Supplementary Information

Kinetics of OH + SO_2 + M: Temperature-dependent rate coefficients in the fall-off regime and the influence of water vapour

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Table S1. Values of k_1 measured in N_2 bath gas.

p (Torr)	*T* (K)	M (×10^{18} molecule cm^{-3})	precursor	$[OH]_0$ (×10^{11} molecule cm^{-3})	k_1 [1] (×10^{-13} cm^3 $molecule^{-1}$ s^{-1})
26.8	220	1.18	HNO_3	4.4	4.57 ± 0.14
39.9		1.75	HNO_3	2.3	5.58 ± 0.31
65.2		2.86	HNO_3	0.7	7.25 ± 0.18
89.6		3.93	HNO_3	1.4	8.29 ± 0.48
121.1		5.31	HNO_3	0.9	9.46 ± 0.28
151.4		6.64	HNO_3	0.9	9.97 ± 0.53
181.5		7.96	HNO_3	1.3	10.82 ± 0.58
222.5		9.76	HNO_3	4.2	11.06 ± 0.46
301.1		13.21	HNO_3	1.2	12.07 ± 0.60
400.4		17.57	HNO_3	1.5	13.71 ± 0.41
23.8	250	0.92	HNO_3	6.2	3.11 ± 0.15
45.0		1.74	HNO_3	5.0	4.03 ± 0.29
74.4		2.87	HNO_3	3.7	5.43 ± 0.23
98.7		3.81	HNO_3	5.0	6.32 ± 0.40
130.0		5.02	HNO_3	5.9	7.24 ± 0.42
160.4		6.19	HNO_3	7.8	8.21 ± 0.19
195.5		7.55	HNO_3	6.0	8.96 ± 0.48
243.2		9.39	HNO_3	5.8	9.32 ± 0.48
298.3		11.52	HNO_3	3.9	9.68 ± 0.66
398.7		15.40	HNO_3	3.6	11.31 ± 0.42
499.2		19.28	HNO_3	3.4	11.87 ± 0.67
23.6	273	0.83	HNO_3	5.1	2.17 ± 0.07
35.0		1.24	H_2O_2	4.3	2.83 ± 0.12
44.2		1.56	HNO_3	3.7	3.26 ± 0.08
58.9		2.08	H_2O_2	13.6	3.91 ± 0.26
69.9		2.47	H_2O_2	2.9	4.41 ± 0.24
80.4		2.84	HNO_3	2.9	4.70 ± 0.19
98.5		3.48	H_2O_2	7.0	5.02 ± 0.12
108.8		3.85	H_2O_2	5.9	5.15 ± 0.22
121.3		4.29	HNO_3	6.2	5.43 ± 0.19
148.7		5.26	H_2O_2	4.5	6.25 ± 0.34
174.8		6.18	HNO_3	5.9	6.64 ± 0.15
216.4		7.65	HNO_3	5.0	7.35 ± 0.27
247.9		8.77	H_2O_2	6.6	8.17 ± 0.40
301.2		10.65	H_2O_2	9.3	9.02 ± 0.35
398.3		14.08	H_2O_2	11.4	10.25 ± 0.19

502.3		17.76	H_2O_2	15.2	10.72 ± 0.38
14.2	298	0.46	H_2O_2	5.8	1.30 ± 0.07
17.8		0.58	H_2O_2	3.2	1.49 ± 0.08
20.4		0.66	HNO_3	4.3	1.46 ± 0.04
22.1		0.72	H_2O_2	8.7	1.49 ± 0.06
30.5		0.99	H_2O_2	4.0	1.88 ± 0.02
43.5		1.41	HNO_3	4.2	2.24 ± 0.12
46.8		1.52	H_2O_2	2.1	2.46 ± 0.10
59.9		1.94	H_2O_2	4.7	2.97 ± 0.10
67.6		2.19	HNO_3	7.2	3.18 ± 0.14
74.8		2.42	H_2O_2	3.6	3.56 ± 0.15
97.9		3.17	HNO_3	2.4	3.74 ± 0.23
105.4		3.41	H_2O_2	2.5	4.06 ± 0.30
125.7		4.07	H_2O_2	5.9	4.01 ± 0.15
126.0		4.08	H_2O_2	4.4	4.20 ± 0.16
134.4		4.35	H_2O_2	3.6	4.70 ± 0.08
146.9		4.76	H_2O_2	4.2	4.88 ± 0.11
163.4		5.29	H_2O_2	2.3	5.50 ± 0.10
174.4		5.65	H_2O_2	3.0	5.45 ± 0.29
195.0		6.32	H_2O_2	3.6	5.54 ± 0.15
201.1		6.51	HNO_3	2.6	5.52 ± 0.21
247.5		8.02	H_2O_2	3.8	6.50 ± 0.31
298.6		9.67	H_2O_2	4.0	7.34 ± 0.24
299.0		9.69	HNO_3	3.5	6.87 ± 0.23
348.5		11.29	H_2O_2	8.5	7.35 ± 0.29
396.6		12.85	H_2O_2	7.5	7.58 ± 0.32
403.5		13.07	HNO_3	6.3	7.99 ± 0.32
453.2		14.68	H_2O_2	10.4	8.70 ± 0.19
503.4		16.31	H_2O_2	10.0	8.69 ± 0.26
510.3		16.53	HNO_3	6.1	9.02 ± 0.55
562.5		18.22	H_2O_2	9.4	9.45 ± 0.19
595.4		19.29	HNO_3	5.9	9.02 ± 0.98
612.4		19.84	H_2O_2	7.7	9.52 ± 0.17
652.7		21.14	H_2O_2	9.3	10.02 ± 0.32
698.7		22.63	H_2O_2	6.3	10.23 ± 0.41
725.0		23.49	H_2O_2	11.3	10.49 ± 0.42
742.0		24.04	H_2O_2	7.3	10.53 ± 0.41
30.6	333	0.89	H_2O_2	1.8	1.37 ± 0.06
49.4		1.43	H_2O_2	2.3	1.77 ± 0.11

78.6	2.28	H_2O_2	3.0	2.59 ± 0.23
100.7	2.92	H_2O_2	2.3	2.99 ± 0.10
134.7	3.90	H_2O_2	2.9	3.12 ± 0.17
165.5	4.80	H_2O_2	29.2	3.61 ± 0.32
198.9	5.77	H_2O_2	2.5	4.53 ± 0.13
252.4	7.32	H_2O_2	22.4	4.96 ± 0.12
301.5	8.74	H_2O_2	2.6	5.71 ± 0.18
350.0	10.15	H_2O_2	5.4	5.53 ± 0.46
398.7	11.56	H_2O_2	2.8	6.55 ± 0.44
449.1	13.02	H_2O_2	5.2	6.38 ± 0.48
499.5	14.48	H_2O_2	3.4	6.76 ± 0.24
597.4	17.32	H_2O_2	2.7	7.76 ± 0.31
702.7	20.37	H_2O_2	2.8	7.87 ± 0.21

Notes: [1]The uncertainty in k_1 is statistical only and does not incude uncertainty in the SO_2 cross-section.

Table S2. Values of k_1 measured in N_2-H_2O bath gas.[1]

T (K)	*p* (Torr)	M (10^{18} molecule/cm^3)	[H_2O] (10^{17} molecule/cm^3)	x_{H_2O}	x_{N_2}	k_1 [2] (10^{-13} cm^3 molecule^{-1} s^{-1})
273	49.3	1.74	0.00	0.000	1.000	3.42 ± 0.19
	50.6	1.79	0.22	0.012	0.988	3.49 ± 0.15
	49.5	1.75	0.28	0.016	0.984	3.52 ± 0.28
	50.4	1.78	0.44	0.024	0.976	3.67 ± 0.25
	49.9	1.76	0.54	0.031	0.969	3.69 ± 0.16
	50.6	1.79	0.64	0.036	0.964	3.68 ± 0.32
	50.5	1.79	0.84	0.047	0.953	3.81 ± 0.34
298	49.1	1.59	0.00	0.000	1.000	2.59 ± 0.10
	49.5	1.60	0.31	0.020	0.980	2.71 ± 0.17
	49.8	1.61	0.43	0.027	0.973	2.78 ± 0.07
	50.3	1.63	0.77	0.047	0.953	2.94 ± 0.13
	50.6	1.64	1.14	0.070	0.930	3.03 ± 0.13
	50.3	1.63	1.54	0.095	0.905	3.13 ± 0.16
	50.8	1.65	1.93	0.118	0.882	3.29 ± 0.15
	52.3	1.69	2.53	0.149	0.851	3.65 ± 0.12
	51.6	1.67	2.87	0.172	0.828	3.79 ± 0.34
	50.4	1.63	3.02	0.185	0.815	4.14 ± 0.42
	54.8	1.78	3.41	0.192	0.808	4.18 ± 0.13
333	49.9	1.45	0.00	0.000	1.000	1.70 ± 0.04
	50.0	1.45	0.36	0.025	0.975	1.89 ± 0.11
	50.1	1.45	0.70	0.048	0.952	1.96 ± 0.07
	50.6	1.47	0.74	0.050	0.950	2.11 ± 0.15
	50.2	1.46	1.17	0.081	0.919	2.32 ± 0.20
	50.2	1.46	1.39	0.095	0.905	2.23 ± 0.18
	50.2	1.46	1.96	0.135	0.865	2.20 ± 0.14
	49.8	1.44	2.13	0.148	0.852	2.36 ± 0.34
	50.2	1.46	2.49	0.171	0.829	2.65 ± 0.37

[1] H_2O_2 was used as OH precursor in all measurements. [2]The uncertainty in k_1 is statistical only and does not incude uncertainty in the SO_2 cross-section.

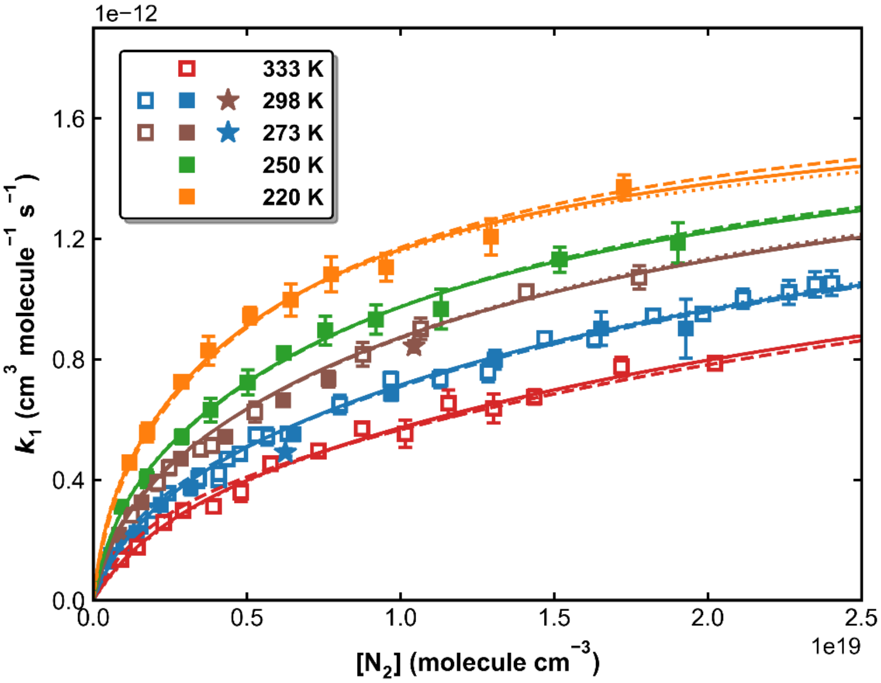

Figure S1. Measured (symbols) values of k_1 in N_2 bath gas and parameterization (lines) using the different methods listed in **Table 2** (Method 1: solid lines; Method 2: dashed lines; Method 3: dotted lines).

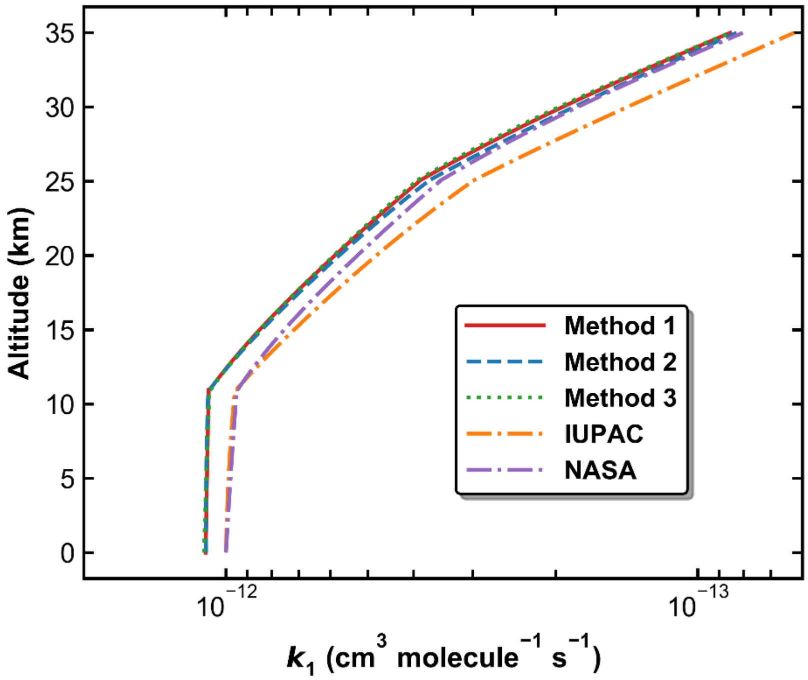

Figure S2. Values of k_1 using the three different parameterisation methods listed in **Table 2** at different altitudes and a comparison with the IUPAC and NASA recommendations. The altitude dependent pressure and temperature were calculated using parameters given in an Earth atmosphere model (https://www.grc.nasa.gov/www/BGH/atmosmet.html).

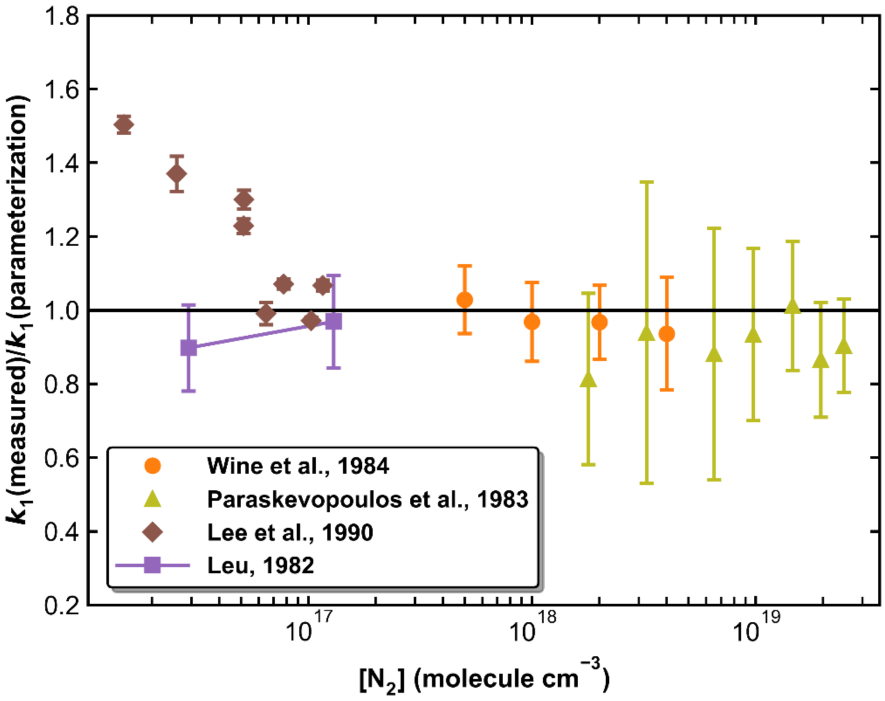

Figure S3. The ratio of rate coefficients obtained in N_2 bath-gas reported by (Leu, 1982; Paraskevopoulos et al., 1983; Wine et al., 1984; Lee et al., 1990) to the current parameterization as a function of N_2 molecular density at around 298 K.

Further parameterization methods for termolecular reactions

The NASA evaluation panel uses a simplified form of the Troe expression for termolecular reactions, with

$$k_{NASA}\ (P,T) = \frac{k_0\left(\frac{T}{298}\right)^{-n}[M]}{1+\frac{k_0\left(\frac{T}{298}\right)^{-n}[M]}{k_\infty\left(\frac{T}{298}\right)^{-m}}} 0.6^{\left\{1+\left[log\left(\frac{k_0\left(\frac{T}{298}\right)^{-n}[M]}{k_\infty\left(\frac{T}{298}\right)^{-m}}\right)\right]^2\right\}^{-1}} \tag{S1}$$

where [M] = molecular density (in molecule cm^{-3}), T is in kelvin. This expression should be used when inputting the “NASA” parameters from **Table 2**.

Blitz et al. (2017) used a more detailed form of the Troe expression (Troe and Ushakov, 2014) which is applicable to the cases of “broad” fall-off curves and characterized by the following equations:

$$\frac{k}{k_\infty\left(\frac{T}{298}\right)^{-m}} = \frac{x}{1+x} F(x) \tag{S2}$$

where

$$x = \frac{k_0(T/298)^{-n}}{k_\infty(T/298)^{-m}}[M] \tag{S3}$$

and

$$F(x) = \left(1+\frac{x}{x_0}\right)/[1+(x/x_0)^p]^{\frac{1}{p}} \tag{S4}$$

with

$$p = \left[\frac{\ln 2}{\ln\left(\frac{2}{F_\mathrm{C}}\right)}\right]\left[1-b+b\left(\frac{x}{x_0}\right)^q\right] \tag{S5}$$

where

$$q = (F_\mathrm{C}-1)/\ln(F_\mathrm{C}/10) \tag{S6}$$

Besides those listed in **Table 2**, the parameters x_0= 0.94 and b = 0.19 are also required. These values were provided by Mark Blitz in a personal communication.

Parametrization for k_1 in N_2-H_2O bath using different F_C for N_2 and H_2O

According to the approach proposed by Burke and Song (2017), the broadening factor for a gas-mixture can also expressed by the weighed sum of the broadening factors in the two individual bath gases, in this case N_2 and H_2O:

$$\log F^{\mathrm{N_2-H_2O}} = X_{\mathrm{N_2}} \log F^{\mathrm{N_2}} + X_{\mathrm{H_2O}} \log F^{\mathrm{H_2O}} \tag{S1}$$

where

$$\log F^{\mathrm{N_2}} = \frac{\log F_{\mathrm{C}}^{\mathrm{N2}}}{1+[\log(\frac{(x_{\mathrm{N2}} k_{1,0}^{\mathrm{N2}}\left(\frac{T}{300}\right)^{-n} + x_{\mathrm{H_2O}} k_{1,0}^{\mathrm{H2O}}\left(\frac{T}{300}\right)^{-o})[M]}{k\infty\left(\frac{T}{300}\right)^{-m}})/(0.75-1.27\log F_{\mathrm{C}}^{\mathrm{N2}})]^2} \tag{S2}$$

$$\log F^{\mathrm{H_2O}} = \frac{\log F_{\mathrm{C}}^{\mathrm{H2O}}}{1+[log(\frac{(x_{\mathrm{N_2}} k_{1,0}^{\mathrm{N2}}\left(\frac{T}{300}\right)^{-n} + x_{\mathrm{H_2O}} k_{1,0}^{\mathrm{H2O}}\left(\frac{T}{300}\right)^{-o})[M]}{k\infty\left(\frac{T}{300}\right)^{-m}})/(0.75-1.27\log F_{\mathrm{C}}^{\mathrm{H2O}})]^2} \tag{S3}$$

, and the weights for the N_2 and the H_2O terms are characterized by:

$$X_{\mathrm{N_2}} = \frac{x_{\mathrm{N_2}} k_{1,0}^{\mathrm{N2}}\left(\frac{T}{300}\right)^{-n}[M]}{(x_{\mathrm{N_2}} k_{1,0}^{\mathrm{N2}}\left(\frac{T}{300}\right)^{-n} + x_{\mathrm{H_2O}} k_{1,0}^{\mathrm{H2O}}\left(\frac{T}{300}\right)^{-o})[M]} \tag{S4}$$

$$X_{\mathrm{H_2O}} = \frac{x_{\mathrm{H_2O}} k_{1,0}^{\mathrm{H2O}}\left(\frac{T}{300}\right)^{-o}[M]}{(x_{\mathrm{N_2}} k_{1,0}^{\mathrm{N2}}\left(\frac{T}{300}\right)^{-n} + x_{\mathrm{H_2O}} k_{1,0}^{\mathrm{H2O}}\left(\frac{T}{300}\right)^{-o})[M]} \tag{S5}$$

where $F_{\mathrm{C}}^{\mathrm{N2}}$and $F_{\mathrm{C}}^{\mathrm{H2O}}$ are the broadening factors at the center of the fall-off curves of N_2 and H_2O, respectively.

If a value of 0.6 (normally an upper limit for F_C in IUPAC evaluations) is used for $F_{\mathrm{C}}^{\mathrm{H2O}}$, the fit with Eqs. (5), (S1)–(S5) would give $k_{1,0}^{\mathrm{H2O}}$ = 1.56×10^{-30} cm^{6}molecule^{-2}s^{-1}, which is about 5.5% lower than the value derived through the first method, and o = 4.80. For the current SO_2+OH case, since our preferred $F_{\mathrm{C}}^{\mathrm{N2}}$ value of 0.58 is close to 0.6, the resulting $k_{1,0}^{\mathrm{H2O}}$s derived via the two different methods are similar.

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