 ± 27	613 ± 20	301 ± 17
8.64	1226 ± 28	649 ± 21	345 ± 17
13.0	1496 ± 19	902 ± 21	429 ± 18
17.3	1782 ± 24	1203 ± 28	565 ± 24
21.6	1953 ± 31	1396 ± 36	595 ± 31
25.9	2181 ± 37	1627 ± 41	656 ± 35
25.9	1973 ± 30	1530 ± 35	545 ± 30
30.2	2193 ± 39	1787 ± 47	606 ± 39
34.6	2361 ± 27	1939 ± 37	636 ± 33
38.9	2658 ± 29	2259 ± 42	767 ± 36
43.2	2750 ± 27	2361 ± 38	543 ± 27
43.2	2662 ± 21	2194 ± 31	705 ± 32
86.4	4555 ± 59	4037 ± 69	693 ± 58
130	6287 ± 125	5616 ± 137	580 ± 114
173	8263 ± 159	7550 ± 182	798 ± 151
216	9896 ± 310	9035 ± 342	590 ± 326

#### Numerical modelling of the CH<sub>2</sub>OO + SO<sub>2</sub> reaction at low [SO<sub>2</sub>]

Numerical simulations were performed for reaction of CH<sub>2</sub>OO with SO<sub>2</sub> at low SO<sub>2</sub> concentration using FACSIMILE to test the validity of a pseudo first order approximation in regimes where the concentrations of SO<sub>2</sub> and CH<sub>2</sub>OO are comparable. The approximation is robust only if the concentration of SO<sub>2</sub> does not change significantly over the course of our measurements. Simulations were performed for different initial [SO<sub>2</sub>] with fixed values of the initial concentration of CH<sub>2</sub>OO + CH<sub>2</sub>OO corresponding to experimental values. Rate coefficients for the CH<sub>2</sub>OO + SO<sub>2</sub> and CH<sub>2</sub>OO + CH<sub>2</sub>OO reactions were chosen that are appropriate for 10 Torr, using values determined in this work ( $k_4$  = 3.93 x 10<sup>-11</sup> cm<sup>2</sup> molecule<sup>-1</sup> and  $k_{obs}$  = 1.06 x 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). Figure S7 shows concentration profiles of all the chemical species involved in the reactions for the lowest initial [SO<sub>2</sub>] value used in our experiments (1.08 × 10<sup>12</sup> cm<sup>-3</sup>).

Similar simulations were carried out for other initial  $SO_2$  concentrations and the results are summarized in Table S6. In all cases, use of a pseudo first order approximation is validated; the fast  $CH_2OO$  self-reaction rate ensures only small changes in [SO<sub>2</sub>]. The simulated time-dependences of [ $CH_2OO$ ] fit very well to combined first and second order decay terms, as used in our experimental data fitting.

Table S6. Changes in SO<sub>2</sub> concentration obtained from numerical simulations of the  $CH_2OO + SO_2$  reaction system for different initial concentrations of SO<sub>2</sub> under conditions typical of our experiments. The pseudo first-order rate coefficients obtained for  $CH_2OO + SO_2$  reaction are also listed.

Initial $[SO_{2}] / 10^{12} \text{ cm}^{-3}$	1 08	2 16	4 32	8 64
	1.00	2.10	1.52	0.01
Final [SO <sub>2</sub> ] / 10 <sup>12</sup> cm <sup>-3</sup>	0.71	1.45	3.04	6.55
	-	_		
Change / %	24	22	27	24
Change / 70	54	55	27	Z4
$k / s^{-1}$	33 85 + 0 37	68 03 + 0 70	1392+013	2913+21
Npseudo / S	55.05 ± 0.57	00.05 ± 0.70	$135.2 \pm 0.1.3$	251.5 - 2.1
Final [SO <sub>2</sub> ] / 10 <sup>12</sup> cm <sup>-3</sup> Change / % k <sub>pseudo</sub> / s <sup>-1</sup>	0.71 34 33.85 ± 0.37	1.45 33 68.03 ± 0.70	3.04 27 139.2 ± 0.1.3	6.55 24 291.3 ± 2.1



Figure S8. Top: Simulated changes in concentration of key species in the  $CH_2OO + SO_2$  reaction system for an initial concentration of  $SO_2$  of 1.08 x  $10^{12}$  cm<sup>-3</sup> and an initial concentration of  $CH_2OO$  typical of our experimental conditions. Bottom: Fit of the simulated  $CH_2OO$  decay profile to analytical first and second order kinetic functions.

# References

- S. P. Sander, J. Abbatt, J. R. Barker, J. B. Burkholder, R. R. Friedl, D. M. Golden, R. E. Huie, C. E. Kolb, M. J. Kurylo, G. K. Moortgat, V. L. Orkin and P. H. Wine, National Aeronautics and Space Administration, Jet Propulsion Laboratory California Institute of Technology Pasadena, California 2011, pp. 4H-15.
- 2. L. Sheps, J. Phys. Chem. Lett., 2013, 4, 4201-4205.
- 3. W. L. Ting, Y. H. Chen, W. Chao, M. C. Smith and J. J. M. Lin, *Phys. Chem. Chem. Phys.*, 2014, **16**, 4039-4049.
- 4. J. M. Beames, F. Liu, L. Lu and M. I. Lester, J. Am. Chem. Soc. , 2012, **134**, 20045-20048.
- S. P. Sander, J. Abbatt, J. R. Barker, J. B. Burkholder, R. R. Friedl, D. M. Golden, R. E. Huie, C. E. Kolb, M. J. Kurylo, G. K. Moortgat, V. L. Orkin and P. H. Wine, National Aeronautics and Space Administration, Jet Propulsion Laboratory California Institute of Technology Pasadena, California2011, pp. 4D-5.
- 6. D. Stone, M. Blitz, L. Daubney, T. Ingham and P. Seakins, *PCCP*, 2013, 19119-19124.
- S. P. Sander, J. Abbatt, J. R. Barker, J. B. Burkholder, R. R. Friedl, D. M. Golden, R. E. Huie, C. E. Kolb, M. J. Kurylo, G. K. Moortgat, V. L. Orkin and P. H. Wine, National Aeronautics and Space Administration, Jet Propulsion Laboratory California Institute of Technology Pasadena, California2011, pp. 4H-5.
- 8. H. Huang, A. J. Eskola and C. A. Taatjes, *J. Phys. Chem. Lett.*, 2012, **3**, 3399-3403.
- 9. L. Vereecken, H. Harder and A. Novelli, *Phys. Chem. Chem. Phys.*, 2012, **14**, 14682-14695.
- B. Long, X.-F. Tan, Z.-W. Long, Y.-B. Wang, D. S. Ren and W.-J. Zhang, J. Phys. Chem. A, 2011, 115, 6559-6567.