Supporting Information for

Reactions of Criegee Intermediates with Acrolein: Kinetics and Atmospheric Implication

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I. Kinetic model for the *syn*-CH_3CHOO + CH_2=CHCHO reaction

The formation of *syn*-CH_3CHOO includes reactions listed below:

$$CH_3CHI_2 + h\nu \xrightarrow{k_8} CH_3CHI + I \quad \text{(R8)}$$

$$CH_3CHI + O_2 \xrightarrow{k_{9a}} syn\text{-}CH_3CHOO + I \quad \text{(R9a)}$$

$$\xrightarrow{k_{9b}} anti\text{-}CH_3CHOO + I \quad \text{(R9b)}$$

$$\xrightarrow{k_{9c}} \text{other products} \quad \text{(R9c)}$$

The consumption of *syn*-CH_3CHOO results from the following reactions:

$$syn\text{-}CH_3CHOO \xrightarrow{k_{10a}} OH \quad \text{(R10a)}$$

$$\xrightarrow{k_{10b}} \text{other products} \quad \text{(R10b)}$$

$$syn\text{-}CH_3CHOO + CH_2{=}CHCHO \xrightarrow{k_{11}} \text{products} \quad \text{(R11)}$$

$$syn\text{-}CH_3CHOO + X \xrightarrow{k_{12}} \text{products} \quad \text{(R12)}$$

$$syn\text{-}CH_3CHOO + syn\text{-}CH_3CHOO \xrightarrow{k_{13}} \text{products} \quad \text{(R13)}$$

Reaction (R7) describes the consumption of OH:

$$OH + Y \xrightarrow{k_{14}} \text{products} \quad \text{(R14)}$$

Where X in reaction (R12) denotes the species that react with *syn*-CH_3CHOO, such as I and CH_3CHI_2. Y in reaction (R14) denotes the species that consume the OH, e.g., IO, CH_3CHI_2, CH_3CHO, and CH_2=CHCHO. We neglected the cross-self-reaction of *syn*-CH_3CHOO with *anti*-CH_3CHOO as it is hardly discernible under similar experimental condition.[1]

The OH(v″=0) decay profiles were fitted with the expression (II) (for details see our previous publication)[2]:

$$S_{OH} = \frac{A_0 (k_{10}+k'_{11}+k'_{12})}{(k_{10}+k'_{11}+k'_{12}) e^{(k_{10}+k'_{11}+k'_{12})t} + 2k_{13}[syn-CH_3CHOO]_0 \left(e^{(k_{10}+k'_{11}+k'_{12})t}-1\right)} - A_1 e^{-k'_{14}t} \quad \text{(SI)}$$

where $A_0 = \gamma \frac{k_{10a}[syn-CH_3CHOO]_0}{k'_{14}-(k_{10}+k'_{11}+k'_{12})}$, $A_1 = \gamma \left(\frac{k_{10a}[syn-CH_3CHOO]_0}{k'_{14}-(k_{10}+k'_{11}+k'_{12})} - [OH]_0 \right)$.

In expression (II), $k'_{11} = k_{11}[CH_2{=}CHCHO]$; $k'_{12} = k_{12}[X]$; k_{13} was fixed to a reported value of 1.6×10^{-10} cm^3 s^{-1},[1] $k'_{14} = k_{14}[Y]$. The initial concentration of *syn*-CH_3CHOO, [*syn*-CH_3CHOO]$_0$, was fixed to a calculated value during the fitting. $[OH]_0$ is the concentration of OH from the decomposition of energized CH_3CHOO; γ is the OH detection efficiency.

II. Summary of experimental conditions

Table S1. Summary of the experimental conditions for CH_2OO reaction with CH_2=CHCHO at different temperatures. The total pressure is 10 Torr; $[CH_2I_2]$ ~ (1.54 ± 0.18) × 10^{14} cm^{-3}; $[CH_2OO]$ ~ (3.59 ± 0.86) × 10^{12} cm^{-3}; $[O_2]$ = 2.50 × 10^{16} cm^{-3}; I_{248} ~15 mJ cm^{-2}.

Exp #	T / K	$k_3 + k_6^{'}$ / s^{-1}	k_5 /10^{-12} cm^3 s^{-1}
1-1	281.3	451	1.80 ± 0.23
1-2	281.5	480	1.80 ± 0.22
1-3	281.2	514	1.87 ± 0.23
1-4	281.3	422	1.85 ± 0.23
Average			**1.83 ± 0.23**
1-5	298.4	427	1.61 ± 0.20
1-6	298.3	584	1.64 ± 0.20
1-7	298.5	673	1.69 ± 0.21
1-8	298.4	504	1.60 ± 0.20
Average			**1.64 ± 0.20**
1-9	308.5	520	1.35 ± 0.17
1-10	308.1	504	1.45 ± 0.17
1-11	308.4	476	1.39 ± 0.18
1-12	308.2	445	1.47 ± 0.18
Average			**1.42 ± 0.17**
1-13	318.1	405	1.25 ± 0.15
1-14	318.5	413	1.31 ± 0.16
1-15	318.2	599	1.36 ± 0.17
1-16	318.1	467	1.35 ± 0.17
Average			**1.32 ± 0.16**

Table S2. Summary of the experimental conditions for *syn*-CH_3CHOO reaction with CH_2=CHCHO at different temperatures. The total pressure is 15 Torr; [CH_3CHI_2]~ (1.30 ± 0.16) × 10^{14} cm^{-3}; [*syn*-CH_3CHOO] ~ (2.44 ± 0.75) × 10^{12} cm^{-3}; [O_2] = 2.50 × 10^{16} cm^{-3}; I_{248} ~15 mJ cm^{-2}.

Exp #	T / K	$k_{10} + k_{12}^{'}$ / s^{-1}	k_{11} / 10^{-13} cm^3 s^{-1}
2-1	282.9	456	1.38 ± 0.23
2-2	282.8	439	1.29 ± 0.19
2-3	282.8	424	1.33 ± 0.23
2-4	282.7	353	1.42 ± 0.22
Average			**1.36 ± 0.21**
2-5	298.5	296	1.33 ± 0.19
2-6	298.4	537	1.22 ± 0.23
2-7	298.3	313	1.25 ± 0.23
2-8	298.3	543	1.19 ± 0.19
2-9	298.1	451	1.24 ± 0.17
Average			**1.25 ± 0.21**
2-10	308.3	257	1.18 ± 0.22
2-11	308.7	303	1.04 ± 0.21
2-12	308.6	324	1.19 ± 0.18
2-13	308.2	301	1.16 ± 0.18
Average			**1.14 ± 0.19**
2-14	318.5	283	1.03 ± 0.16
2-15	318.3	374	0.86 ± 0.14
2-16	318.3	284	1.11 ± 0.18
2-17	318.0	361	1.00 ± 0.15
Average			**1.00 ± 0.16**

III. Error analysis

The overall errors for the rate coefficients k_5 and k_{11}, as shown in Table S1 and S2, are determined as follow:

a) The estimation of [CH_2OO]$_0$ and [*syn*-CH_3CHOO]$_0$

[CH_2OO]$_0$ and [*syn*-CH_3CHOO]$_0$ was calculated as y × f ×b×[CH_2I_2]$_0$ (or [CH_3CHI_2]$_0$).

y is the fraction of CH_2I_2/CH_3CHI_2 that were photolyzed by 248 nm laser and it was calculated as (F/$h\nu_{248}$) × σ_{248}. F denotes the laser fluence (0.5 cm beam diameter), and σ_{248} is the absorption cross-section of CH_2I_2/CH_3CHI_2 at 248 nm (1.61×10^{-18} and 1.57×10^{-18} cm^2 $molecule^{-1}$).[3] In the current experimental condition, y is about 3%.

f is the fractional yield of CH_2OO/CH_3CHOO from the reaction of CH_2I/CH_3CHI with O_2, which was pressure-dependent.[4] The yield of CH_2OO was reported to be ca. 0.76 at 7.6 Torr and 0.52 at 200 Torr.[4] For the CH_3CHOO, the fractional yield was reported as 0.86 ± 0.11 at 2 Torr [5] and 0.9 at pressures between 5 and 20 Torr,[6] but no available knowledge about the f at higher pressure was reported and therefore we adopted a value of 0.9 for f at 5-150 Torr pressure range.

b is the ratio of [*syn*-CH_3CHOO] to [CH_3CHOO] (the existence of *anti*-CH_3CHOO). This value was estimated to be 0.7.[6] This value is 1 for CH_2OO.

The [CH_2I_2]$_0$ / [CH_3CHI_2]$_0$ was measured by a deep UV LED (DUV325-H46, Roithner Lasertechnik, centered at 322.4 nm) and a balanced amplified photodetector (PDB450A, Thorlabs), with known absorption cross-section and LED emission profile.

b) Error analysis

Considering errors in the measurement of flow rate (1%), pressure (3%), temperature (1%), the fluence of the LED light source (10%) and the UV absorption cross-section of CH_2I_2 (5%), we estimated the errors of [CH_2I_2] to be 12%. With the errors of the fractional yield of CH_2OO from the CH_2I + O_2 reaction (20%), the fluence of photolysis laser (5%), the UV absorption cross-section of CH_2I_2 at 248 nm (5%) and [CH_2I_2] (12%), the uncertainty of [CH_2OO]$_0$ was calculated to be 24%.

Similarly, considering the errors of [CH_3CHI_2] (12%), the errors of the fractional yield of CH_3CHOO from the CH_3CHI + O_2 reaction (20%), the branching of *syn*-CH_3CHOO (20%), the fluence of photolysis laser (5%), and the UV absorption cross-section of CH_3CHI_2 at 248 nm (5%). we estimated the uncertainty of [*syn*-CH_3CHOO]$_0$ to be 31%.

During fitting the OH decay profiles, the CH_2OO self-reaction rate coefficient, k_4, was fixed to 8×10^{-11} cm^3 s^{-1}, the uncertainty of which was estimated to be 50%.[4] And the *syn*-CH_3CHOO self-reaction rate coefficient was fixed to 1.6×10^{-10} cm^3 s^{-1} with uncertainty of 33%.[1] Therefore, the error of [CH_2OO]$_0$ ×

k_4 and [*syn*-CH_3CHOO]$_0$ × k_{13} is about 56% and 46%, respectively. Table S3 and S4 shows the values of k_5 and k_{11} when varying the value of [CH_2OO]$_0$ × k_4 and [*syn*-CH_3CHOO]$_0$ × k_{13}. According to Table S2 and S3, we estimated the error of k_5 and k_{11} caused by the uncertainty of [CH_2OO]$_0$ × k_4 and [*syn*-CH_3CHOO]$_0$ × k_{13} to be 5% and 8%, respectively.

For the reaction of CH_2OO with CH_2=CHCHO, considering the errors from fitting the OH decay profiles (5%), the linear fits (1%-14%) that depend on the total pressure, the absolute [CH_2=CHCHO] (10%) and the error of k_5 caused by the uncertainty of [CH_2OO]$_0$ × k_6 (5%), the overall error of k_5 was estimated to be 12-19%. Similarly, we estimated the overall error of the k_{11} for the reaction of *syn*-CH_3CHOO with CH_2=CHCHO to be 15-20%.

Table S3. The error of k_5 resulting from the 56% uncertainty of [CH_2OO]$_0$ × k_4.

Exp #	[CH_2OO]$_0$ × k_4 / s^{-1}	[CH_2OO]$_0$ × k_4 × (1 ± 56%) /s^{-1}	k_5 /10^{-12} cm^3 s^{-1}	k_5 /10^{-12} cm^3 s^{-1}	Uncertainty / %
1-1	287	445 [a]	1.78 [a]	1.80	1.1 [a]
		129 [b]	1.81 [b]		0.6 [b]
1-5	287	445	1.58	1.61	1.9
		129	1.63		1.2
1-9	287	445	1.34	1.35	0.7
		129	1.36		0.7
1-13	287	445	1.22	1.25	2.4
		129	1.34		7.2
3_a	280	434	1.97	2.05	3.9
		126	2.12		3.4
3_d	294	455	1.33	1.38	3.6
		132	1.47		6.5
3_f	279	433	1.58	1.59	0.6
		126	1.60		0.6
3_h	274	424	1.56	1.66	6.0
		123	1.73		4.2

[a] The data highlighted in yellow shows the values and uncertainties of k_4 when fixing the [CH_2OO]$_0$×k_4 to

its upper-limit value, (1.56×[$CH_2OO]_0$×k_4).

[b] The data highlighted in grey shows the values and uncertainties of k_4 when fixing the [$CH_2OO]_0$×k_4 to its lower-limit value, (0.44×[$CH_2OO]_0$×k_4).

Table S4. The error of k_{11} resulting from the 46% uncertainty of [*syn*-$CH_3CHOO]_0$ × k_{13}.

Exp #	[*syn*-$CH_3CHOO]_0$ × k_{13} / s^{-1}	[*syn*-$CH_3CHOO]_0$ × k_{13} × (1 ± 46%) /s^{-1}	k_{11} /10^{-13} cm^3 s^{-1}	k_{11} /10^{-13} cm^3 s^{-1}	Uncertainty / %
2-2	390	570 [a]	1.27 [a]	1.29	1.6 [a]
		211 [b]	1.36 [b]		5.4 [b]
2-9	390	570	1.22	1.24	1.6
		211	1.27		2.4
2-13	390	570	1.11	1.16	4.3
		211	1.17		0.9
2-14	390	570	0.92	1.03	10
		211	1.06		2.9
4_a	477	696	1.30	1.34	3
		257	1.43		6.7
4_e	426	621	1.07	1.17	8.5
		230	1.18		1
4_g	504	736	0.99	1.05	5.7
		272	1.16		10
4_i	482	703	1.17	1.31	10
		260	1.43		9.2

[a] The data highlighted in yellow shows the values and uncertainties of k_{13} when fixing the [*syn*-$CH_3CHOO]_0$×k_{13} to its upper-limit value, (1.46×[*syn*-$CH_3CHOO]_0$×k_{13}).

[b] The data highlighted in grey shows the values and uncertainties of k_{13} when fixing the [*syn*-$CH_3CHOO]_0$× k_{13} to its lower-limit value, (0.54×[*syn*-$CH_3CHOO]_0$×k_{13}).

IV. Sensitivity analysis of the fit on A_1 and k'_{14}

During fits the OH time-dependent profiles of *syn*-CH_3CHOO + CH_2=CHCHO reaction, the parameters of A_0, A_1, $k_{10} + k'_{11} + k'_{12}$ (corresponding to the $k_3 + k'_5 + k'_6$ in the CH_2OO + CH_2=CHCHO reaction), and k'_{14} (the overall loss rate of OH) were floated. The fits are not sensitive to either A_1 or k'_{14}, as shown in Table S5-S7.

OH is expected to be consumed mainly by reacting with CH_3CHI_2 and acrolein. Thus, the predicted k'_{14} value can be calculated as follows:

$$k'_{14} = k_{CH3CHI2}[CH_3CHI_2] + k_{acrolein}[acrolein] \qquad \text{(SII)}$$

where, the $k_{CH3CHI2}$ and $k_{acrolein}$ are the rate coefficient for OH +CH_3CHI_2 and OH + acrolein reaction, respectively. $k_{CH3CHI2}$ is not available; we take the rate coefficient for OH + CH_2I_2 reaction($(4.45 \pm 0.32) \times 10^{-12}$ cm^3 s^{-1}) as a reference.[7] The values of $k_{acrolein}$ was reported to be $(1.99 \pm 0.24) \times 10^{-11}$ cm^3 s^{-1}.[8]

The fitted values of A_0, A_1, $k_{10} + k'_{11} + k'_{12}$—with k'_{14} floated or fixed to the calculated values—are listed in Table S5. It shows that the fitted values of A_0 and $k_{10} + k'_{11} + k'_{12}$ did not change when k'_{14} were either floated or fixed to calculated values. This is because the decrease portion of OH profiles is mainly described by the first term of eqn (SI).[2] Table S5 also shows that the output values of A_1 are exceptionally small when k'_{14} were fixed to calculated values. This could be because the fits are not sensitive to A_1. We fixed k'_{14} to calculated values and fixed A_1 to different values, as shown in Table S6 and Table S7. It shows that the $k_{10} + k'_{11} + k'_{12}$ barely change when increasing A_1 from 0 to 500 ([acrolein] ~ 0.37×10^{15} cm^{-3}) and 0 to 5000 ([acrolein] ~ 2.4×10^{15} cm^{-3}).

Table S5. The fitted values of A_0, A_1, $k_{10} + k'_{11} + k'_{12}$—with k'_{14} floated or fixed to the calculated values. The total pressure is 15 Torr; [CH_3CHI_2]~ (1.30 ± 0.16) × 10^{14} cm^{-3}; [*syn*-CH_3CHOO] ~ (2.44 ± 0.75) × 10^{12} cm^{-3}; [O_2] = 2.50 × 10^{16} cm^{-3}; I_{248} ~15 mJ cm^{-2}.

Exp #	[acrolein] /10^{15} cm^{-3}	A_0, A_1, $k_{10} + k'_{11} + k'_{12}$ and k'_{14} are floated					k'_{14} [a] (calculated) /s^{-1}	fix k'_{14} to calculated value			
		k'_{14} /s^{-1}	A_0	A_1	$k_{10} + k'_{11} + k'_{12}$ /s^{-1}	R^2 [b]		A_0	A_1	$k_{10} + k'_{11} + k'_{12}$ /s^{-1}	R^2
2-9-1	0.37	385910	22433	28970	500	0.997	7957	22433	2.8E-12	500	0.997
2-9-2	0.74	401190	19845	77478	543	0.998	15337	19845	3.2E-12	543	0.997
2-9-3	1.12	768250	17703	77605	590	0.998	22717	17703	2.3E-12	590	0.998
2-9-4	1.49	690600	15069	32855	632	0.998	30097	15069	6.8E-13	632	0.998
2-9-5	1.87	553220	13318	36460	684	0.998	37477	13318	6.5E-11	684	0.998
2-9-6	2.42	436140	10202	16520	755	0.997	44857	10202	4.9E-11	755	0.997

a. the values of k'_{14} are calculated from eqn (SII).

b. R^2 is the coefficient of determination of the fits.

Table S6. The fittd values of $k_{10} + k'_{11} + k'_{12}$ when fixed k'_{14} to calculated values and fixed A_1 to different values. The total pressure is 15 Torr; [CH_3CHI_2]~ (1.30 ± 0.16) × 10^{14} cm^{-3}; [*syn*-CH_3CHOO] ~ (2.44 ± 0.75) × 10^{12} cm^{-3}; [O_2] = 2.50 × 10^{16} cm^{-3}; [CH_2=CHCHO]~ 3.70×10^{14} cm^{-3}; I_{248} ~15 mJ cm^{-2}.

Exp #	($k_{10} + k'_{11} + k'_{12}$) s^{-1} [a]	A_1 (fix)	fix A_1 and k'_{14} k'_{14} = 7957 s^{-1}		
			A_0	$k_{10} + k'_{11} + k'_{12}$ /s^{-1}	R^2
2-9-1	500	0	22433	500	0.997
		500	22562	504	0.997
		1000	22692	509	0.997

		2000	22956	519	0.996
		4000	23495	539	0.995

a. the fitted value of $k_{10} + k'_{11} + k'_{12}$ when A_0, A_1, $k_{10} + k'_{11} + k'_{12}$ and k'_{14} are floated during the fit.

Table S7. The fittd values of $k_{10} + k'_{11} + k'_{12}$ when fixed k'_{14} to calculated values and fixed A_1 to different values. The total pressure is 15 Torr; [CH_3CHI_2]~ (1.30 ± 0.16) × 10^{14} cm^{-3}; [*syn*-CH_3CHOO] ~ (2.44 ± 0.75) × 10^{12} cm^{-3}; [O_2] = 2.50 × 10^{16} cm^{-3}; [CH_2=CHCHO]~ 2.42×10^{15} cm^{-3}; I_{248} ~15 mJ cm^{-2}.

Exp #	($k_{10} + k'_{11} + k'_{12}$) s^{-1} [a]	A_1 (fix)	fix A_1 and k'_{14} k'_{14} = 44857 s^{-1}		
			A_0	$k_{10} + k'_{11} + k'_{12}$ /s^{-1}	R^2
2-9-6	755	0	10202	755	0.997
		1000	10207	755	0.998
		5000	10228	758	0.998
		10000	10254	761	0.998
		30000	10359	772	0.997

a. the fitted value of $k_{10} + k'_{11} + k'_{12}$ when A_0, A_1, $k_{10} + k'_{11} + k'_{12}$ and k'_{14} are floated during the fit.

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