Supplement of Atmos. Chem. Phys., 20, 13541–13555, 2020
https://doi.org/10.5194/acp-20-13541-2020-supplement

Atmospheric Chemistry and Physics
Open Access
EGU

Supplement of

Reaction between $CH_3C(O)OOH$ (peracetic acid) and OH in the gas phase: a combined experimental and theoretical study of the kinetics and mechanism

Matias Berasategui et al.

Correspondence to: John N. Crowley (john.crowley@mpic.de)

Table S1. Rate constants for the reaction OH (k_6) and OD (k_7) with $CH_3C(O)OH$ at 298 K.

Precursor	Pressure (Torr)	$[CH_3C(O)OH]$ [a]	[Precursor] [b]	$[OH]_0$ [c]	k' [d]	k_6 or k_7 [e]
H_2O_2 (OH)	102 ± 2	0	19.42	6.47	472.67 ± 2.3	6.95 ± 0.08
		19.54 ± 1.20	19.42	6.48	1679.33 ± 6.2	
		24.70 ± 1.25	19.42	6.48	2016.66 ± 12.3	
		30.76 ± 1.31	19.41	6.47	2606.32 ± 9.2	
		36.82 ± 1.37	19.42	6.48	3046.21 ± 8.7	
		41.76 ± 1.04	19.42	6.47	3363.66 ± 10.6	
H_2O_2 (OH)	57 ± 0.3	0	4.85	1.62	668.94 ± 10.4	7.04 ± 0.28
		4.01 ± 1.04	3.33	1.11	986.54 ± 17.2	
		11.64 ± 1.17	2.99	1.00	1512.84 ± 30.4	
		17.75 ± 1.18	3.83	1.28	1930.14 ± 59.3	
		18.51 ± 1.19	3.23	1.08	1972.35 ± 43.9	
		21.95 ± 1.22	2.99	1.00	2229.59 ± 35.0	
		24.81 ± 1.25	2.56	0.85	2393.95 ± 39.4	
DNO_3 (OD)	66 ± 1	0	5.84	1.95	1129.54 ± 26.5	7.30 ± 0.26
		4.27 ± 1.04	5.88	1.96	1436.82 ± 43.0	
		9.88 ± 1.10	6.31	2.11	1865.88 ± 60.2	
		11.45 ± 1.11	5.95	1.99	1960.29 ± 48.0	
		14.15 ± 1.14	5.95	1.98	2153.9 ± 58.2	
		16.17 ± 1.16	6.32	2.11	2312.91 ± 47.5	

[a] in 10^{14} molecule cm^{-3} (errors are total uncertainty, 2σ).
[b] in 10^{14} molecule cm^{-3}.
[c] Calculated from $[H_2O_2]$ or $[DNO_3]$, in 10^{11} molecule cm^{-3}.
[d] First-order decay constant for OH or OD (s^{-1}).
[e] 10^{-13} cm^3 $molecule^{-1}$ s^{-1}.

Table S2. Reaction between OH or OD and $CH_3C(O)OOH$: Experimental conditions and results.

Temp (K)	Pressure (Torr)	Pre-cursor	$[CH_3C(O)OH]$ [a]	$[CH_3C(O)OOH]$ [b]	$[OH]_0$ [c]	$k_4'+k_6'+k_d$	k_6'	$k_4'+k_d$	k_4
298	103 ± 2	PAA	2.52 ± 0.58	6.17 ± 1.84	3.1	302 ± 2	178 ± 28	124±25	3.2 ± 0.6
			4.82 ± 0.53	11.6 ± 2.11	5.8	470 ± 3	340 ± 53	130±48	
			8.20 ± 0.47	16.7 ± 2.36	8.3	715 ± 3	579 ± 90	136±82	
			12.8 ± 0.41	26.8 ± 2.87	13.4	1089 ± 5	904 ± 141	185±128	
			14.5 ± 0.40	33.5 ± 3.21	16.8	1254 ± 4	1024 ±160	230±145	
			15.6 ± 0.39	35.7 ± 3.32	17.9	1337 ± 3	1102 ±172	235±156	
306	104 ± 2	PAA	8.62 ± 0.48	12.9 ± 2.17	6.4	744 ± 6	570 ± 89	174±81	4.3 ± 0.5
			13.0 ± 0.42	21.9 ± 2.63	10.9	1081 ± 8	859 ± 134	222±122	
			15.8 ± 0.40	28.0 ± 2.93	14.0	1299 ± 11	1044 ± 163	255±148	
			18.3 ± 0.37	32.5 ± 3.15	16.2	1459 ± 12	1210 ± 189	249±172	
			20.2 ± 0.36	37.8 ± 3.42	18.9	1611 ± 12	1335 ± 209	276±189	
316	103 ± 2	PAA	3.90 ± 0.56	6.79 ± 1.87	3.4	377 ± 2	239 ± 37	138±34	3.7 ± 0.6
			8.49 ± 0.48	13.7 ± 2.22	6.9	665 ± 5	520 ± 81	145±74	
			12.8 ± 0.42	22.7 ± 2.66	11.3	1005 ± 6	784 ± 123	220±111	
			15.4 ± 0.40	28.8 ± 2.97	14.4	1160 ± 8	944 ± 147	217±134	
			18.1 ± 0.38	32.6 ± 3.16	16.3	1322 ± 8	1109 ± 173	213±157	
			20.2 ± 0.36	38.5 ± 3.45	19.2	1498 ± 9	1238 ± 193	260±175	
326	102 ± 2	PAA	4.70 ± 0.56	8.21 ± 1.94	4.1	421 ± 3	269 ± 42	152±38	2.5 ± 0.8
			8.35 ± 0.49	14.4 ± 2.25	7.2	616 ± 6	478 ± 75	138±68	
			15.2 ± 0.41	29.1 ± 2.98	14.5	1061 ± 10	871 ± 136	190±124	
			12.4 ± 0.45	22.9 ± 2.68	11.5	882 ± 8	710 ± 111	172±101	
			17.7 ± 0.40	33.2 ± 3.19	16.6	1226 ± 11	1014 ± 158	212±144	
			19.9 ± 0.38	37.8 ± 3.42	18.9	1400 ± 8	1140 ± 178	260±161	
335	102 ± 2	PAA	4.35 ± 0.54	7.96 ± 1.93	4.0	397 ± 7	235 ± 37	163±34	2.9 ± 0.6
			8.92 ± 0.49	14.9 ± 2.28	7.5	643 ± 7	481 ± 75	162±68	
			12.4 ± 0.44	20.7 ± 2.56	10.3	852 ± 11	669 ± 104	184±95	
			15.8 ± 0.41	28.1 ± 2.93	14.0	1070 ± 10	852 ± 133	218±121	
			17.9 ± 0.39	32.3 ± 3.15	16.2	1195 ± 15	965 ± 151	229±137	
			19.4 ± 0.39	37.3 ± 3.40	18.7	1321 ± 9	1046 ± 163	275±148	
345	101 ± 2	PAA	5.66 ± 0.54	10.4 ± 2.05	5.2	406 ± 6	288 ± 45	118±41	3.5 ± 0.4
			8.91 ± 0.50	14.4 ± 2.25	7.2	589 ± 8	454 ± 71	135±65	
			12.6 ± 0.45	22.5 ± 2.66	11.3	787 ± 11	642 ± 100	145±91	
			15.7 ± 0.42	28.3 ± 2.95	14.2	995 ± 13	800 ± 125	195±114	
			17.9 ± 0.40	31.9 ± 3.13	16.0	1104 ± 13	912 ± 142	192±130	
			19.3 ± 0.39	36.3 ± 3.35	18.2	1193 ± 13	983 ± 154	209±140	
353	101 ± 2	PAA	5.46 ± 0.57	8.83 ± 1.97	4.4	351 ± 8	266 ± 42	85±38	4.0 ± 0.4
			8.81 ± 0.50	14.8 ± 2.27	7.4	548 ± 16	429 ± 67	120±63	
			12.8 ± 0.45	22.6 ± 2.66	11.3	776 ± 14	623 ± 97	154±89	
			15.6 ± 0.42	28.4 ± 2.95	14.2	915 ± 15	759 ± 119	156±108	
			17.3 ± 0.40	32.5 ± 3.16	16.3	1013 ± 10	842 ± 132	171±119	
			19.6 ± 0.39	35.5 ± 3.31	17.8	1155 ± 10	954 ± 149	201±135	
298	57 ± 1	$DONO_2$	8.89 ± 0.28	18.4 ± 2.45	2	1686 ± 36	628 ± 98	1058±96	4.3 ± 0.5
			12.6 ± 0.52	26.9 ± 2.87	2	1993 ± 41	890 ± 139	1104±132	
			15.8 ± 0.41	33.3 ± 3.20	2	2218 ± 54	1116 ±174	1102±167	
			23.5 ± 0.64	49.0 ± 3.98	2	2862 ± 73	1659 ± 259	1202±246	
			29.4 ± 0.66	61.9 ± 4.63	2	3325 ± 71	2076 ± 324	1249±302	

[a]Concentration of $CH_3C(O)OH$ in 10^{14} molecule cm^{-3}. [b]Concentration of $CH_3C(O)OOH$ in 10^{14} molecule cm^{-3} [c]OH concentration in 10^{11} molecule cm^{-3}. PAA = $CH_3C(O)OOH$.

Table S3. Reaction scheme used in the numerical simulations.

Reaction	**Rate coefficient**	**Reference**
$OH + CH_3COOH \rightarrow H_2O + CH_3 + CO_2$	$8.4 \times 10^{-20} T^2 \exp(1356/T)$	(IUPAC, 2020) [a]
$OH + CH_3C(O)OOH \rightarrow H_2O + CH_3C(O)O_2$	varied	This work
$OH + CH_3 \rightarrow CH_3OH$	1.2×10^{-10} [b]	(Sangwan et al., 2012) (Pereira et al., 1997)
$OH + CH_3C(O)O_2 \rightarrow HO_2 + CH_3 + CO_2$	1×10^{-10}	Analogy to $OH + CH_3O_2$ [a]
$OH + HO_2 \rightarrow H_2O + O_2$	$4.8 \times 10^{-11} \exp(250/T)$	(IUPAC, 2020)
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2.0×10^{-12}	(IUPAC, 2020)
$HO_2 + CH_3C(O)O_2 \rightarrow CH_3C(O)OOH + O_2$	$1.5 \times 10^{-12} \exp(480/T)$	(IUPAC, 2020)
$HO_2 + CH_3C(O)O_2 \rightarrow CH_3C(O)OH + O_3$	$4.4 \times 10^{-15} \exp(1910/T)$	(IUPAC, 2020)
$HO_2 + CH_3C(O)O_2 \rightarrow OH + CH_3 + CO_2 + O_2$	$4.66 \times 10^{-12} \exp(235/T)$	(IUPAC, 2020) [a]
$CH_3 + CH_3 \rightarrow C_2H_6$	5×10^{-11}	(Slagle et al., 1988)
$HO_2 + CH_3 \rightarrow CH_3O + OH$	3×10^{-11}	(Baulch et al., 2005)
$CH_3C(O)O_2 + CH_3C(O)O_2 \rightarrow 2\ CH_3 + 2\ CO_2 + O_2$	$2.9 \times 10^{-12} \exp(500/T)$	(IUPAC, 2020) [a]

[a]Assumes rapid decomposition of the initially formed $CH_3C(O)O$ radical. [b]Termolecular reaction at the high-pressure limit under our experimental conditions.

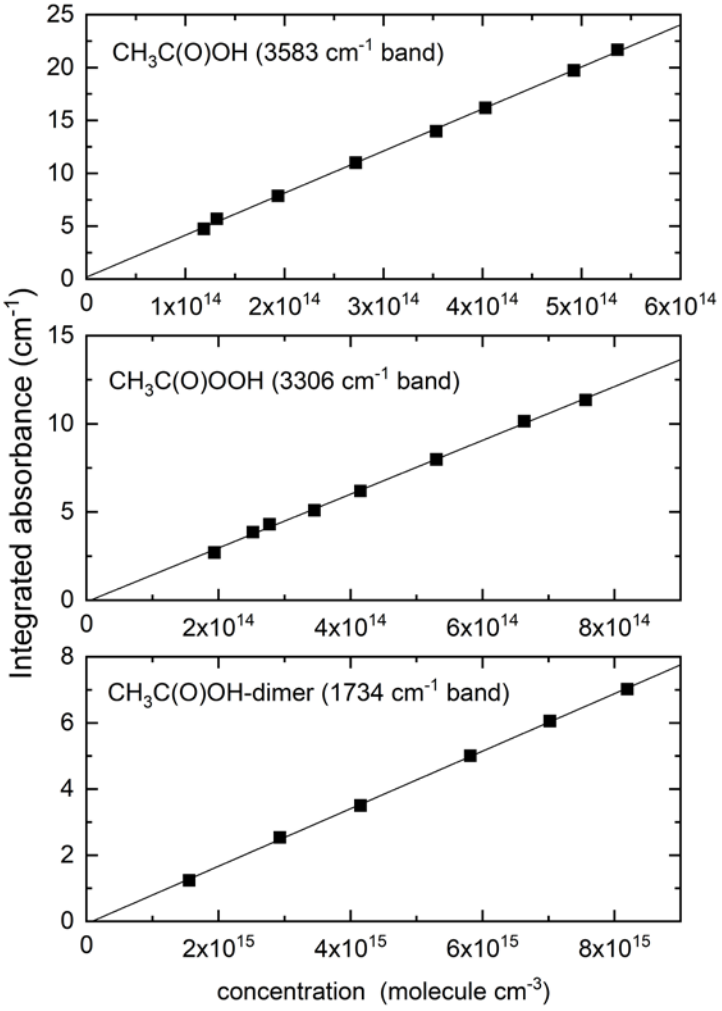

Figure S1. Beer-Lambert plots of integrated absorption versus concentration of $CH_3C(O)OH$, $CH_3C(O)OOH$ and $CH_3C(O)OH$-dimer.

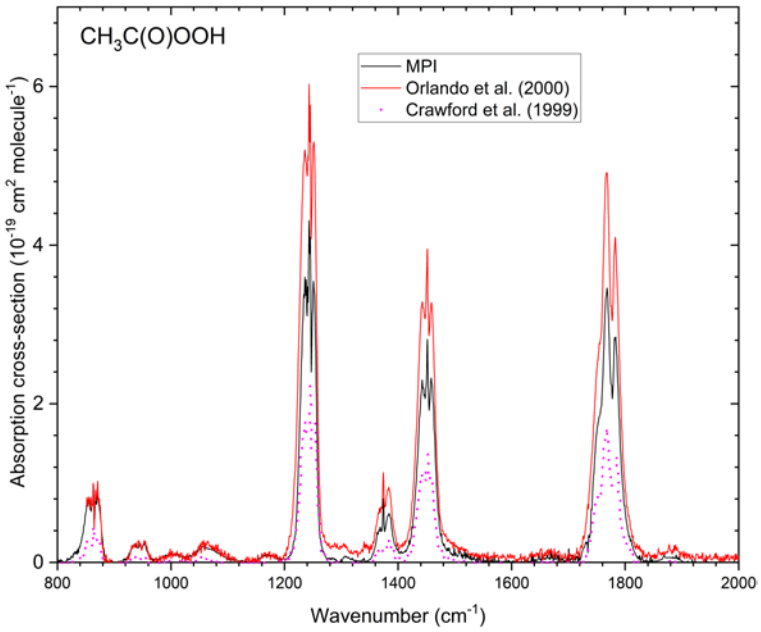

Figure S2. IR spectra of $CH_3C(O)OOH$ recorded in this work (MPI), and those published by Orlando et al. (2000) (who reported a single value at 1251 cm^{-1}) and Crawford et al. (1999). The spectrum of Crawford et al. was digitized from their Figure 2, that of Orlando et al. was kindly provided by the authors.

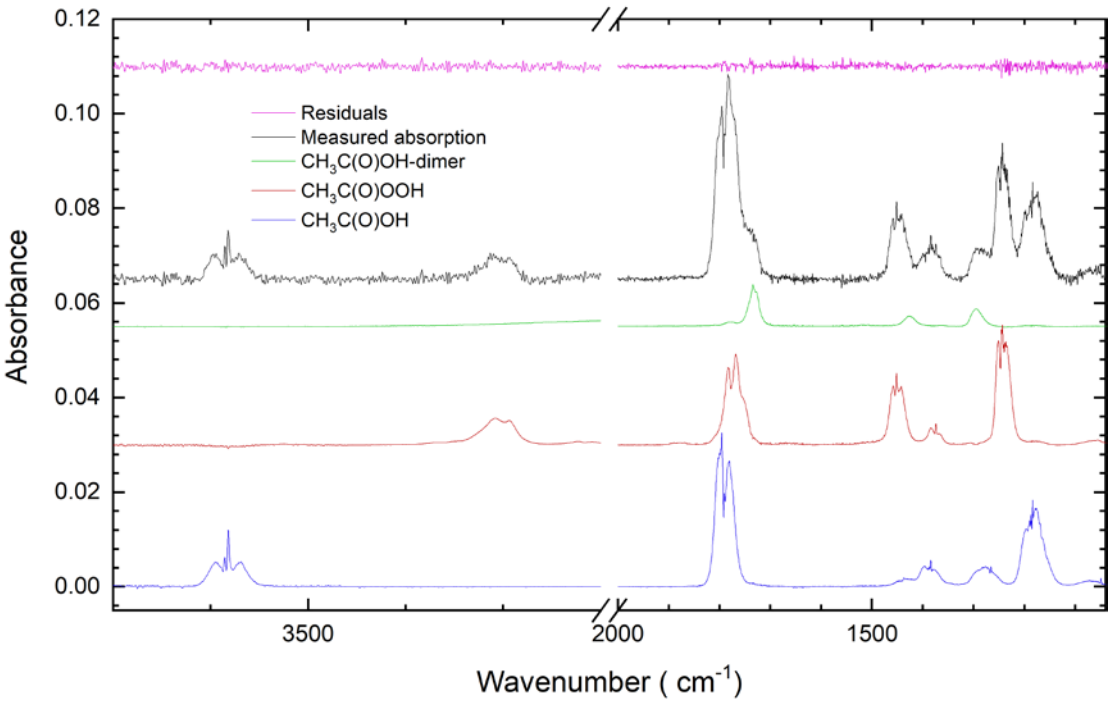

Figure S3. IR-absorbance (black trace) measured during an experiment to determine k_4 at 298 K and 125 Torr N_2. The scaled reference spectra of $CH_3C(O)OOH$, $CH_3C(O)OH$ and $CH_3C(O)OH$-dimer as well as the residual obtained by subtraction are also displayed.

References

Baulch, D. L., Bowman, C. T., Cobos, C. J., Cox, R. A., Just, T., Kerr, J. A., Pilling, M. J., Stocker, D., Troe, J., Tsang, W., Walker, R. W., and Warnatz, J.: Evaluated kinetic data for combustion modeling: Supplement II, J. Phys. Chem. Ref. Data, 34, 757-1397, 2005.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation, (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.) http://iupac.pole-ether.fr/index.html., 2020. 2020.

Pereira, R. D., Baulch, D. L., Pilling, M. J., Robertson, S. H., and Zeng, G.: Temperature and pressure dependence of the multichannel rate coefficients for the CH_3+OH system, J. Phys. Chem. A, 101, 9681-9693, 1997.

Sangwan, M., Chesnokov, E. N., and Krasnoperov, L. N.: Reaction CH_3 + OH Studied over the 294-714 K Temperature and 1-100 bar Pressure Ranges, J. Phys. Chem. A, 116, 8661-8670, 2012.

Slagle, I. R., Gutman, D., Davies, J. W., and Pilling, M. J.: Study of the recombination reaction CH_3 + CH_3 -> C_2H_6. 1. Experiment, J. Phys. Chem., 92, 2455-2462, 1988.