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Supporting Information

Temperature- and Pressure-dependent Rate Coefficient measurement for the Reaction of CH_2OO with CH_3CH_2CHO

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Table of Contents:

Experimental conditions

Table S1. Summary of experimental conditions for the reaction of CH_2OO + CH_3CH_2CHO at 298 K and different pressures. I_{248} ~17.8mJ cm^{-2}.

Exp #	P / Torr	CH_2I_2 / 10^{14} cm^{-3}	O_2 / 10^{16} cm^{-3}	$k_3 + k_5'$ / s^{-1}	k_4 / 10^{-12} cm^3 s^{-1}
1-1	10	2.04	1.57	378	2.79 ± 0.21
1-2	5	2.54	1.35	484	2.39 ± 0.22
1-3	50	2.48	1.89	857	3.12 ± 0.19
1-4	200	1.77	2.10	1419	3.39 ± 0.21
1-5	100	2.27	2.08	1423	3.08 ± 0.19
2-1	5.2	2.54	1.63	491	2.52 ± 0.24
2-2	10	2.24	1.82	576	2.58 ± 0.24
2-3	25	2.46	1.81	769	3.07 ± 0.20
2-4	75	1.91	1.97	1030	3.30 ± 0.20
2-5	150	2.32	2.90	1517	3.18 ± 0.20
2-6	100	2.21	2.16	1317	3.09 ± 0.19
2-7	75	1.91	1.97	1255	3.08 ± 0.19
2-8	200	1.86	2.43	1532	3.04 ± 0.19
3-1	5.2	2.53	1.57	551	2.42 ± 0.23
3-2	50	2.47	1.89	903	3.21 ± 0.20
3-3	100	2.25	1.98	1259	3.25 ± 0.20
3-4	150	2.44	2.30	1465	3.19 ± 0.20
3-5	200	2.11	2.67	1628	3.18 ± 0.20
3-6	10	2.28	1.82	610	2.58 ± 0.19
3-7	25	2.37	1.81	740	3.02 ± 0.19
3-8	75	2.04	1.96	1310	3.13 ± 0.19

The k_4 in Table S1 was plotted against the total number of density, as shown in Figure 4 of the Main Text. The error of k_4 is the combination of 1σ value of k_4 form the linear fit of k_4' against [CH_3CH_2CHO] and the error arises from neglecting the decomposition of OH ($v'' \geq 1$) in fitting the temporal profiles of OH(v'' =0). Systematic uncertainty is not included.

Table S2. Summary of experimental conditions for the reaction of CH_2OO with CH_3CH_2CHO at several temperatures and 50 Torr. I_{248} = ~17.8mJ cm^{-2}, [CH_2I_2] = ~2.5×10^{14} cm^{-3}. The error of k_4 is 14%.

Exp #	T / K	O_2 / 10^{16} cm^{-3}	$k_3 + k_5'$ / s^{-1}	k_4 / 10^{-12} cm^3 s^{-1}
4-1	318	1.83	662	2.41 ± 0.34
4-2	318	1.83	760	2.27 ± 0.32
4-3	308	1.89	767	2.66 ± 0.37
4-4	308	1.89	881	2.71 ± 0.38
4-5	298	1.96	831	2.90 ± 0.41
4-6	298	1.96	802	3.36 ± 0.47
4-7	298	1.96	854	3.11 ± 0.44
4-8	283	2.06	878	3.58 ± 0.50
4-9	283	2.06	839	3.55 ± 0.50
4-10	283	2.06	808	3.56 ± 0.50
5-1	318	1.83	753	2.44 ± 0.34
5-2	318	1.83	811	2.43 ± 0.34
5-3	318	1.83	843	2.35 ± 0.33
5-4	308	1.89	863	2.58 ± 0.36
5-5	308	1.89	955	2.68 ± 0.38
5-6	308	1.89	920	2.57 ± 0.36
5-7	298	1.96	933	2.87 ± 0.40
5-8	298	1.96	989	3.06 ± 0.43
5-9	298	1.96	859	3.03 ± 0.42
5-10	298	1.96	878	3.17 ± 0.44
5-11	283	2.06	792	3.58 ± 0.50
5-12	283	2.06	1404	3.46 ± 0.48

II. Error analysis

The error for the rate coefficients k_4 is determined as the followings:

a) The estimation of $[CH_2OO]_0$

$[CH_2OO]_0$ was calculated as y × f × $[CH_2I_2]$.

y is the fraction of CH_2I_2 that were photolyzed by 248 nm laser ($CH_2I_2 + h\nu \rightarrow CH_2I + I$), and it was calculated as $(F/h\nu_{248}) \times \sigma_{248}$. F denotes the laser fluence, and σ_{248} is the absorption cross-section of CH_2I_2 at 248 nm (1.6×10^{-18} cm^2 molecule^{-1}).[1] In the current experimental condition, y is about 2.55%.

f is the yield of CH_2OO from the reaction of $CH_2I + O_2 \rightarrow CH_2OO + I$. The pressure-dependent yield of this reaction was calculated in reference to previous experimental result.[2]

The $[CH_2I_2]_0$ 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 flow rate (2%), pressure (4%), temperature (1%), the fluence of the LED light source (5%) and the UV absorption cross-section of CH_2I_2 (6%), we estimated the error of $[CH_2I_2]$ to be 9%.

Considering the errors of the CH_2OO yield from $CH_2I + O_2$ reaction (20%), the fluence of photolysis laser (5%), the UV absorption cross-section of CH_2I_2 (6%) and $[CH_2I_2]$ (9%), the error of $[CH_2OO]_0$ was calculated to be 24%.

The error of the self-reaction rate coefficient of CH_2OO, k_6, was estimated to be 50%.[2] Hence, the error of $[CH_2OO]_0 \times k_6$ is about 55%. Table S3 shows the values of k_4 when varying the product of $[CH_2OO]_0$ and k_6. According to Table S3, we estimated the error of k_4 caused by the error of $[CH_2OO]_0 \times k_6$ is 2% (see our previous publication for details).[3]

Considering the errors from fitting the OH decay profiles (5%), neglecting the decomposition of OH ($v'' = 1$) (7% at 5 Torr, 2% at 10 and 25 Torr, 1% for $P \geq 50$ Torr), the linear fits (6%), the absolute $[CH_3CH_2CHO]$ (10%) and $[CH_2OO]_0 \times k_6$ (2%), the overall error of k_4 was estimated to be ~14% (14.6% at 5 Torr, 13.4% at 10 and 25 Torr, 13.0% for P ≥ 50 Torr).

Table S3. The error of k_4 caused by the error of $[CH_2OO]_0 \times k_6$.

Pressure/ Temperature	$[CH_2OO]_0$ / 10^{12} cm^3	$[CH_2OO]_0 \times k_6$ / s^{-1}	$[CH_2OO]_0 \times k_6 \times (1 \pm 55\%)$ / s^{-1}	$k4$ / 10^{-12} cm^3 s^{-1}	$k4$ / 10^{-12} cm^3 s^{-1}	Uncertainty / %
50 Torr 318 K	5.91	473	213	2.418	2.405	0.55
			733	2.438		1.38
50 Torr 308 K	6.45	516	232	2.698	2.707	0.34
			800	2.711		0.15
50 Torr 298 K	6.65	532	239	2.988	3.029	1.36
			825	3.040		0.37
50 Torr 283 K	6.21	497	224	3.538	3.580	1.18
			770	3.579		0.03
298 K 5 Torr	6.09	503	226	2.36	2.39	1.26
			780	2.40		0.42
298 K 25 Torr	5.59	447	201	3.11	3.12	0.32
			693	3.13		0.32
298 K 100 Torr	5.42	434	195	3.08	3.09	0.33
			673	3.10		0.33
298 K 200 Torr	4.24	339	152	3.23	3.18	1.57
			525	3.15		0.95

III. OH (v''= 1) product from the unimolecular reaction of CH_2OO

CH_2OO is produced through the following reactions:

$$\mathrm{CH_2I_2} + h\nu \overset{k_1}{\rightarrow} \mathrm{CH_2I + I} \tag{R1}$$

$$\mathrm{CH_2I + O_2} \xrightarrow{k_{2a}} \mathrm{CH_2OO + I} \tag{R2a}$$

$$\mathrm{CH_2I + O_2} \xrightarrow{k_{2b}} \text{other products} \tag{R2b}$$

The consumption of CH_2OO upon its generation in the experiment included the following reactions:

$$\mathrm{CH_2OO} \xrightarrow{k_{3a}} \mathrm{OH{+}HCO} \tag{R3a}$$

$$\mathrm{CH_2OO} \xrightarrow{k_{3b}} \text{other products} \tag{R3b}$$

$$\mathrm{CH_2OO + CH_3CH_2CHO} \overset{k_4}{\rightarrow} \text{products} \tag{R4}$$

$$\mathrm{CH_2OO + X} \overset{k_5}{\rightarrow} \text{products} \tag{R5}$$

$$\mathrm{CH_2OO + CH_2OO} \overset{k_6}{\rightarrow} \text{products} \tag{R6}$$

The formation of CH_2OO and OH (v''= 0, 1) takes place on the time scale of a few microseconds.[4-6] The consumption of OH (v''= 0, 1) are from reaction (R7) and (R8):

$$\mathrm{OH}\ (v''{=}\ 0) + \mathrm{Y} \overset{k_7}{\rightarrow} \text{products} \tag{R7}$$

$$\mathrm{OH}\ (v''{=}\ 1) + \mathrm{Z} \overset{k_8}{\rightarrow} \mathrm{OH}\ (v''{=}\ 0) + \mathrm{Z} \tag{R8}$$

Here, X denotes the species that react with CH_2OO, such as I and CH_2I_2. Y denotes species that contribute to the loss of OH (v''= 0), e.g., IO and CH_2I_2. Z denotes the species that contribute to the collisional relaxation of OH (v''= 1) to OH (v''= 0), mainly by O_2 [7] and Ar [8] (for details, see Table S4).

Without considering the effect of OH (v''= 1), the time-dependent OH concentration can be written as ES1:

$$\frac{d[\mathrm{OH}](v''{=}0)}{dt} = -k_7'[\mathrm{OH}](v'' = 0) + k_{3a}[\mathrm{CH_2OO}] \tag{ES1}$$

The time-dependent of OH (v''= 0) signal can be given as (ES2). A detail derivation for this expression was provided in our previous publication.[9]

$$S_{\mathrm{OH}(v''=0)}(t) = \frac{A_0(k_3+k_4'+k_5')}{(k_3+k_4'+k_5')e^{(k_3+k_4'+k_5')t}+2k_6[\mathrm{CH_2OO}]_0\left(e^{(k_3+k_4'+k_5')t}-1\right)} - A_1 e^{k_7' t} \quad \text{(ES2)}$$

where $A_0 = \gamma\frac{k_{3a}[\mathrm{CH_2OO}]_0}{k_7'-(k_3+k_4'+k_5')}$, $A_1 = \gamma(\frac{k_{3a}[\mathrm{CH_2OO}]_0}{k_7'-(k_3+k_4'+k_5')} - [\mathrm{OH}]_0(v''=0))$, γ is the detection efficiency of OH (v''= 0). k_4'= $k_4[\mathrm{CH_3CH_2CHO}]$, k_5'= k_5[X], k_7'= k_7[Y]. k_6 was fixed at 8 × 10^{-11} $\mathrm{cm^3\ s^{-1}}$ from the results of Ting *et al.*[2]

Considering the OH (v''= 1), the time-dependent OH concentration can be obtained by the ES3 expression instead of ES1:

$$\frac{d[\mathrm{OH}](v''=0)}{dt} = -k_7'[\mathrm{OH}](v''=0) + k_8'[\mathrm{OH}](v''=1) + k_{3a}[\mathrm{CH_2OO}] \quad \text{(ES3)}$$

k_8'= k_8[Z] represent the collisional relaxation rate of OH (v''= 1) to OH (v''= 0). Then, the new expression of time-dependent of OH (v''= 0) signal could be derived as:

$$S'_{\mathrm{OH}(v''=0)}(t) = \frac{A_0'(k_3+k_4'+k_5')}{(k_3+k_4'+k_5')e^{(k_3+k_4'+k_5')t}+2k_6[\mathrm{CH_2OO}]_0\left(e^{(k_3+k_4'+k_5')t}-1\right)} - A_1' e^{k_7' t} - A_2' e^{k_8' t} \quad \text{(ES4)}$$

in the expression (ES4), $A_0' = \gamma\frac{k_{3a}[\mathrm{CH_2OO}]_0}{k_7'-(k_3+k_4'+k_5')}$, $A_1' = \gamma(\frac{k_{3a}[\mathrm{CH_2OO}]_0}{k_7'-(k_3+k_4'+k_5')} - [\mathrm{OH}]_0(v''=0) - \frac{k_8'[\mathrm{OH}]_0(v''=1)}{k_8'-k_7'})$, $A_2' = \gamma\frac{k_8'[\mathrm{OH}]_0(v''=1)}{k_8'-k_7'}$, γ is the detection efficiency of OH (v''= 0).

Using the expression (ES4), kinetic fitting was performed for OH decay trace by varying the parameters A_0', A_1', A_2', (k_3 + k_4' + k_5'), k_7' and k_8'. A comparison of k_4 from the fit between (ES2) and (ES4) are shown in table S5. The difference between the two fitting models decreases as pressure increases, and the value is about 1% at the pressure higher than 25 Torr.

Table S4. A list of the relaxation rate of OH (v''= 1) by O_2, Ar, and from the single exponential fit to the OH (v''= 1) profiles in Figure 1.

Pressure / Torr	[Ar] / $\mathrm{cm^{-3}}$	[O_2] / $\mathrm{cm^{-3}}$	[a] k_{Ar} × [Ar] / $\mathrm{s^{-1}}$	[b] k_{O2} × [O_2] / $\mathrm{s^{-1}}$	exponential fit / $\mathrm{s^{-1}}$
10	2.8 × 10^{17}	1.7 × 10^{16}	< 280	2669 ± 527	2857
50	1.4 × 10^{18}	7.2 × 10^{16}	< 1400	11304 ± 2232	11322

[a] k_{Ar} is the relaxation rate coefficient of OH (v''= 1) by Ar. An upper limit value of 1 ×

10^{-15} cm^3 s^{-1} at 298 K was adopted.[8] [b] k_{O2} is the relaxation rate coefficient of OH (v''=1) by O$_2$. k_{O2} = (1.57 ± 0.31) × 10^{-13} cm^3 s^{-1} at 295 K.[7]

Table S5. A list of k_4 from fitting temporal profiles of OH (v''= 0) at 298 K and pressures ranging from 5 to 200 Torr with equation ES2 and ES4.

Exp #	Pressure / Torr	k_4 / 10^{-12} cm^3 s^{-1}		Difference / 10^{-12} cm^3 s^{-1}	Percentage / %
		ES2	ES4		
1-2	5	2.39	2.53	0.14	5.9
2-1	5.2	2.52	2.61	0.09	3.6
3-1	5.2	2.42	2.59	0.17	7.0
1-1	10	2.79	2.91	0.12	4.3
2-2	10	2.58	2.60	0.02	0.8
3-6	10	2.58	2.54	-0.04	1.6
2-3	25	3.07	3.01	-0.06	2.0
3-7	25	3.02	2.95	-0.07	2.3
1-3	50	3.12	3.15	0.03	1.0
2-4	75	3.30	3.34	0.04	1.2
3-4	150	3.19	3.16	-0.03	0.9
1-4	200	3.39	3.38	0.01	0.3

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