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Kinetics of the simplest Criegee intermediate reaction with ammonia: a combination of experiment and theory

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Table S1. Reaction rate coefficients for calculated by variational transition state theory at temperatures between -50°C and 50°C, covering the temperature range of the atmosphere. The unit of equilibrium constant K_{eq} between the reactants (CH_2OO + NH_3/ND_3) and the vdW complex ($CH_2OO…NH_3/ND_3$) is cm^{-3}. The unimolecular rate coefficient of the vdW complex, k_{uni}, is calculated by conventional transition state theory, in s^{-1}. Tunneling correction κ is estimated using the asymmetric Eckart barrier approximation. Variational correction is denoted as v. The final reaction rate, k_{total} , is the product of the three numbers along with the variational correction factor. (a) & (b) are calculated using rigid rotor harmonic oscillation approximation (RRHO) while (c) & (d) are vibrational second order perturbation theory.

CH_2OO + NH_3	K_{eq}	k_{uni}	κ	v	k_{total}
223.15	2.66E-21	2.27E+07	1.10	0.82	1.10E-13
228.15	2.12E-21	2.77E+07	1.10	0.82	1.07E-13
233.15	1.71E-21	3.36E+07	1.09	0.82	1.04E-13
238.15	1.39E-21	4.03E+07	1.09	0.82	1.01E-13
243.15	1.14E-21	4.81E+07	1.09	0.82	9.84E-14
248.15	9.49E-22	5.69E+07	1.08	0.82	9.61E-14
253.15	7.93E-22	6.68E+07	1.08	0.82	9.40E-14
258.15	6.68E-22	7.79E+07	1.08	0.82	9.21E-14
263.15	5.67E-22	9.03E+07	1.07	0.82	9.03E-14
268.15	4.85E-22	1.04E+08	1.07	0.82	8.87E-14
273.15	4.17E-22	1.19E+08	1.07	0.82	8.71E-14
278.15	3.61E-22	1.36E+08	1.06	0.82	8.55E-14
283.15	3.14E-22	1.54E+08	1.06	0.82	8.42E-14
288.15	2.75E-22	1.74E+08	1.06	0.82	8.29E-14
293.15	2.42E-22	1.96E+08	1.06	0.82	8.16E-14
298.15	2.14E-22	2.19E+08	1.06	0.81	8.05E-14
303.15	1.90E-22	2.44E+08	1.05	0.81	7.94E-14
308.15	1.70E-22	2.71E+08	1.05	0.81	7.85E-14
313.15	1.52E-22	3.00E+08	1.05	0.81	7.76E-14
318.15	1.37E-22	3.31E+08	1.05	0.81	7.67E-14
323.15	1.24E-22	3.64E+08	1.05	0.81	7.59E-14

(a)

CH_2OO + ND_3	K_{eq}	k_{uni}	κ	v	k_{total}
223.15	3.15E-21	2.50E+07	1.09	0.83	1.42E-13
228.15	2.50E-21	3.03E+07	1.09	0.83	1.36E-13
233.15	2.00E-21	3.64E+07	1.08	0.83	1.30E-13
238.15	1.62E-21	4.35E+07	1.08	0.82	1.25E-13
243.15	1.32E-21	5.15E+07	1.08	0.82	1.20E-13
248.15	1.09E-21	6.05E+07	1.07	0.82	1.16E-13
253.15	9.04E-22	7.06E+07	1.07	0.82	1.12E-13
258.15	7.57E-22	8.19E+07	1.07	0.82	1.09E-13
263.15	6.39E-22	9.44E+07	1.06	0.82	1.05E-13
268.15	5.44E-22	1.08E+08	1.06	0.82	1.02E-13
273.15	4.66E-22	1.23E+08	1.06	0.82	9.97E-14
278.15	4.02E-22	1.40E+08	1.06	0.82	9.72E-14
283.15	3.48E-22	1.58E+08	1.05	0.82	9.48E-14
288.15	3.04E-22	1.78E+08	1.05	0.82	9.27E-14
293.15	2.66E-22	1.99E+08	1.05	0.81	9.06E-14
298.15	2.35E-22	2.22E+08	1.05	0.81	8.87E-14
303.15	2.08E-22	2.47E+08	1.05	0.81	8.69E-14
308.15	1.85E-22	2.73E+08	1.05	0.81	8.53E-14
313.15	1.65E-22	3.01E+08	1.04	0.81	8.37E-14
318.15	1.48E-22	3.31E+08	1.04	0.80	8.23E-14
323.15	1.34E-22	3.63E+08	1.04	0.80	8.09E-14

(b)

CH_2OO + NH_3	K_{eq}	k_{uni}	κ	ν	k_{total}
223.15	6.09E-21	8.74E+06	1.15	0.35	4.31E-14
228.15	4.89E-21	1.06E+07	1.14	0.36	4.24E-14
233.15	3.97E-21	1.27E+07	1.13	0.37	4.19E-14
238.15	3.25E-21	1.52E+07	1.13	0.37	4.13E-14
243.15	2.68E-21	1.80E+07	1.12	0.38	4.08E-14
248.15	2.23E-21	2.11E+07	1.12	0.38	4.04E-14
253.15	1.87E-21	2.47E+07	1.11	0.39	3.99E-14
258.15	1.58E-21	2.87E+07	1.11	0.39	3.95E-14
263.15	1.34E-21	3.31E+07	1.10	0.40	3.92E-14
268.15	1.15E-21	3.81E+07	1.10	0.41	3.89E-14
273.15	9.84E-22	4.36E+07	1.10	0.41	3.86E-14
278.15	8.50E-22	4.97E+07	1.09	0.42	3.83E-14
283.15	7.38E-22	5.64E+07	1.09	0.42	3.81E-14
288.15	6.44E-22	6.38E+07	1.09	0.42	3.79E-14
293.15	5.65E-22	7.18E+07	1.08	0.43	3.77E-14
298.15	4.97E-22	8.06E+07	1.08	0.43	3.75E-14
303.15	4.39E-22	9.01E+07	1.08	0.44	3.74E-14
308.15	3.90E-22	1.01E+08	1.08	0.44	3.72E-14
313.15	3.47E-22	1.12E+08	1.07	0.45	3.71E-14
318.15	3.10E-22	1.24E+08	1.07	0.45	3.71E-14
323.15	2.78E-22	1.37E+08	1.07	0.45	3.70E-14

(c)

CH_2OO + ND_3	K_{eq}	k_{uni}	κ	ν	k_{total}
223.15	5.91E-21	1.16E+07	1.13	0.34	5.24E-14
228.15	4.67E-21	1.40E+07	1.12	0.34	5.02E-14
233.15	3.73E-21	1.69E+07	1.12	0.34	4.83E-14
238.15	3.01E-21	2.01E+07	1.11	0.35	4.66E-14
243.15	2.45E-21	2.39E+07	1.11	0.35	4.50E-14
248.15	2.01E-21	2.81E+07	1.10	0.35	4.36E-14
253.15	1.66E-21	3.29E+07	1.10	0.35	4.23E-14
258.15	1.39E-21	3.83E+07	1.09	0.35	4.11E-14
263.15	1.16E-21	4.44E+07	1.09	0.36	4.00E-14
268.15	9.81E-22	5.11E+07	1.09	0.36	3.91E-14
273.15	8.34E-22	5.87E+07	1.08	0.36	3.82E-14
278.15	7.13E-22	6.69E+07	1.08	0.36	3.74E-14
283.15	6.12E-22	7.62E+07	1.08	0.36	3.66E-14
288.15	5.29E-22	8.62E+07	1.08	0.37	3.59E-14
293.15	4.59E-22	9.73E+07	1.07	0.37	3.53E-14
298.15	4.00E-22	1.10E+08	1.07	0.37	3.47E-14
303.15	3.50E-22	1.23E+08	1.07	0.37	3.41E-14
308.15	3.08E-22	1.37E+08	1.07	0.37	3.36E-14
313.15	2.72E-22	1.53E+08	1.06	0.38	3.32E-14
318.15	2.41E-22	1.70E+08	1.06	0.38	3.28E-14
323.15	2.14E-22	1.88E+08	1.06	0.38	3.24E-14

(d)

Table S2. The optimized XYZ geometries (in Ångström) studied in this work, including CH_2OO, NH_3, vdW complex, transition state, and product of the reaction. Obtained by B3LYP/6-311+G(2d,2p).

NH_3			
N	-0.07915	-0.05308	0.01039
H	0.08668	-0.04126	1.00976
H	0.82094	0.04409	-0.44434
H	-0.61954	0.77399	-0.21394
CH_2OO			
C	-1.12167	-0.25566	0.08037
O	0.12217	-0.40115	0.14990
O	0.92634	0.62059	-0.21778
H	-1.52655	0.68453	-0.27245
H	-1.70370	-1.11155	0.38952
vdW complex			

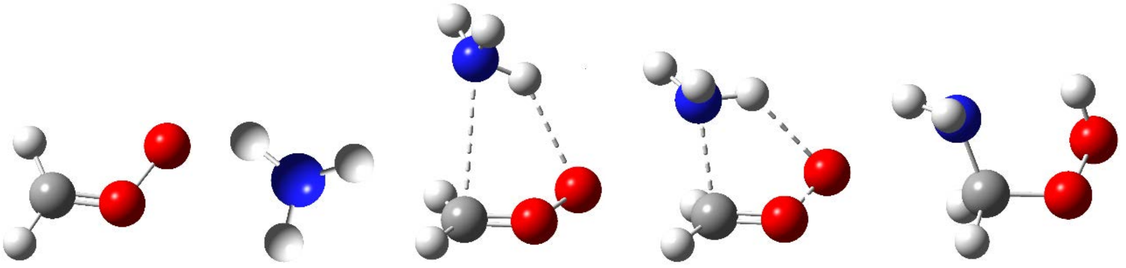
C	0.66578	1.07879	0.22093
H	0.19035	0.97665	1.18470
H	0.84250	2.02020	-0.28089
O	1.07498	0.06585	-0.38546
O	0.83450	-1.16097	0.18561
N	-1.97607	0.02369	-0.04639
H	-1.34930	-0.77694	0.01229
H	-2.70802	-0.10554	0.64140
H	-2.41363	0.00800	-0.95960
transition state			
C	0.01727	0.98914	0.26308
H	-0.07556	0.79178	1.32214
H	-0.31841	1.92650	-0.16563
O	0.89739	0.37090	-0.40272
O	1.14901	-0.92115	0.17196
N	-1.56866	-0.34017	-0.06962
H	-0.84233	-1.06861	-0.01375
H	-2.29690	-0.50154	0.61306
H	-1.96098	-0.29981	-1.00080
product			
C	-0.57355	0.60443	0.27508
H	-0.45839	0.60159	1.35961
H	-0.99381	1.55879	-0.05239
O	0.70610	0.61524	-0.33963
O	1.43563	-0.53186	0.15621
N	-1.33691	-0.55226	-0.13080
H	0.92659	-1.25546	-0.24385
H	-1.89533	-0.94265	0.61269
H	-1.91324	-0.39017	-0.94357

Table S3. Relative energies for the van der Waals, (vdW), transition state (TS), and product (Prod) for the CH_2OO+NH_3 and CH_2OO+ND_3 reaction optimized by B3LYP/ 6-311+G(2d,2p). The relative zero point corrected energy, in kcal mol^{-1}, are refined with QCISD(T)/CBS with core correlation. The zero of energy is set to infinitely separated reactants. The imaginary frequency at the transition state is given in cm^{-1}. We list the values by Misiewicz et al.[1] in parenthesis.

	QCISD(T)/CBS with core correlation			B3LYP/6-311+G(2d,2p)
	vdW	TS	Prod	imaginary frequency
CH_2OO+NH_3	-4.63 (-4.36)	-0.19 (0.42)	-43.26 (-42.11)	238.91 (302)
CH_2OO+ND_3	-4.94	-0.64	-43.80	226.05

Table S4. Frequencies of CH_2OO, NH_3, vdW complex, transition state, and product of the reaction. Obtained by B3LYP/6-311+G(2d,2p).

NH_3	CH_2OO	vdW complex	transition state	product
1036.57	531.21	76.24	221.95	172.68
1673.53	672.88	141.76	266.52	224.30
1673.55	923.43	166.75	337.50	375.72
3482.88	948.56	204.65	505.69	448.46
3598.86	1247.17	237.34	565.70	603.82
3598.89	1402.66	404.21	681.20	732.49
	1544.01	522.84	802.67	880.30
	3123.75	667.58	869.34	952.28
	3276.26	875.11	1095.25	1010.82
		976.27	1139.88	1073.00
		1081.42	1220.32	1261.52
		1243.05	1383.42	1343.50
		1415.10	1540.83	1409.12
		1567.34	1628.90	1414.64
		1665.49	1679.88	1487.07
		1688.76	3112.19	1662.42
		3139.84	3234.81	3029.81
		3287.04	3256.07	3082.95
		3438.58	3551.06	3551.67
		3559.77	3631.58	3639.10
		3601.61		3697.36



CH_2OO NH_3 vdW complex transition state product

Figure S1. The optimized geometries studied in this work. Obtained by B3LYP/6-311+G(2d,2p).

Derivation of the reaction rate fitting formula

CH_2OO was generated through the following reactions:

$$CH_2I_2 + hv \rightarrow CH_2I + I \qquad \text{(R1)}$$

$$CH_2I + O_2 \rightarrow CH_2OO + I \qquad \text{(R2)}$$

$$CH_2I + O_2 \rightarrow other\ products \qquad \text{(R3)}$$

The consumption of CH_2OO upon their generation included reactions as follows:

$$CH_2OO \xrightarrow{k_{uni}} products \qquad \text{(R4)}$$

$$CH_2OO + CH_2OO \xrightarrow{k_{self}} products \qquad \text{(R5)}$$

$$CH_2OO + X \xrightarrow{k_{other}} products \qquad \text{(R6)}$$

$$CH_2OO + NH_3 \xrightarrow{k_{rxn}} products \qquad \text{(R7)}$$

The formation of CH_2I comes from photolysis of CH_2I_2, the time-dependent concentration of CH_2I can be described as:

$$\frac{d[CH_2I]}{dt} = -(k_2 + k_3)[CH_2I][O_2] \qquad \text{(S1)}$$

The solution of Eq. (S1) gives a time-dependent concentration of CH_2I as shown in Eq. (S2):

$$[CH_2I]_t = [CH_2I]_0 \exp(-(K_2 + K_3)\, t) \qquad \text{(S2)}$$

Where k_2 and k_3 are the rate coefficients of reaction (R2) and (R3); and $\mathrm{K}_2 = \mathrm{k}_2[O_2]$ is the reaction rate of (R2), likewise, $\mathrm{K}_3 = \mathrm{k}_3[O_2]$ is the reaction rate of (R3). $[\mathrm{CH_2I}]_0$ is the concentration of $\mathrm{CH_2I}$ at time zero, which is corresponding to the time the photolysis laser was fired.

Similarly, the formation of CH_2OO can be written as:

$$\frac{d[CH_2OO]_f}{dt} = k_2[CH_2I][O_2] \qquad \text{(S3)}$$

Combine Eq. (S2) and Eq. (S3), the time-dependent formation of CH_2OO is

$$[CH_2OO]_f = \frac{K_2}{K_2 + K_3}[CH_2I]_0(1 - e^{-(K_2+K_3)t}) \qquad \text{(S4)}$$

The consumption of CH_2OO can be expressed by combining both the first- and second-order kinetics of CH_2OO

$$\frac{d[CH_2OO]_c}{dt} = -2k_{self}[CH_2OO]_c{}^2 - K_{obs}[CH_2OO]_c \qquad (S5)$$

Numerical solution of Eq. (S5) gives a time-dependent decay of CH_2OO as shown in Eq. (S6):

$$[CH_2OO]_c = \frac{K_{obs}[CH_2OO]_0}{K_{obs}e^{K_{obs}t} - 2k_{self}[CH_2OO]_0 + 2k_{self}[CH_2OO]_0e^{K_{obs}t}} \qquad (S6)$$

where K_{obs} is the overall pseudo first-order loss rate of CH_2OO, k_{self} is the effective second-order rate coefficient of CH_2OO and $[CH_2OO]_0$ is the initial CH_2OO concentration.

When omitting the correlation between the formation and consumption of CH_2OO, the time-dependent trace of CH_2OO can be approximately described by combining of Eq. (S4) and Eq. (S6) as follows:

$$[CH_2OO]_t = \frac{K_{obs}[CH_2OO]_0}{K_{obs}e^{K_{obs}t} - 2k_{self}[CH_2OO]_0 + 2k_{self}[CH_2OO]_0e^{K_{obs}t}}$$

$$+\frac{K_2}{K_2 + K_3}[CH_2I]_0(1 - e^{-(K_2+K_3)t}) \qquad (S7)$$

In the current experiment, OH radicals originated from the unimolecular decomposition of CI and the loss of OH radicals comes from reactions with CH_2I_2, bath gas in the reactor and the wall loss, etc.

$$\frac{d[OH]}{dt} = K_d[CH_2OO] - K_{loss}[OH] \qquad (S8)$$

where K_d is the rate of the formation of OH radicals from the unimolecular decomposition of CH_2OO and K_{loss} is the overall loss rate of OH radial. Applying steady-state approximation to OH, [OH] is obtained as follows:

$$[\mathrm{OH}] = \frac{K_d}{K_{loss}}[CH_2OO] \qquad (S9)$$

Combining expressions (S7) and (S9), the time-dependent OH signal is given by

$$S_{OH}(t) = \frac{K_{obs}A_0}{K_{obs}e^{K_{obs}t} - 2k_{self}[CH_2OO]_0 + 2k_{self}[CH_2OO]_0 e^{K_{obs}t}}$$

$$+A_1(1 - e^{-(K_2+K_3)t}) \qquad (S10)$$

where $\mathrm{A_0} = \alpha\frac{\mathrm{k_d}}{\mathrm{k_{loss}}}[\mathrm{CH_2OO}]_0$, $\mathrm{A_1} = \alpha\frac{\mathrm{k_d}}{\mathrm{k_{loss}}}\frac{\mathrm{k_2}}{\mathrm{k_2+k_3}}[\mathrm{CH_2I}]_0$, α is the detection efficiency of OH. During the fitting of the OH signal, $\mathrm{A_0}$, $\mathrm{A_1}$, $\mathrm{k_{obs}}$, $(\mathrm{k_2} + \mathrm{k_3})$ and $[CH_2OO]_0$ were allowed to vary, while $\mathrm{k_{self}}$ was fixed to 8×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, in reference to the results of Ting et al.[2]

1. J. P. Misiewicz, S. N. Elliott, K. B. Moore and H. F. Schaefer, *Phys. Chem. Chem. Phys.*, 2018, **20**, 7479-7491.
2. W. L. Ting, C. H. Chang, Y. F. Lee, H. Matsui, Y. P. Lee and J. J. Lin, *J. Chem. Phys.*, 2014, **141**, 104308.