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Electronic Supplementary Information

Kinetics of the simplest Criegee intermediate reaction with ozone studied by high resolution mid-infrared quantum cascade laser spectrometer

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I. Experimental conditions and tests of possible factors of interference

Table S1. Summary of the experimental conditions and effective rate coefficients of CH_2OO reaction with O_3 at 298 K.

Expt. #[a]	P_{CH2I2} / mTorr	Laser fluence / mJ cm^{-2}	$[CH_2OO]_0$ / 10^{11} cm^{-3}	$P_{Total} = P_{O2}$ / Torr	k_0 / sec^{-1}	k_{incpt} / sec^{-1}	k_{O3} / 10^{-14} cm^3 sec^{-1}	Number of data points
1	1.9	19.9	8.0	30.3	207.3	303.4	6.95±0.16	18
2	2.2	7.5	3.6	30.5	88.8	158.4	5.88±0.21	19
3	1.2	19.9	4.5	30.2	111.0	190.0	5.78±0.16	22
4	1.8	16.9	6.8	30.1	145.1	244.9	6.72±0.12	20
5	3.9	24.9	20.1	30.1	375.8	647.4	6.94±0.25	16
6	4.1	12.4	9.2	30.3	207.5	326.9	6.77±0.10	19
7	6.9	14.9	17.6	30.4	364.7	580.3	7.49±0.27	21
8	6.9	11.2	15.4	30.2	313.6	493.3	7.28±0.22	20
9	6.9	19.9	21.2	30.0	436.0	732.6	6.71±0.18	20
10	1.6	7.5	2.0	29.4	74.2	87.9	6.84±0.23	18
11	1.8	7.5	2.4	30.0	80.7	120.7	6.40±0.09	45
12	3.4	19.6	11.0	30.2	261.0	386.9	6.95±0.17	20
13	1.2	16.9	4.0	30.0	110.0	169.3	6.28±0.17	20
14	3.1	13.0	7.1	100.3	156.4	191.4	7.08±0.20	21
Average							6.72±0.46[b]	

a. The IR pulse period in Expt. 10−13 was 18 μs, 120μs for the rest.

b. The error bar is one standard deviation.

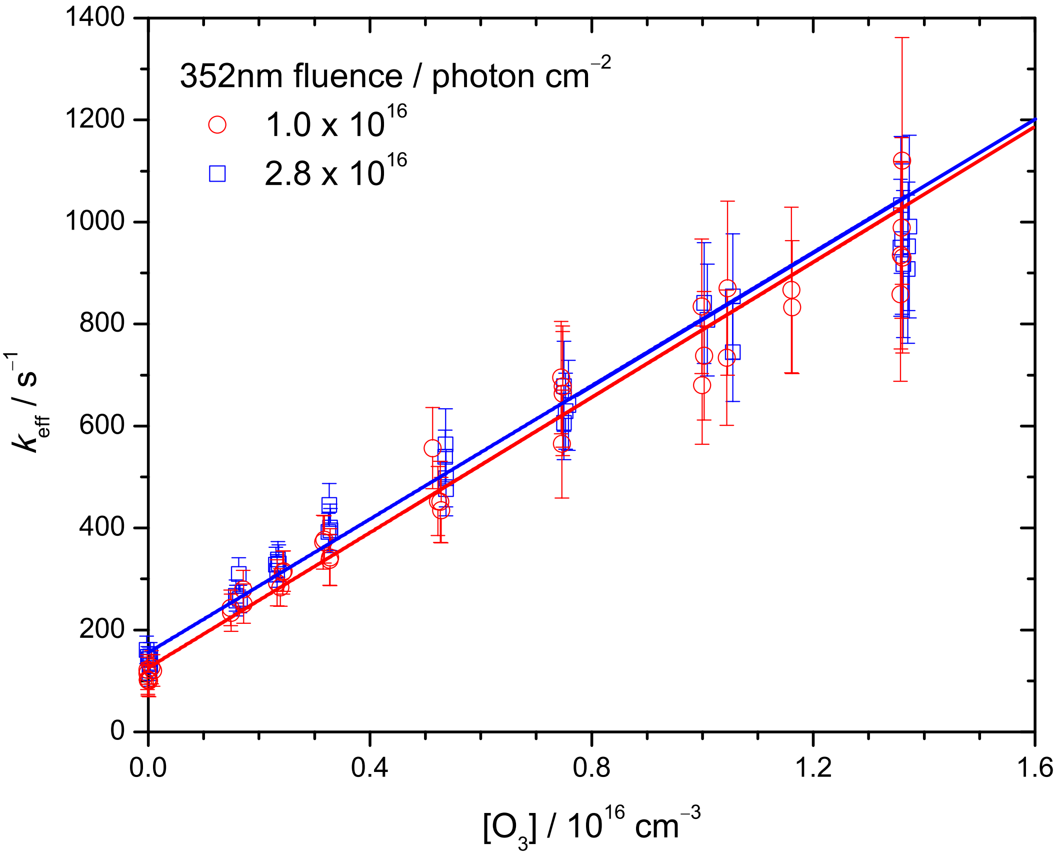

FIG. S1. Effect of the photolysis laser fluence in the kinetics of CH_2OO reaction with O_3 (expt. 2 and 3). k_{eff} is the effective first-order rate coefficient of CH_2OO decay.

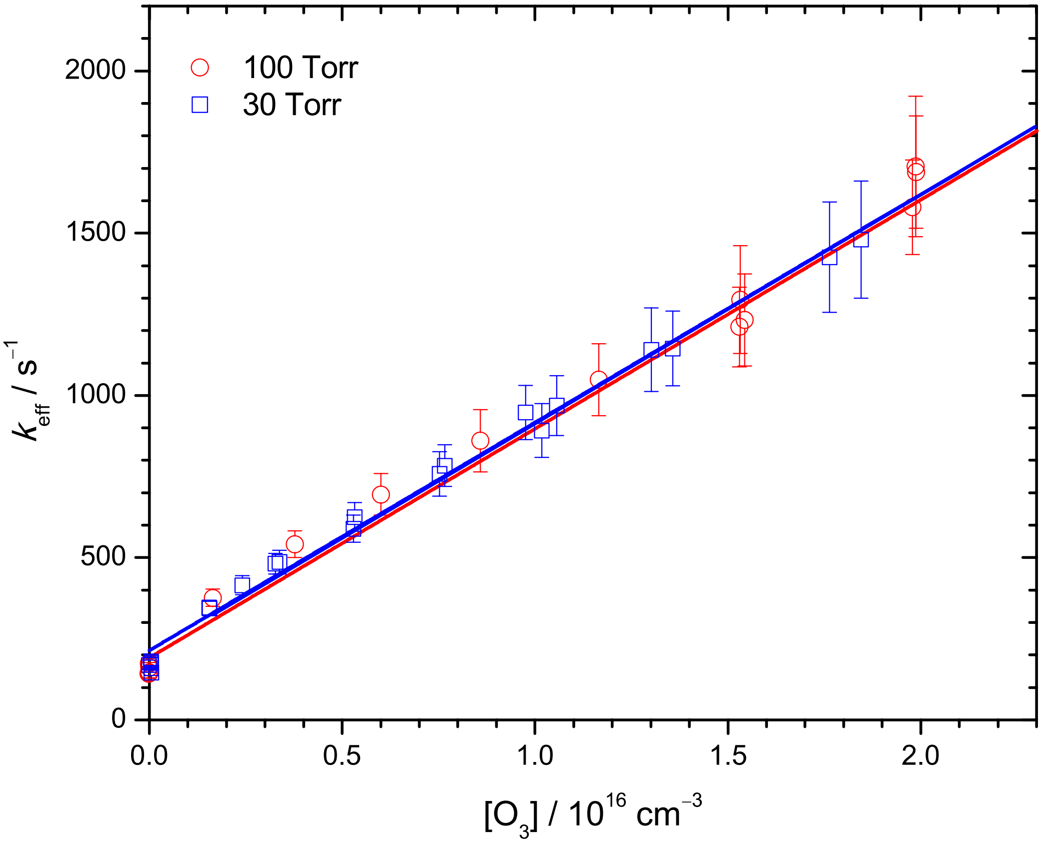

FIG. S2. Effect of the total pressure in the kinetics of CH_2OO reaction with O_3. (expt. 4 and 14). k_{eff} is the effective first-order rate coefficient of CH_2OO decay.

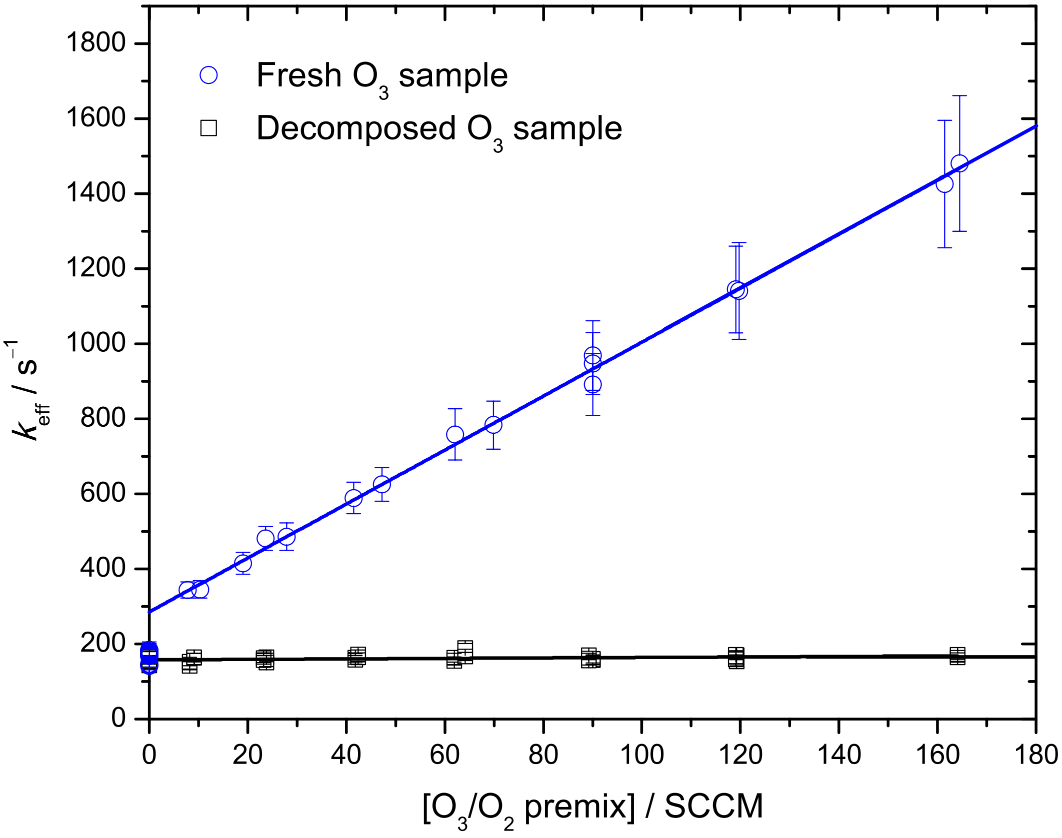

FIG. S3 Effective CH_2OO decay rate coefficient (k_{eff}) as a function of the reactant gas (O_3/O_2 premix) flow rate. SCCM stands for standard cubic centimeter per minute. The total flow rate was kept at 760 sccm (O_2 balance). The “fresh ozone sample” means the ozone gas prepared within 3 hours and kept under dry-ice temperature (~200 K) (expt. 4); the “decomposed ozone sample” means the ozone gas prepared 3 days ago and kept under room temperature until all ozone had fully decomposed. Other experimental conditions were kept the same. No reaction can be observed by using the “dead ozone” gas, indicating negligible effect of the impurity in the ozone gas.

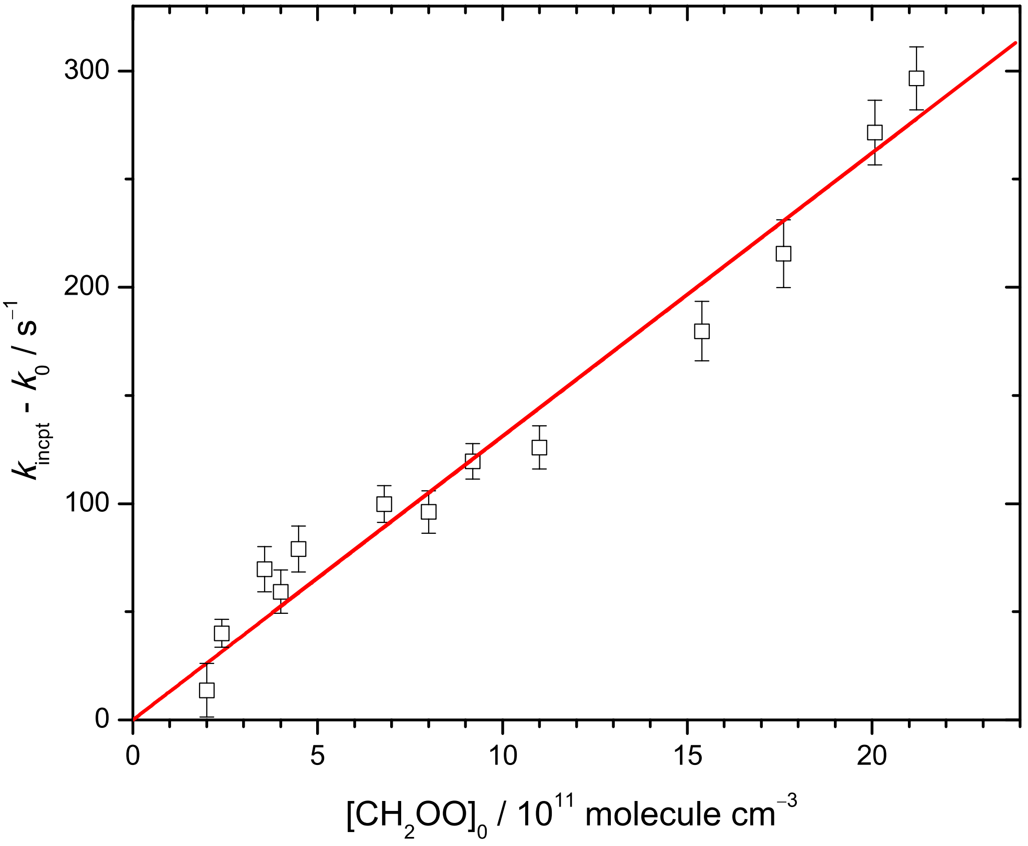

FIG. S4 Difference between the k_{incpt} (intercept of k_{eff}) and the measured k_0 as a function of [CH$_2$OO]$_0$. See the main text for details.

II. Kinetic modelling

To gain more insights from the concentration-time profiles of CH_2OO obtained in this work, we adapted the kinetic model developed by Ting *et al.*[1] to describe the CH_2I_2/O_2 photolysis system. The used rate coefficients are listed in Table S2, which uses the same notations of rate coefficients as Ting *et al.*[1] In addition, we added 3 more reactions,

$O_3 + I \rightarrow IO + O_2$ $\quad k_8$

$O_3 + CH_2OO \rightarrow CH_2O + 2O_2$ $\quad k_9$

$IO + CH_2OO \rightarrow CH_2O + IO_2$ $\quad k_{10}$

to describe the kinetics when O_3 is present.

Figure S5 shows the simulated time profiles of CH_2I, I, ICH_2OO, H_2CO, IO, CH_2OO, which show reasonable agreement with the recorded time profile of CH_2OO without O_3. Figure S6 shows the simulated time profiles of various species under $[O_3] = 1.7\times10^{15}$ cm^{-3}. Figures S6 and S7 show the simulated time profiles of CH_2OO at various concentrations of O_3, under the conditions of low and high $[CH_2OO]_0$, respectively. Each figure also includes the simulated time profiles with and without considering the reaction of CH_2OO with IO ($k_{10} = 1.50 \times 10^{-10}$ or 0 cm^3 s^{-1}). As shown in these two Figures, the simulations assuming $k_{10} = 0$ do not agree with the experimental data.

Table S2 Rate coefficients used in the kinetic model.

Reaction			Rate coefficient[a]	
			Fig. S3-S5[b]	Fig S6[b]
$CH_2I + O_2 \rightarrow CH_2OO + I$	k_{1a}'	=	1.09×10^{-12}	1.11×10^{-12}
$CH_2I + O_2 \rightarrow ICH_2OO$	k_{1b}	=	2.92×10^{-13}	1.30×10^{-13}
$CH_2I + O_2 \rightarrow$ products other than CH_2OO or ICH_2OO	k_{1c}	=	1.21×10^{-13}	2.60×10^{-13}
$CH_2OO + I \rightarrow CH_2I + O_2$	k_{2a}	=	6.65×10^{-11}	7.54×10^{-11}
$CH_2OO + I \rightarrow ICH_2OO$	k_{2b}	=	1.60×10^{-11}	7.13×10^{-12}
$CH_2OO + I \rightarrow H_2CO + IO$	k_{2c}	=	9.00×10^{-12}	9.00×10^{-12}
$CH_2OO + CH_2OO \rightarrow 2H_2CO + O_2$	k_3	=	8.00×10^{-11}	
$ICH_2OO + ICH_2OO \rightarrow 2ICH_2O + O_2$	k_4	=	9.00×10^{-11}	
$ICH_2OO + I \rightarrow ICH_2O + IO$	k_5	=	3.50×10^{-11}	
$ICH_2O \rightarrow H_2CO + I$	k_6	=	1.00×10^{5}	
$IO + IO \rightarrow$ products	k_7	=	9.90×10^{-11}	
$O_3 + I \rightarrow IO + O_2$	k_8	=	1.28×10^{-12}	
$O_3 + CH_2OO \rightarrow CH_2O + 2O_2$	k_9	=	6.72×10^{-14}	
$IO + CH_2OO \rightarrow CH_2O + IO_2$	k_{10}	=	1.50×10^{-10}	

a. unit for k_6 is s^{-1}, unit of the other rate coefficients is $cm^3\ sec^{-1}$.

b. k_1 to k_7 are derived from the kinetic model of Ref. 1 using $y = 0.73$ and $\beta = 0.90$ for $P_{Total} = P_{O2} = 30$ Torr (Figure S3-S5) and $y = 0.74$ and $\beta = 0.81$ for $P_{Total} = P_{O2} = 30$ Torr (Figure S6). k_8 is from Ref. 2. k_9 is from this work. k_{10} is derived from this simulation.

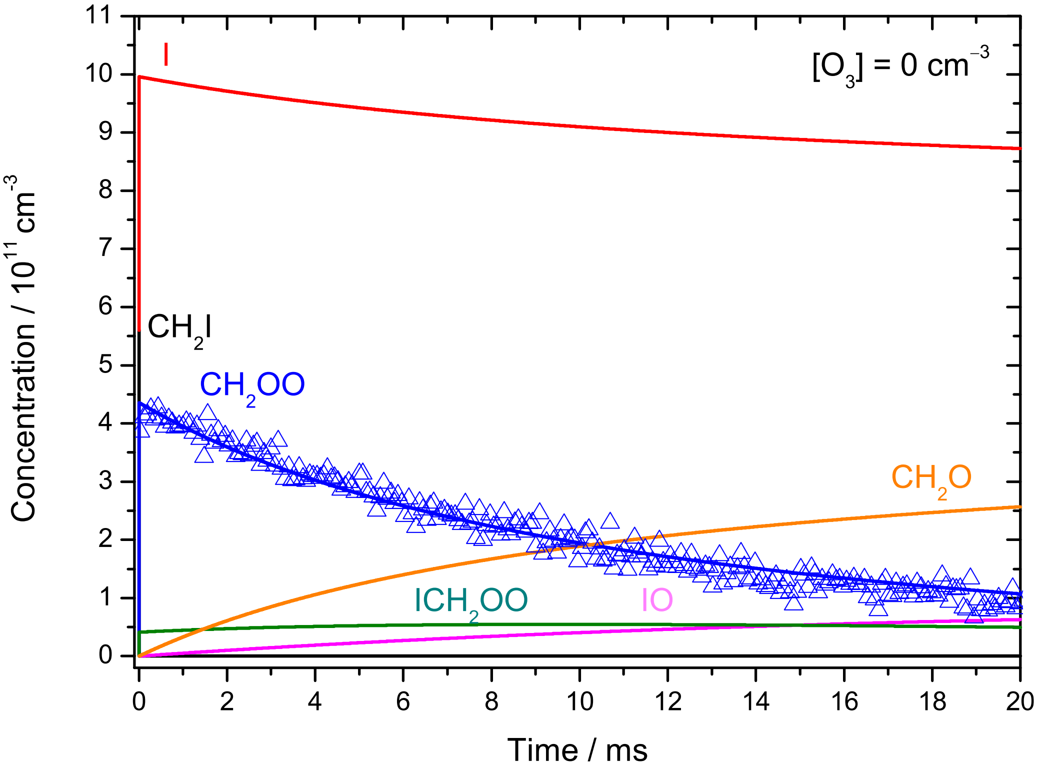

Figure S5 Concentrations of IO (pink), CH_2OO (blue), CH_2I (black), ICH_2OO (green), I (red) and CH_2O (orange) simulated with a model described in Ref. 1 are shown as lines. The rate coefficients used are listed in Table S2. The initial conditions are: $[CH_2I]_0 = 5.6\times10^{11}$ cm^{-3}, $P_{\text{Total}} = P_{\text{O2}} = 30$ Torr . $[O_3] = 0$ cm^{-3}. The temporal profile of CH_2OO recorded upon photolysis of a mixture of CH_2I_2/O_2 (0.01 Torr/30 Torr) at 298 K in Figure 2 (expt. 11) is also shown as symbol Δ. Under the same condition, the measured $[CH_2OO]_{\text{max}}$ by UV absorption is 2.4×10^{11} cm^{-3}.

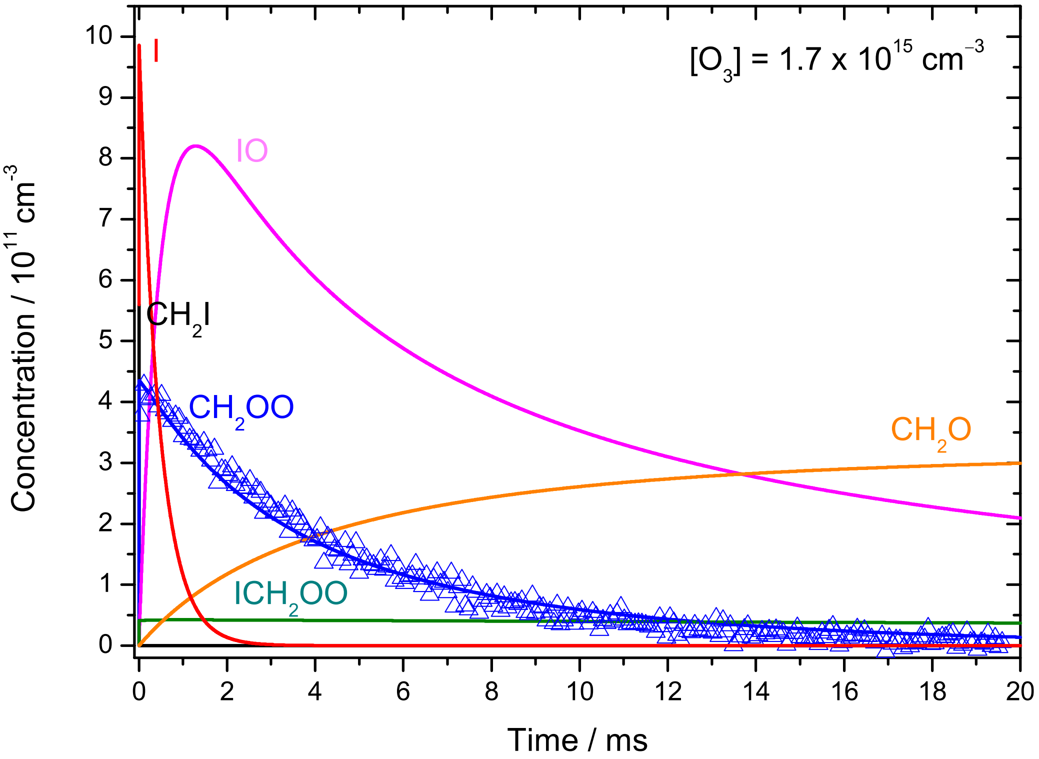

Figure S6 Concentrations of IO (pink), CH_2OO (blue), CH_2I (black), ICH_2OO (green), I (red) and CH_2O (orange) simulated with a model described in Ref. 1 (with 3 more reactions added, k_8 to k_{10}, for $[O_3]>0$) are shown as lines. The rate coefficients used are listed in Table S2. The initial conditions used are: $[CH_2I]_0 = 5.6\times10^{11}$ cm^{-3}, $P_{\mathrm{Total}} = P_{\mathrm{O2}} = 30$ Torr. $[O_3] = 1.7\times10^{15}$ cm^{-3}. The temporal profile of CH_2OO recorded upon photolysis of a mixture of CH_2I_2/O_2 (0.01 Torr/30 Torr) at 298 K in Figure 2 (expt. 11) is also shown as symbol Δ. Under the same condition, the measured $[CH_2OO]_{\max}$ by UV absorption is 2.4×10^{11} cm^{-3}.

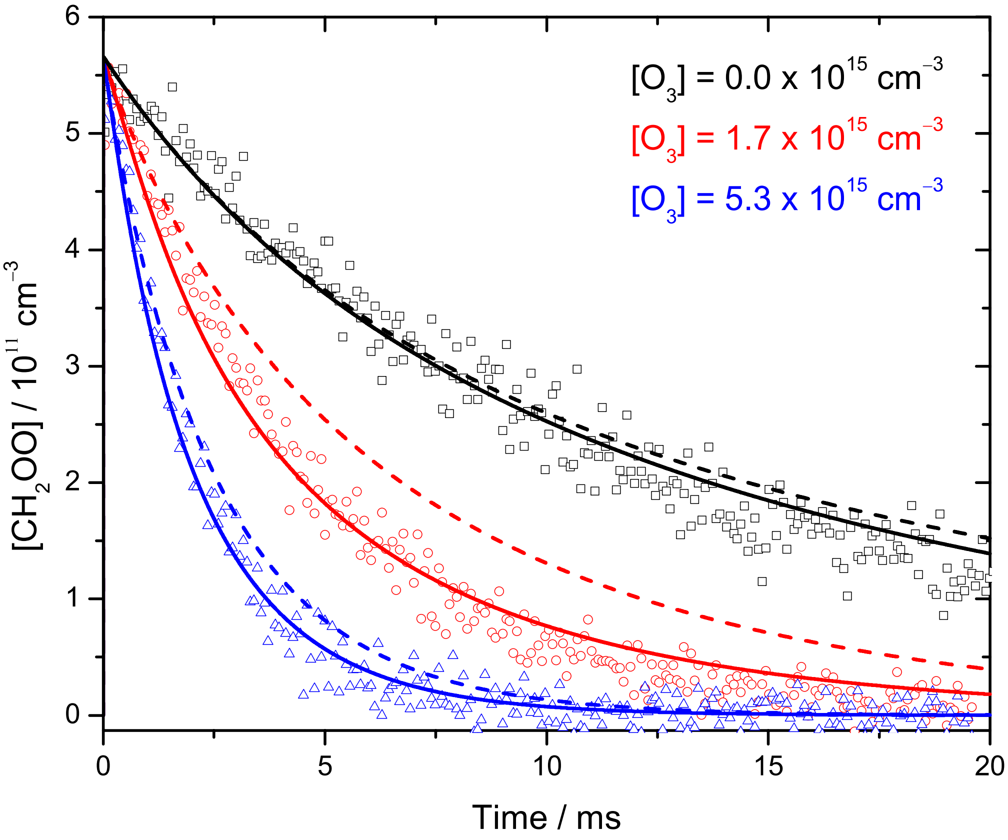

Figure S7 $[CH_2OO]$ time profiles under different $[O_3]$ simulated with a model described in Ref. 1 (with 3 more reactions added, k_8 to k_{10}, for $[O_3]>0$) are shown as solid lines. The rate coefficients used are listed in Table S2. The dashed lines are modeled profiles without considering the reaction of CH_2OO with IO (by setting k_{10} to 0). The initial conditions used in this simulation are: $[CH_2I]_0 = 5.6\times10^{11}$ cm^{-3}, $P_{\text{Total}} = P_{O2} = 30$ Torr. The temporal profiles of CH_2OO recorded upon photolysis of a mixture of CH_2I_2/O_2 (0.01 Torr/30 Torr) at 298 K under different $[O_3]$ are shown as symbols (expt. 11). Under the same condition, the measured $[CH_2OO]_{\text{max}}$ by UV absorption is about 2.5×10^{11} cm^{-3}.

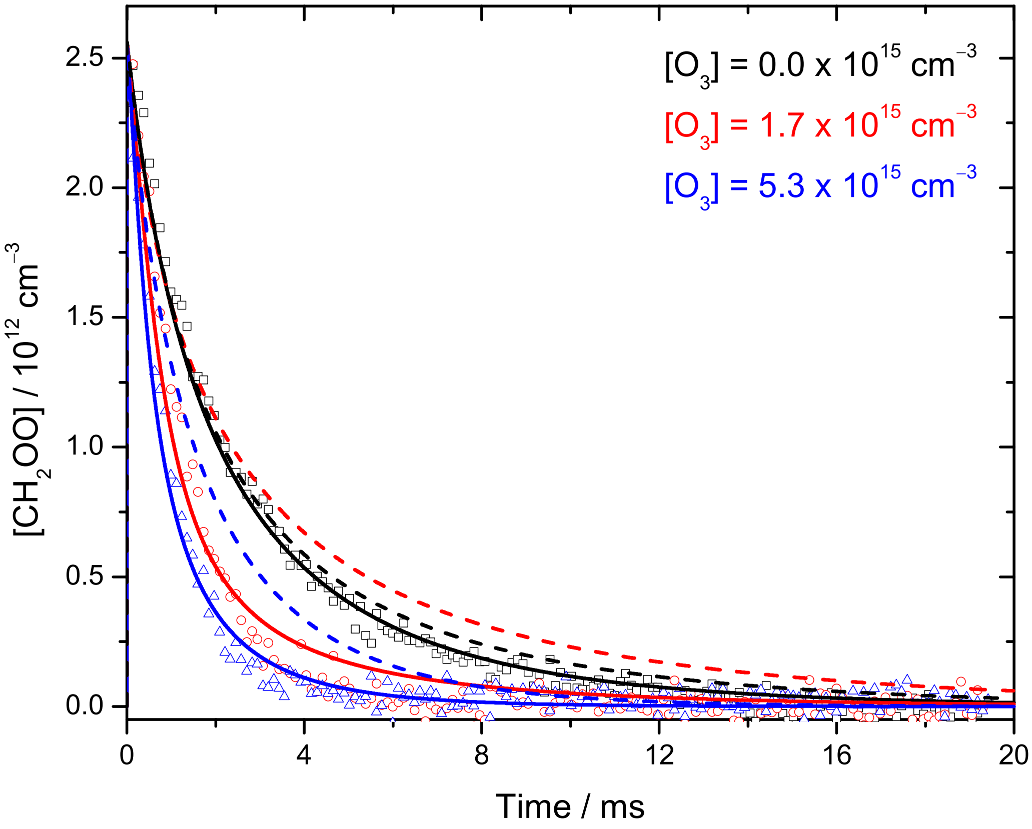

Figure S8 [CH_2OO] time profiles under different [O_3] simulated with a model described in Ref. 1 (with 3 more reactions added, k_8 to k_{10}, for [O_3]>0) are shown as solid lines. The rate coefficients used in this simulation are listed in Table S2. The dashed lines are modeled profiles without considering the reaction of CH_2OO with IO (by setting k_{10} to 0). The initial conditions used are: $[CH_2I]_0 = 3.3\times10^{12}$ cm^{-3}, $P_{\mathrm{Total}} = P_{O2} = 30$ Torr. The temporal profiles of CH_2OO recorded upon photolysis of a mixture of CH_2I_2/O_2 (0.01 Torr/30 Torr) at 298 K under different [O_3] are shown as symbols (expt. 9). Under the same condition, the measured $[CH_2OO]_{\max}$ by UV absorption is 2.1×10^{12} cm^{-3}.

References

1. W.-L. Ting, C.-H. Chang, Y.-F. Lee, H. Matsui, Y.-P. Lee, and J..J.-M. Lin, J. Chem. Phys. **141**, 104308 (2014).
2. M. E. Tucceri, T. J. Dillon, J. N. Crowley, Phys. Chem. Chem. Phys. **7**, 1657 (2005).