Supplementary for

Kinetics of Dimethyl Sulfide (DMS) Reactions with Isoprene-derived Criegee Intermediates Studied with Direct UV Absorption

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S1 Summary of the experimental conditions and results

Table S1. Summary of the experimental conditions and results for the reaction CH₂OO+DMS at 308 nm photolysis. T = 296.8 - 297.2 K; $[O_2] = (3.28 - 3.32) \times 10^{17}$ cm⁻³; $P_{\text{total}} = 299.9 - 301.5$ Torr.

Exp#	$\left[CH_{2}I_{2}\right]$	<i>I</i> _{308nm}	k_0	$k_{ m DMS}$
_	$/10^{13} \text{ cm}^{-3}$	$/\mathrm{mJcm}^{-2}$	$/s^{-1}$	$/10^{-16} \text{ cm}^3 \text{s}^{-1}$
1	16.1	1.19	232±2 ^{<i>a</i>}	7.8±4.1 ^a
2	16.3	2.35	464±3	10.9±5.6
3	16.2	3.63	698±3	22.0±5.5
4	16.5	4.83	956±5	-4.1±10.4
5	12.6	0.34	54±2	9.1±4.5
6	21.2	0.31	79±2	10.2±4.1
7	20.7	0.31	90±2	8.6±4.9
8	21.1	0.74	188±1	-3.2±1.7
9	19.6	0.95	240±2	12.0±3.5
10	2.30	9.97	261±8	28.7±16.7
11	25.4	2.27	680±4	24.1±8.2
		avera	11.5	
		standard deviation ^b		10.3

^{*a*} averaged value ± 1 sigma error of the mean (statistical only, not including systematic errors). Note: 1 sigma error of the mean = standard deviation / sqrt(degrees of freedom)

^{*b*} Standard deviation of the 11 data points of k_{DMS} .

Table S2. Summary of the experimental conditions and results for the reaction CH₂OO+DMS at 248 nm photolysis. T = 296.7K-296.8 K; $[O_2] = 3.29$ x 10^{17} cm $^{-3}$; $P_{total} = 299.5 - 299.7$ Torr.

Exp#	$[CH_2I_2]$	I_{248nm}	k_0	$k_{\rm DMS}$
	$/10^{13} \text{ cm}^{-3}$	$/mJ \text{ cm}^{-2}$	$/s^{-1}$	$/10^{-16} \text{ cm}^3 \text{s}^{-1}$
12	19.3	1.10	109±1 ^{<i>a</i>}	16.2 ± 10.3^{a}
13	19.0	2.18	197±1	25.5±8.6
14	18.9	3.17	275±1	31.6±11.5
		avera	24.4	
		standard de	7.8	

^{*a*} averaged value ± 1 sigma error of the mean (statistical only, not including systematic errors). Note: 1 sigma error of the mean = standard deviation / sqrt(degrees of freedom)

^{*b*} Standard deviation of the 3 data points of k_{DMS} .

Exp#	Precursor Abs	P _{total}	<i>I</i> _{248nm}	<i>k</i> _r	adduct yield $1-\alpha$	k_0	k _{DMS}
		/Torr	$/mJ cm^{-2}$	$/s^{-1}$	/%	$/s^{-1}$	$/10^{-16} \text{ cm}^3 \text{s}^{-1}$
15	0.100	301.4	1.09	1182 ± 14^{b}	91.8 ± 0.3^{b}	115 ± 2^{b}	116.5 ± 34.3^{b}
16	0.220	303.0	1.06	1442±7	89.2±0.1	151±2	94.7±34.5
17	0.331	301.6	1.03	1641±5	87.2±0.1	182±2	73.2±24.0
18	0.334	301.9	0.58	1386±10	90.4±0.2	140±1	99.9±19.1
19	0.056	302.1	1.25	1033±48	91.1±1.6	123±8	75.0±70.7
20	0.151	302.2	1.23	1109±14	91.2±0.3	131±2	44.2±22.5
21	0.057	302.5	2.45	1203±14	90.6±0.2	146±2	19.6±17.0
22	0.158	302.3	2.43	1395±6	87.0±0.1	179±5	78.7±56.1
23	0.056	302.3	3.72	1330±5	88.9±0.3	229±2	33.2±15.9
24	0.160	302.4	3.67	1652±8	84.0±0.1	274±1	-15.0±16.7
25	0.179	30.6	1.19	1297±7	57.0±0.2	138±2	70.3±58.1
26	0.558	30.2	1.14	2123±19	49.2±0.1	255±2	67.8±59.3
27	0.289	100.2	1.18	1481±12	79.2±0.2	153±1	68.4±7.7
28	0.746	99.9	1.11	2146±8	70.7±0.1	321±2	39.6±25.8
29	0.142	299.5	1.19	1362±11	88.7±0.1	126±1	57.1±14.8
					average		61.6
		standard deviation ^c		33.4			

Table S3. Summary of the experimental conditions and results for the reaction MVKO + DMS at 248 nm photolysis. T = 297.0-298.1 K; $[O_2] = (3.28-3.41)\times10^{17}$ cm⁻³.

^{*a*} The estimated absorbance of the precursor (1,3-diiodo-2-butene) at 238 nm in the photolysis reactor (using L = 426 cm).

^{*b*} averaged value ± 1 sigma error of the mean (statistical only, not including systematic errors).

Note: 1 sigma error of the mean = standard deviation / sqrt(degrees of freedom)

^{*c*} Standard deviation of the 15 data points of k_{DMS} .

S2 Observed decay rate coefficient of CH₂OO at various conditions



Fig. S1. First-order decay rate coefficient of CH₂OO, k_{obs} , against [DMS] at various experimental conditions (Exp#5–11, Table S1). The wavelength of the photolysis laser is 308 nm.



Fig. S2. First-order decay rate coefficient of CH₂OO, k_{obs} , against [DMS] at various photolysis laser fluence (Exp#12–14, Table S2). The wavelength of the photolysis laser is 248 nm.

S3 Kinetic model for MVKO reactions

To obtain more quantitative values for k_{DMS} , we performed kinetic analysis with the following model. At t = 0, the precursor ICH₂-CH=C(I)-CH₃ is photodissociated into CH₃(C₂H₃)CI + I. Under the high [O₂] conditions (~3.3x10¹⁷ cm⁻³) in our experiment, the reaction of CH₃(C₂H₃)CI + O₂ (R3a) and (R3b) proceeds within a very short time (< 0.1 ms). However, different from the case of CH₂OO, an additional MVKO signal rises slowly until about 2 ms (R3c), followed by a decay in longer reaction times (due to (R4) and (R5)). The formation/decomposition of the adduct of MVKO and I atom (R3b)/(R3c) are pressure dependent.

$$\begin{aligned} \mathrm{CH}_3(\mathrm{C}_2\mathrm{H}_3)\mathrm{CI} + \mathrm{O}_2 &\rightarrow \mathrm{I} + \mathrm{CH}_3(\mathrm{C}_2\mathrm{H}_3)\mathrm{COO} \ (\mathrm{MVKO}) & (\mathrm{R3a}; \ \alpha k_{\mathrm{O2}}) \\ \mathrm{CH}_3(\mathrm{C}_2\mathrm{H}_3)\mathrm{CI} + \mathrm{O}_2 + \mathrm{M} &\rightarrow \mathrm{CH}_3(\mathrm{C}_2\mathrm{H}_3)\mathrm{CIOO} + \mathrm{M} & (\mathrm{R3b}; \ (1-\alpha)k_{\mathrm{O2}}) \\ \mathrm{CH}_3(\mathrm{C}_2\mathrm{H}_3)\mathrm{CIOO} + \mathrm{M} &\rightarrow \mathrm{I} + \mathrm{CH}_3(\mathrm{C}_2\mathrm{H}_3)\mathrm{COO} + \mathrm{M} & (\mathrm{R3c}; k_r) \\ \mathrm{CH}_3(\mathrm{C}_2\mathrm{H}_3)\mathrm{COO} \ (\mathrm{MVKO}) + \mathrm{DMS} &\rightarrow \mathrm{Products} & (\mathrm{R4}; k_{\mathrm{DMS}}) \\ \mathrm{CH}_3(\mathrm{C}_2\mathrm{H}_3)\mathrm{COO} \ (\mathrm{MVKO}) + \mathrm{X} \ (\mathrm{radicals}) &\rightarrow \mathrm{Products} & (\mathrm{R5}; k_{\mathrm{X}}) \end{aligned}$$

The detail kinetics of the adduct decomposition into MVKO + I will be published elsewhere. In brief, MVKO is either formed directly (R3a), or via the formation and consecutive decomposition of an adduct of $CH_3(C_2H_3)CIOO$ ((R3b) and (R3c)). From the differential rate equations of these three reactions, the following analytical expression for [MVKO](t) can be derived:

$$[MVKO](t) = [MVKO]_{0}e^{-k_{obs}t} + [adduct]_{0}\frac{k_{r}}{k_{r} - k_{obs}}[e^{-k_{obs}t} - e^{-k_{r}t}]$$

$$= [MVKO]_{total} \{\alpha e^{-k_{obs}t} + (1 - \alpha)\frac{k_{r}}{k_{r} - k_{obs}}[e^{-k_{obs}t} - e^{-k_{r}t}]\}$$
(3)

with α and $(1-\alpha)$ as the yields of the prompt MVKO and the adduct ([MVKO]_{total} = [MVKO]₀ + [adduct]₀) and $k_{obs} = k_0 + k_{DMS}$ [DMS] as in the case of CH₂OO. Fitting this equation to the measured absorbance–time profiles treating k_{obs} , k_r , and α as variable parameters, we obtained k_{obs} . Selected results of k_{obs} are presented in Figure 4 and all results are summarized in Table S3.





Fig. S3. First-order decay rate coefficient of MVKO, k_{obs} , against [DMS] at various experimental conditions (Exp#19–29). The wavelength of the photolysis laser is 248 nm.

S5 Effect of DMS photolysis

Assuming the photolysis yield of DMS is unity, the concentration of the photodissociated DMS, [DMS]_{diss}, can be deduced from the following equation:

$$[DMS]_{diss} = [DMS]\rho c$$
$$\rho = I \frac{\lambda}{hc}$$

where $\rho = I\lambda/hc$ is the number of photons per unit area and σ is the absorption cross section of DMS; *I* and λ are the fluence and wavelength of the photolysis laser; *h* and *c* are the Planck constant and speed of light, respectively. The maximum values of photodissociated DMS and CH₂I₂ precursor are estimated as in Table S4.

Wavelength	I / mL cm ⁻²	ρ / cm ⁻²	σ	[DMS] _{diss} /[DMS]	[DMS]	[DMS] _{diss}
		/ 0111	/ СШ		/0111	/0111
248 nm	3.72	4.64×10^{15}	1.28×10^{-20}	5.9×10^{-5}	1.7×10^{15}	1.0×10^{11}
308 nm	9.97	1.55×10^{16}	$<1 \times 10^{-22}$	$<1.5 \times 10^{-6}$	8.1×10^{15}	$< 1.3 \times 10^{10}$
					$[CH_2I_2]$	$[CH_2I_2]_{diss}$
				$[C\Pi_2I_2]_{diss}/[C\Pi_2I_2]$	$/cm^{-3}$	$/cm^{-3}$
248 nm	3.17	3.96×10 ¹⁵	1.6×10^{-18}	6.3×10^{-3}	1.9×10 ¹⁴	1.2×10^{12}
308 nm	9.97	1.55×10^{16}	3.3×10^{-18}	5.1×10^{-2}	2.3×10^{13}	1.2×10^{12}

Table S4. Estimation for the photodissociated DMS and CH₂I₂.

High [DMS]_{diss} at 248 nm photolysis would generate radical products, which may react with CH₂OO or MVKO and may absorb light at our probe wavelength (see **Figure S4**). On the other hand, the very minor [DMS]_{diss} at 308 nm photolysis would not cause a problem. Hence, at 248 nm photolysis, we limit [DMS] $\leq 1.7 \times 10^{15}$ cm⁻³ and $I_{248nm} \leq 3.72$ mJ cm⁻² (Exp#23–24) to constraint [DMS]_{diss} $\leq 1.0 \times 10^{11}$ cm⁻³. **Figure S5** shows the background trace at 248 nm photolysis with constraint [DMS] and I_{248nm} . No significant background due to [DMS]_{diss} is observed, except absorption caused from the optics. Besides, in **Figure S9**, we can see that the results of CH₂OO+DMS reaction at 248 nm photolysis are quite similar to those at 308 nm, while a slightly higher k_{DMS} can be observed for 248 nm at high $I_{248 nm}$, indicating that [DMS]_{diss} only has a minor effect.



Fig. S4. Background traces recorded under extra-high [DMS]. The traces were obtained with 248 nm photolysis laser ($I_{248nm} = 3.34 \text{ mJ cm}^{-2}$). The experimental conditions are : $P_{\text{total}} = 297.2 \text{ Torr}$, $[O_2] = 3.23 \times 10^{17} \text{ cm}^{-3}$, T=299K. The length of the cell for monitoring [DMS] is 1 cm. The photolysis laser pulse defines t = 0. The absorbance change under zero [DMS] comes from the interaction of the optics and the photolysis laser pulse. Note that in the kinetic experiments, the used [DMS] was much lower ($< 1.7 \times 10^{15} \text{ cm}^{-3}$) such that the background did not depend on [DMS] (see Figure S5).



Fig. S5. Background traces under normal DMS concentrations obtained with 248 nm photolysis laser ($I_{248nm} = 3.72 \text{ mJ cm}^{-2}$). See Exp# 23 of Table S3 for the experimental condition.



Fig. S6. Background traces under various [DMS] obtained with 308 nm photolysis laser $(I_{308nm} = 4.83 \text{ mJ cm}^{-2})$. See Exp#4 of Table S1 for the experimental condition. Note that the optics (long pass filters) are different from those at 248 nm.

S6 Dependence of k_0 and k_{DMS} on laser fluence and precursor concentration



Fig. S7. Plot of k_0 against the product of the laser fluence (I_{248nm} or I_{308nm}) and the precursor concentration [CH₂I₂] for the experiments (Exp#1–14, Tables S1–S2) of CH₂OO+DMS reaction. The x-axis essentially represents the total amounts of radical species generated through the photolysis of the precursor (R1) and the subsequent reactions (R2). Higher radical concentration results in faster CH₂OO decay, thus higher k_0 . The difference of the slopes mainly comes from the difference of CH₂I₂ absorption cross sections at these two wavelengths (see Table S4). Note that there are experiments having different combinations of [CH₂I₂] and I_{308nm} , but very similar I_{308nm} **x**[CH₂I₂] (like Exp#3,11; Exp#1,9).



Fig. S8. As Figure S7, but for the experiments (Exp#15–29) of MVKO+DMS reaction. Because the absorption cross section of the precursor is not available, we use its absorbance to represent its concentration.



Fig. S9. Plot of k_{DMS} against the product of the laser fluence (I_{248nm} or I_{308nm}) and the precursor concentration [CH₂I₂] for the experiments (Exp#1–14, Tables S1–S2) of CH₂OO+DMS reaction. The x-axis essentially represents the total amounts of radical species generated through the photolysis of the precursor (R1) and the subsequent reactions (R2). No observable trend of k_{DMS} can be found for the data of 308 nm photolysis, whereas k_{DMS} at 248 nm photolysis increases as I_{248nm} x[CH₂I₂] increases, which may result from the increased radical generation from the DMS photolysis. Note that there are experiments having different combinations of [CH₂I₂] and I_{308nm} , but very similar I_{308nm} x[CH₂I₂] (like Exp#3,11; Exp#1,9).



Fig. S10. As Figure S9, but for k_{DMS} in Exp#15–29 of MVKO+DMS reaction. No significant trend for k_{DMS} is observed.

S7 Representative time traces for the CH₂OO+DMS reaction obtained with 308 nm photolysis



Fig. S11. Representative time traces of CH₂OO absorption at 340±5nm at various [DMS] (Exp#1–4). The wavelength of the photolysis laser was 308 nm and the laser pulse is set at the time zero. In each experiment, [DMS] was scanned from 0 to the maximum (labeled as "up"), and scanned from maximum to 0 (labeled as "down"). The negative baseline is resulted from the depletion of the precursor CH_2I_2 .



Fig. S12. As Fig. S11, but different experiment sets (Exp#5-8)



Fig. S13. As Fig. S11, but different experiment sets (Exp#9-11)

S8 Representative time traces for the CH₂OO+DMS reaction obtained with 248 nm photolysis



Fig. S14. Representative time traces of CH_2OO at $340\pm5nm$ at various [DMS] (Exp# 12–14). The wavelength of the photolysis laser was 248 nm and the laser pulse is set at the time zero. In each experiment, [DMS] was scanned from 0 to the maximum (labeled as "up"), and scanned from maximum to 0 (labeled as "down"). The negative baseline resulted from the depletion of the precursor CH_2I_2 .

S9 Representative time traces for the MVKO+DMS reaction obtained with 248 nm photolysis



Fig. S15. Representative time traces of MVKO at 340±5nm at various [DMS] (Exp#15–18). The wavelength of the photolysis laser was 248 nm and the laser pulse is set at the time zero. In each experiment, [DMS] was scanned from 0 to the maximum (labeled as "up"), and scanned from maximum to 0 (labeled as "down").



Fig. S16. Representative time traces of MVKO at 340±5nm at various [DMS] (Exp#19–24). The wavelength of the photolysis laser was 248 nm and the laser pulse is set at the time zero.



Fig. S17. As Fig. S16, but different experiment sets (Exp#25-29)