ELECTRONIC SUPPLEMENTARY INFORMATION

January 22, 2017

Reaction of SO_2 with OH in the Atmosphere

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Basis set abbreviations

Basis set	Reference	Abbrev.
cc-pVDZ-F12	1	DZF
cc-pVTZ-F12	1	TZF
aug-cc-pV(T+d)Z	2	aTZ
maug-cc-pV(T+d)Z	3	maTZ
6-311++G(2df,2p)	4	STZ
modified G3Large semidiffuse	5	MG3S

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2 Dunning, T. H. Jr.; Peterson, K. A.; Wilson, A. K. Gaussian basis sets for use in correlated molecular calculations. X. The atoms aluminum through argon revisited. *J. Chem. Phys.* **2001,** *114*, 9244-9253.

3 Papajak, E.; Leverentz, H. R.; Zheng, J.; Truhlar, D. G. Efficient Diffuse Basis Sets: cc-pV*x*Z+ and maug-cc-pV*x*Z. *J. Chem. Theory. Comput.* **2009**, *5*, 1197-1202.

4 Frisch, M. J.; Pople, J. A.; Binkley, J. S. Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets. *J. Chem. Phys.* **1984***, 80*, 3265-3269.

5 Lynch, B. J.; Zhao, Y.; Truhlar, D. G. The Effectiveness of Diffuse Basis Functions for Calculating Relative Energies by Density Functional Theory. *J. Phys. Chem. A* **2003***, 107*, 1384-1388.

Table S1. The optimized bond lengths (in Å) of the transition structure for the OH + SO_2 reaction by spin-orbit-free theoretical methods with mean unsigned error (MUE) and maximum absolute derivation (MAD)

Method	HO1	SO1	SO2	SO3	MUE	MAD
CCSD(T)-F12a/TZF	0.973	2.472	1.431	1.434	0.000	0.000
CCSD(T)-F12a/DZF	0.973	2.472	1.431	1.435	0.000	0.000
M06/MG3S	0.973	2.464	1.425	1.432	0.004	0.008
M06/STZ	0.973	2.463	1.431	1.439	0.004	0.009
PW6B95/STZ	0.971	2.462	1.430	1.438	0.004	0.010
MPW1B95/STZ	0.971	2.462	1.430	1.438	0.004	0.010
BMK/STZ	0.972	2.464	1.425	1.431	0.005	0.008
mPW1PW91/STZ	0.972	2.493	1.433	1.440	0.008	0.021
SOGGA11-X/STZ	0.970	2.493	1.427	1.432	0.008	0.021
wB97XD/STZ	0.971	2.507	1.429	1.435	0.010	0.035
CCSD(T)/aTZ	0.975	2.438	1.440	1.443	0.014	0.034
MPW3LYP/STZ	0.975	2.510	1.439	1.447	0.015	0.038
BB1K/STZ	0.966	2.437	1.418	1.423	0.017	0.035
TPSSIKCIS/STZ	0.977	2.507	1.445	1.454	0.018	0.035
MPW1K/STZ	0.964	2.436	1.417	1.422	0.018	0.036
B97-1/STZ	0.974	2.524	1.440	1.448	0.019	0.052
B98/STZ	0.974	2.539	1.437	1.444	0.021	0.067
MN12-L/STZ	0.971	2.402	1.421	1.427	0.022	0.070
M11-L/STZ	0.965	2.433	1.404	1.408	0.025	0.039
B1LYP/STZ	0.974	2.564	1.438	1.443	0.027	0.092
B3LYP/STZ	0.976	2.552	1.441	1.448	0.027	0.080
M05/STZ	0.970	2.574	1.434	1.439	0.028	0.102
M05-2X/STZ	0.972	2.365	1.428	1.434	0.028	0.107
MN12-SX/STZ	0.975	2.371	1.423	1.429	0.029	0.101
M11/STZ	0.975	2.349	1.431	1.438	0.032	0.123
B97-3/STZ	0.971	2.594	1.434	1.439	0.033	0.122
B97-2/STZ	0.970	2.594	1.434	1.440	0.034	0.122
M06-2X/STZ	0.973	2.334	1.426	1.430	0.037	0.138
CCSD/aTZ	0.973	2.334	1.427	1.430	0.037	0.138
M08-SO/STZ	0.978	2.320	1.429	1.435	0.040	0.152
M08-HX/maTZ	0.972	2.303	1.422	1.426	0.047	0.169
M08-HX/aTZ	0.972	2.307	1.422	1.426	0.046	0.165
BHandHLYP/STZ	0.963	2.320	1.415	1.419	0.048	0.152
M08-HX/STZ	0.972	2.289	1.426	1.431	0.048	0.183
M08-HX/MG3S	0.972	2.291	1.421	1.425	0.050	0.181
MP2(Full)/aTZ	0.971	2.219	1.436	1.441	0.067	0.253
BHandH/STZ	0.968	2.245	1.408	1.421	0.067	0.227
MP2(Full)/STZ	0.970	2.197	1.440	1.445	0.075	0.275
M06-L/STZ	0.973	2.657	1.441	1.449	0.053	0.185
O3LYP/STZ	0.973	2.779	1.443	1.446	0.083	0.307
τ-HCTHhyb/STZ	0.976	2.843	1.444	1.444	0.099	0.371
TPSSh/STZ	0.978	2.838	1.447	1.452	0.101	0.366
BLYP/STZ	0.984	2.790	1.468	1.477	0.102	0.318

Table S2. The optimized bond angles (in degrees) of the transition structure for the OH + SO_2 reaction by spin-orbit-free theoretical methods

Method	Bend HO1S	Bend O1SO2	Bend O1SO3	Torsion HO1SO2	Torsion HO1SO3	MUE	MAD
CCSD(T)-F12a/TZF	100.2	107.4	104.5	169.9	41.9	0.0	0.0
CCSD(T)-F12a/DZF	100.1	107.4	104.5	169.9	41.8	0.0	0.1
M08-HX/MG3S	99.9	106.7	104.8	167.3	39.8	1.2	2.6
M08-HX/maTZ	100.0	106.9	104.7	167.1	39.6	1.2	2.8
M08-HX/STZ	100.0	106.9	104.4	165.4	38.3	1.8	4.5
M08-HX/aTZ	99.8	106.8	104.3	164.7	37.5	2.2	5.2
BHandHLYP/STZ	101.5	106.7	107.0	174.8	46.2	2.7	4.9
CCSD(T)/aTZ	99.1	108.4	108.1	176.4	45.3	3.1	6.5
CCSD/aTZ	99.6	106.7	107.7	176.5	46.8	3.2	6.6
MP2(Full)/STZ	99.3	107.0	107.9	180.0	50.0	4.6	10.1
MP2(Full)/aTZ	99.9	106.2	108.4	176.6	53.5	4.7	11.6
M06-2X/STZ	98.9	108.3	103.3	159.3	32.1	4.8	10.6
M08-SO/STZ	98.8	108.9	101.9	154.4	27.8	7.0	15.5
MPW1K/STZ	100.5	108.9	100.9	151.5	25.7	8.0	18.4
M11-L/STZ	98.9	109.6	98.4	142.4	17.4	12.3	27.5
O3LYP/STZ	105.4	111.1	101.5	143.6	16.4	12.7	26.3
MN12-SX/STZ	99.8	109.4	97.8	140.3	16.0	12.9	29.6
M05-2X/STZ	97.3	110.2	97.8	140.8	16.2	13.4	29.1
B97-3/STZ	101.4	112.3	98.6	140.7	14.7	13.7	29.2
M11/STZ	97.6	110.2	96.7	138.5	14.3	14.4	31.4
BB1K/STZ	98.0	111.5	96.1	137.0	12.8	15.3	32.9
SOGGA11-X/STZ	99.2	112.3	95.6	134.6	10.4	16.3	35.3
BMK/STZ	98.1	113.4	95.3	134.9	10.4	16.8	35.0
TPSSh/STZ	98.6	100.1	82.0	145.1	27.9	17.6	24.8
B1LYP/STZ	101.5	112.6	94.7	128.9	5.2	18.8	41.0
M05/STZ	100.7	112.7	93.4	125.9	3.0	20.0	44.0
wB97XD/STZ	99.4	112.2	93.9	128.8	5.6	23.4	-41.1
MN12-L/STZ	97.9	109.7	96.5	139.1	115.3	23.4	73.4
M06/STZ	99.7	113.1	87.7	117.3	-2.6	24.0	52.6
M06/MG3S	99.0	113.1	88.5	117.2	-3.5	24.2	52.7
mPW1PW91/STZ	100.7	110.7	89.3	109.4	-10.8	26.4	60.5
MPW1B95/STZ	99.7	112.4	86.9	110.4	-9.1	26.7	59.5
PW6B95/STZ	99.7	112.4	86.9	110.4	-9.1	26.7	59.5
B97-2/STZ	101.4	111.9	89.0	109.1	-11.3	27.0	60.8
B3LYP/STZ	102.1	112.3	87.4	105.8	-13.8	28.7	64.1
B98/STZ	101.4	111.8	87.2	105.3	-14.2	28.7	64.6
MPW3LYP/STZ	102.0	111.7	86.5	104.2	-14.9	29.3	-65.7
B97-1/STZ	101.5	111.1	85.1	97.7	-20.6	31.8	72.2
TPSSIKCIS/STZ	100.9	109.2	82.8	83.9	-33.3	37.1	86.0
BHandH/STZ	101.7	108.3	83.8	100.0	-17.3	40.7	69.9
M06-L/STZ	97.9	106.2	75.6	70.7	-44.6	43.6	99.2
BLYP/STZ	109.2	149.7	67.2	87.4	-17.5	46.1	82.5
τ-HCTHhyb/STZ	99.6	91.4	91.4	56.0	-59.0	61.2	113.9

Table S3. The enthalpies of activation ($\Delta H_0^{\ddagger,\circ}$, 0 K) and reaction ($\Delta H_0$, 0 K) of the OH + SO_2 reaction by spin-orbit-free theoretical methods (in kcal/mol)

Method[a,b]	$\Delta H_0^{\ddagger,\circ}$	ΔH_0°	MUE[b]	Scale factor[c]
MW3.2//C	0.07	−26.57	0.00	0.984[d]
W3X-L//C	0.01	−26.64	0.07	0.984[d]
M08-HX/MG3S	0.15	−26.65	0.08	0.973[e]
W3X//C	−0.02	−26.32	0.17	0.984[d]
CCSD(T)-F12a/TZF	0.33	−26.66	0.18	0.984[d]
W3X-L//QCISD/STZ	−0.39	−26.64	0.27	0.973[d]
W2X//C	0.35	−26.86	0.29	0.984[d]
CCSD(T)-F12a/DZF	0.53	−26.27	0.38	0.983[d]
CCSD(T)-F12b/VQZ-F12//C	0.36	−27.11	0.42	0.984[d]
CCSD(T)-F12b/VQZ-F12//CCSD(T)-F12a/DZF	0.43	−27.12	0.46	0.983[d]
M08-HX/maTZ	0.65	−26.96	0.49	0.975[e]
M08-HX/aTZ	0.22	−27.49	0.54	0.976[e]
M06-2X/maTZ	−0.31	−28.23	1.02	0.971[e]
M06-2X/aTZ	−0.60	−28.60	1.35	0.971[e]
CCSD(T)/aTZ	0.51	−24.03	1.49	0.987[d]
M06/MG3S	−2.41	−27.65	1.78	0.981[e]

[a]//C denotes "at the geometry calculated by CCSD(T)-F12a/TZF".

[b]Mean unsigned error averaged over the two previous columns, rrelative to the first row.

[c]Unitless factor by which vibrational frequencies were scaled.

[d]The scale factor is calculated in the present work.

[e]The scale factor is obtained from reference 6.

[6] Alecu, I. M.; Zheng, J.; Zhao, Y.; Truhlar, D. G. Computational Thermochemistry: Scale Factor Databases and Scale Factors for Vibrational Frequencies Obtained from Electronic Model Chemistries, *J. Chem. Theory Comput.* **2010**, *6*, 2872-2887.

Table S4. The barrier height ($\Delta E^{\ddagger}$, 0 K) and reaction energy (ΔE, 0 K) of the OH + SO_2 reaction by spin-orbit-free theoretical methods (in kcal/mol)

Method[a]	$V^{\ddagger}$	ΔV	MUE[b]
MW3.2//C	−1.20	−30.93	0.00
W3X-L//C	−1.26	−31.00	0.06
M08-HX/MG3S	−1.24	−30.74	0.12
W3X//C	−1.29	−30.68	0.17
CCSD(T)-F12a/TZF	−0.93	−31.01	0.17
W2X//C	−0.92	−31.21	0.28
W3X-L//QCISD/STZ	−1.77	−30.94	0.3
M08-HX/maTZ	−0.71	−31.05	0.31
CCSD(T)-F12a/DZF	−0.81	−30.61	0.35
M08-HX/aTZ	−1.12	−31.59	0.37
CCSD(T)-F12b/VQZ-F12//C	−0.91	−31.47	0.41
CCSD(T)-F12b/VQZ-F12//CCSD(T)-F12a/DZF	−0.91	−31.47	0.41
M06-2X/MG3S	−1.91	−31.93	0.86
M06-2X/maTZ	−1.59	−32.35	0.91
M06/STZ	−3.41	−30.79	1.18
M06-2X/aTZ	−1.92	−32.72	1.26
CCSD(T)/aTZ	−0.76	−28.34	1.51
M06/MG3S	−3.65	−31.90	1.71
MP2(full)/aTZ	1.97	−33.27	2.76

CCSD(T)-F12a/TZF”

[b]Mean unsigned error averaged over the two previous columns

Table S5. The rate constant of the OH + SO_2 reaction at the different temperatures and pressures.

(a) bath gas: N_2

T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})	T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})
200	1.30×10^{-3}	9.25×10^{-15}	250	1.30×10^{-3}	1.03×10^{-15}
200	1.00×10^{-2}	6.68×10^{-14}	250	1.00×10^{-2}	7.91×10^{-15}
200	5.00×10^{-2}	2.61×10^{-13}	250	5.00×10^{-2}	3.84×10^{-14}
200	1.00×10^{-1}	4.10×10^{-13}	250	1.00×10^{-1}	7.40×10^{-14}
200	5.00×10^{-1}	7.59×10^{-13}	250	5.00×10^{-1}	2.89×10^{-13}
200	1.00×10^{0}	8.51×10^{-13}	250	1.00×10^{0}	4.53×10^{-13}
200	5.00×10^{0}	9.46×10^{-13}	250	5.00×10^{0}	8.43×10^{-13}
200	1.00×10^{1}	9.60×10^{-13}	250	1.00×10^{1}	9.51×10^{-13}
200	5.00×10^{1}	9.71×10^{-13}	250	5.00×10^{1}	1.07×10^{-12}
200	1.00×10^{2}	9.72×10^{-13}	250	1.00×10^{2}	1.09×10^{-12}
200	1.00×10^{3}	9.74×10^{-13}	250	1.30×10^{-3}	1.11×10^{-12}
T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})	T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})
298	1.30×10^{-3}	1.07×10^{-15}	350	1.30×10^{-3}	1.03×10^{-15}
298	1.00×10^{-2}	8.21×10^{-15}	350	1.00×10^{-2}	7.89×10^{-15}
298	5.00×10^{-2}	3.98×10^{-14}	350	5.00×10^{-2}	3.84×10^{-14}
298	1.00×10^{-1}	7.69×10^{-14}	350	1.00×10^{-1}	7.42×10^{-14}
298	5.00×10^{-1}	3.01×10^{-13}	350	5.00×10^{-1}	2.95×10^{-13}
298	1.00×10^{0}	4.75×10^{-13}	350	1.00×10^{0}	4.71×10^{-13}
298	5.00×10^{0}	9.05×10^{-13}	350	5.00×10^{0}	9.40×10^{-13}
298	1.00×10^{1}	1.04×10^{-12}	350	1.00×10^{1}	1.10×10^{-12}
298	5.00×10^{1}	1.20×10^{-12}	350	5.00×10^{1}	1.32×10^{-12}
298	1.00×10^{2}	1.22×10^{-12}	350	1.00×10^{2}	1.37×10^{-12}
298	1.00×10^{3}	1.25×10^{-12}	350	1.00×10^{3}	1.41×10^{-12}
T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})	T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})
400	1.30×10^{-3}	4.59×10^{-16}	450	1.30×10^{-3}	9.83×10^{-17}
400	1.00×10^{-2}	3.52×10^{-15}	450	1.00×10^{-2}	7.56×10^{-16}
400	5.00×10^{-2}	1.74×10^{-14}	450	5.00×10^{-2}	3.77×10^{-15}
400	1.00×10^{-1}	3.42×10^{-14}	450	1.00×10^{-1}	7.51×10^{-15}
400	5.00×10^{-1}	1.53×10^{-13}	450	5.00×10^{-1}	3.65×10^{-14}
400	1.00×10^{0}	2.70×10^{-13}	450	1.00×10^{0}	7.06×10^{-14}
400	5.00×10^{0}	7.18×10^{-13}	450	5.00×10^{0}	2.81×10^{-13}
400	1.00×10^{1}	9.33×10^{-13}	450	1.00×10^{1}	4.51×10^{-13}
400	5.00×10^{1}	1.33×10^{-12}	450	5.00×10^{1}	9.51×10^{-13}
400	1.00×10^{2}	1.43×10^{-12}	450	1.00×10^{2}	1.16×10^{-12}
400	1.00×10^{3}	1.57×10^{-12}	450	1.00×10^{3}	1.60×10^{-12}

(b) bath gas: He

T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})	T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})
200	1.30×10^{-3}	2.88×10^{-15}	250	1.30×10^{-3}	3.07×10^{-16}
200	1.00×10^{-2}	2.17×10^{-14}	250	1.00×10^{-2}	2.36×10^{-15}
200	5.00×10^{-2}	9.95×10^{-14}	250	5.00×10^{-2}	1.17×10^{-14}
200	1.00×10^{-1}	1.80×10^{-13}	250	1.00×10^{-1}	2.31×10^{-14}
200	5.00×10^{-1}	5.14×10^{-13}	250	5.00×10^{-1}	1.06×10^{-13}
200	1.00×10^{0}	6.71×10^{-13}	250	1.00×10^{0}	1.93×10^{-13}
200	5.00×10^{0}	8.90×10^{-13}	250	5.00×10^{0}	5.57×10^{-13}
200	1.00×10^{1}	9.30×10^{-13}	250	1.00×10^{1}	7.32×10^{-13}
200	5.00×10^{1}	9.65×10^{-13}	250	5.00×10^{1}	9.94×10^{-13}
200	1.00×10^{2}	9.69×10^{-13}	250	1.00×10^{2}	1.05×10^{-12}
200	1.00×10^{3}	9.73×10^{-13}	250	1.30×10^{-3}	1.10×10^{-12}
T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})	T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})
298	1.30×10^{-3}	3.09×10^{-16}	350	1.30×10^{-3}	2.89×10^{-16}
298	1.00×10^{-2}	2.37×10^{-15}	350	1.00×10^{-2}	2.22×10^{-15}
298	5.00×10^{-2}	1.17×10^{-14}	350	5.00×10^{-2}	1.10×10^{-14}
298	1.00×10^{-1}	2.32×10^{-14}	350	1.00×10^{-1}	2.18×10^{-14}
298	5.00×10^{-1}	1.07×10^{-13}	350	5.00×10^{-1}	1.01×10^{-13}
298	1.00×10^{0}	1.95×10^{-13}	350	1.00×10^{0}	1.86×10^{-13}
298	5.00×10^{0}	5.77×10^{-13}	350	5.00×10^{0}	5.69×10^{-13}
298	1.00×10^{1}	7.71×10^{-13}	350	1.00×10^{1}	7.78×10^{-13}
298	5.00×10^{1}	1.09×10^{-12}	350	5.00×10^{1}	1.16×10^{-12}
298	1.00×10^{2}	1.16×10^{-12}	350	1.00×10^{2}	1.27×10^{-12}
298	1.00×10^{3}	1.24×10^{-12}	350	1.00×10^{3}	1.40×10^{-12}
T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})	T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})
400	1.30×10^{-3}	1.26×10^{-16}	450	1.30×10^{-3}	2.65×10^{-17}
400	1.00×10^{-2}	9.66×10^{-16}	450	1.00×10^{-2}	2.04×10^{-16}
400	5.00×10^{-2}	4.81×10^{-15}	450	5.00×10^{-2}	1.02×10^{-15}
400	1.00×10^{-1}	9.58×10^{-15}	450	1.00×10^{-1}	2.03×10^{-15}
400	5.00×10^{-1}	4.63×10^{-14}	450	5.00×10^{-1}	1.01×10^{-14}
400	1.00×10^{0}	8.90×10^{-14}	450	1.00×10^{0}	2.00×10^{-14}
400	5.00×10^{0}	3.40×10^{-13}	450	5.00×10^{0}	9.29×10^{-14}
400	1.00×10^{1}	5.30×10^{-13}	450	1.00×10^{1}	1.71×10^{-13}
400	5.00×10^{1}	1.02×10^{-12}	450	5.00×10^{1}	5.37×10^{-13}
400	1.00×10^{2}	1.20×10^{-12}	450	1.00×10^{2}	7.54×10^{-13}
400	1.00×10^{3}	1.52×10^{-12}	450	1.00×10^{3}	1.40×10^{-12}

(c) bath gas: Ar

T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})	T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})
200	1.30×10^{-3}	4.40×10^{-15}	250	1.30×10^{-3}	4.78×10^{-16}
200	1.00×10^{-2}	3.28×10^{-14}	250	1.00×10^{-2}	3.67×10^{-15}
200	5.00×10^{-2}	1.44×10^{-13}	250	5.00×10^{-2}	1.81×10^{-14}
200	1.00×10^{-1}	2.51×10^{-13}	250	1.00×10^{-1}	3.55×10^{-14}
200	5.00×10^{-1}	6.13×10^{-13}	250	5.00×10^{-1}	1.56×10^{-13}
200	1.00×10^{0}	7.50×10^{-13}	250	1.00×10^{0}	2.72×10^{-13}
200	5.00×10^{0}	9.17×10^{-13}	250	5.00×10^{0}	6.72×10^{-13}
200	1.00×10^{1}	9.44×10^{-13}	250	1.00×10^{1}	8.27×10^{-13}
200	5.00×10^{1}	9.68×10^{-13}	250	5.00×10^{1}	1.03×10^{-12}
200	1.00×10^{2}	9.71×10^{-13}	250	1.00×10^{2}	1.07×10^{-12}
200	1.00×10^{3}	9.74×10^{-13}	250	1.30×10^{-3}	1.10×10^{-12}
T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})	T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})
298	1.30×10^{-3}	4.87×10^{-16}	350	1.30×10^{-3}	4.61 × 10-16
298	1.00×10^{-2}	3.74×10^{-15}	350	1.00×10^{-2}	3.54 × 10-15
298	5.00×10^{-2}	1.84×10^{-14}	350	5.00×10^{-2}	1.75 × 10-14
298	1.00×10^{-1}	3.62×10^{-14}	350	1.00×10^{-1}	3.44 × 10-14
298	5.00×10^{-1}	1.60×10^{-13}	350	5.00×10^{-1}	1.53 × 10-13
298	1.00×10^{0}	2.80×10^{-13}	350	1.00×10^{0}	2.71 × 10-13
298	5.00×10^{0}	7.07×10^{-13}	350	5.00×10^{0}	7.11 × 10-13
298	1.00×10^{1}	8.84×10^{-13}	350	1.00×10^{1}	9.10 × 10-13
298	5.00×10^{1}	1.14×10^{-12}	350	5.00×10^{1}	1.24 × 10-12
298	1.00×10^{2}	1.19×10^{-12}	350	1.00×10^{2}	1.31 × 10-12
298	1.00×10^{3}	1.25×10^{-12}	350	1.00×10^{3}	1.41 × 10-12
T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})	T/K	P/bar	k (cm^3 $molecule^{-1}$ s^{-1})
400	1.30×10^{-3}	2.02×10^{-16}	450	1.30×10^{-3}	4.29×10^{-17}
400	1.00×10^{-2}	1.55×10^{-15}	450	1.00×10^{-2}	3.30×10^{-16}
400	5.00×10^{-2}	7.73×10^{-15}	450	5.00×10^{-2}	1.65×10^{-15}
400	1.00×10^{-1}	1.54×10^{-14}	450	1.00×10^{-1}	3.29×10^{-15}
400	5.00×10^{-1}	7.28×10^{-14}	450	5.00×10^{-1}	1.63×10^{-14}
400	1.00×10^{0}	1.37×10^{-13}	450	1.00×10^{0}	3.20×10^{-14}
400	5.00×10^{0}	4.67×10^{-13}	450	5.00×10^{0}	1.43×10^{-13}
400	1.00×10^{1}	6.78×10^{-13}	450	1.00×10^{1}	2.53×10^{-13}
400	5.00×10^{1}	1.15×10^{-12}	450	5.00×10^{1}	6.87×10^{-13}
400	1.00×10^{2}	1.30×10^{-12}	450	1.00×10^{2}	9.09×10^{-13}
400	1.00×10^{3}	1.55×10^{-12}	450	1.00×10^{3}	1.49×10^{-12}

Table S6. Computed $p_{1/2}$ (in the unit of bar) for SO_2 + OH reaction with N_2 as bath gas at various temperatures.

T/K	$p_{1/2}$ /bar
190.0	0.04
200.0	0.13
210.0	0.32
220.0	0.62
230.0	0.95
240.0	1.25
250.0	1.47
260.0	1.63
270.0	1.68
298.0	1.70
300.0	1.70
310.0	1.71
320.0	1.75
330.0	1.85
340.0	1.99
350.0	2.19
360.0	2.52
370.0	3.04
380.0	3.75
390.0	4.85
400.0	6.43
410.0	8.64
420.0	10.48
430.0	15.07
440.0	22.16
450.0	33.01

Table S7. Computed $k(T, p)$ (in the unit of cm^3 $molecule^{-1}$ s^{-1}) for SO_2 + OH reaction with N_2 as bath gas, and the fitted $k(T, p)$ at various pressures (bar) and at 190 K, 298 K and 450 K.

T/K	p/bar	B/bar^{-1}	d / bar^2	F [a]	Fitted $k(T, p)$	Computed $k(T, p)$	Error%
298	1.0E-04	6.22E-01	-2.60E+00	6.21E-05	7.80E-17	8.27E-17	-5.7
298	5.0E-04	6.22E-01	-2.60E+00	3.11E-04	3.90E-16	4.13E-16	-5.7
298	1.0E-03	6.22E-01	-2.60E+00	6.21E-04	7.79E-16	8.26E-16	-5.7
298	5.0E-03	6.22E-01	-2.60E+00	3.10E-03	3.89E-15	4.12E-15	-5.6
298	1.0E-02	6.22E-01	-2.60E+00	6.18E-03	7.75E-15	8.21E-15	-5.6
298	5.0E-02	6.22E-01	-2.60E+00	3.01E-02	3.78E-14	3.98E-14	-5.1
298	1.0E-01	6.22E-01	-2.60E+00	5.85E-02	7.34E-14	7.69E-14	-4.5
298	5.0E-01	6.22E-01	-2.60E+00	2.37E-01	2.98E-13	3.01E-13	-1.1
298	8.0E-01	6.22E-01	-2.60E+00	3.33E-01	4.18E-13	4.15E-13	0.6
298	1.0E+00	6.22E-01	-2.60E+00	3.85E-01	4.83E-13	4.75E-13	1.6
298	1.5E+00	6.22E-01	-2.60E+00	4.96E-01	6.22E-13	5.90E-13	5.4
298	5.0E+00	6.22E-01	-2.60E+00	7.55E-01	9.48E-13	9.05E-13	4.7
298	1.0E+01	6.22E-01	-2.60E+00	8.61E-01	1.08E-12	1.04E-12	4.2
450	1.0E-04	3.84E-02	-6.95E+02	3.84E-06	6.72E-18	7.57E-18	-11.2
450	5.0E-04	3.84E-02	-6.95E+02	1.92E-05	3.36E-17	3.78E-17	-11.2
450	1.0E-03	3.84E-02	-6.95E+02	3.84E-05	6.72E-17	7.57E-17	-11.2
450	5.0E-03	3.84E-02	-6.95E+02	1.92E-04	3.36E-16	3.78E-16	-11.2
450	1.0E-02	3.84E-02	-6.95E+02	3.84E-04	6.72E-16	7.56E-16	-11.2
450	5.0E-02	3.84E-02	-6.95E+02	1.92E-03	3.35E-15	3.77E-15	-11.0
450	1.0E-01	3.84E-02	-6.95E+02	3.83E-03	6.69E-15	7.51E-15	-10.9
450	5.0E-01	3.84E-02	-6.95E+02	1.89E-02	3.30E-14	3.65E-14	-9.7
450	8.0E-01	3.84E-02	-6.95E+02	2.98E-02	5.22E-14	5.73E-14	-8.9
450	1.0E+00	3.84E-02	-6.95E+02	3.70E-02	6.48E-14	7.06E-14	-8.3
450	1.5E+00	3.84E-02	-6.95E+02	5.46E-02	9.54E-14	1.03E-13	-7.0
450	5.0E+00	3.84E-02	-6.95E+02	1.62E-01	2.83E-13	2.81E-13	0.9
450	1.0E+01	3.84E-02	-6.95E+02	2.81E-01	4.91E-13	4.51E-13	8.8
190	1.0E-04	2.14E+01	-2.23E-03	2.14E-03	2.03E-15	2.33E-15	-12.6
190	5.0E-04	2.14E+01	-2.23E-03	1.06E-02	1.01E-14	1.15E-14	-12.4
190	1.0E-03	2.14E+01	-2.23E-03	2.10E-02	2.00E-14	2.27E-14	-12.3
190	5.0E-03	2.14E+01	-2.23E-03	9.70E-02	9.22E-14	1.04E-13	-11.0
190	1.0E-02	2.14E+01	-2.23E-03	1.77E-01	1.69E-13	1.87E-13	-9.6
190	5.0E-02	2.14E+01	-2.23E-03	4.15E-01	3.95E-13	5.20E-13	-24.1
190	1.0E-01	2.14E+01	-2.23E-03	6.72E-01	6.40E-13	6.70E-13	-4.5
190	5.0E-01	2.14E+01	-2.23E-03	9.13E-01	8.68E-13	8.74E-13	-0.7
190	8.0E-01	2.14E+01	-2.23E-03	9.44E-01	8.98E-13	9.01E-13	-0.3
190	1.0E+00	2.14E+01	-2.23E-03	9.54E-01	9.08E-13	9.10E-13	-0.2
190	1.5E+00	2.14E+01	-2.23E-03	9.69E-01	9.22E-13	9.23E-13	-0.1
190	5.0E+00	2.14E+01	-2.23E-03	9.91E-01	9.42E-13	9.41E-13	0.1
190	1.0E+01	2.14E+01	-2.23E-03	9.95E-01	9.47E-13	9.45E-13	0.2

[a] The ratio of fitted $k(T, p)$ to fitted $k^{\infty}(T)$.

Table S8. The Cartesian coordinates (Å) of the optimized geometries by different theoretical methods.

Species	Methods	Cartesian Coordindates
OH	CCSD(T)-F12a/TZF	O 0.00000000 0.00000000 0.1088362627 H 0.00000000 0.00000000 -0.8617186527
	CCSD(T)-F12a/DZF	O 0.00000000 0.00000000 0.1089007776 H 0.00000000 0.00000000 -0.8617831676
	CCSD(T)/aTZ	O 0.00000000 0.000000000 -0.1133432910 H 0.00000000 0.000000000 0.8600099510
	M08-HX/MG3S	O 0.00000000 0.00000000 0.10779300 H 0.00000000 0.00000000 -0.86234500
	QCISD/STZ	O 0.00000000 0.00000000 0.10764100 H 0.00000000 0.00000000 -0.86112600
	M08-HX/maTZ	O 0.00000000 0.00000000 0.10781800 H 0.00000000 0.00000000 -0.86254300
	M08-HX/aTZ	O 0.00000000 0.00000000 0.10780400 H 0.00000000 0.00000000 -0.86242900
	M06-2X/MG3S	O 0.00000000 0.00000000 0.10787900 H 0.00000000 0.00000000 -0.86303400
	M06-2X/maTZ	O 0.00000000 0.00000000 0.10799200 H 0.00000000 0.00000000 -0.86393500
	M06-2X/aTZ	O 0.00000000 0.00000000 0.10799200 H 0.00000000 0.00000000 -0.86393700
SO_2	CCSD(T)-F12a/TZF	S 0.0000000000 0.0000000000 0.3604699381 O 0.0000000000 -1.2370798113 -0.3634167190 O 0.0000000000 1.2370798113 -0.3634167190
	CCSD(T)-F12a/DZF	S 0.00000000 0.00000000 0.3602770192 O 0.0000000000 -1.2379025591 -0.3633202596 O 0.0000000000 1.2379025591 -0.3633202596
	CCSD(T)/aTZ	S 0.0000000000 0.0000000000 0.3643273502 O 0.0000000000 -1.2449818111 -0.3653454251 O 0.0000000000 1.2449818111 -0.3653454251
	M08-HX/MG3S	S 0.00000000 0.00000000 0.36300600 O 0.00000000 1.22444100 -0.36300600 O 0.00000000 -1.22444100 -0.36300600
	QCISD/STZ	S 0.00000000 0.00000000 0.36504300 O 0.00000000 1.23596100 -0.36504300 O 0.00000000 -1.23596100 -0.36504300
	M08-HX/maTZ	S 0.00000000 0.00000000 0.36287100 O 0.00000000 1.22567500 -0.36287100 O 0.00000000 -1.22567500 -0.36287100
	M08-HX/aTZ	S 0.00000000 0.00000000 0.36326900 O 0.00000000 1.22555900 -0.36326900 O 0.00000000 -1.22555900 -0.36326900
	M06-2X/MG3S	S 0.00000000 0.00000000 0.36221200 O 0.00000000 1.22496800 -0.36221200 O 0.00000000 -1.22496800 -0.36221200
	M06-2X/maTZ	S 0.00000000 0.00000000 0.36194300

		O 0.00000000 1.22685200 -0.36194300 O 0.00000000 -1.22685200 -0.36194300
	M06-2X/aTZ	S 0.00000000 0.00000000 0.36238100 O 0.00000000 1.22678800 -0.36238100 O 0.00000000 -1.22678800 -0.36238100
$HOSO_2$	CCSD(T)-F12a/TZF	S 0.0004710960 -0.0014666539 0.0015885695 O 0.0002101956 0.0007530638 1.4422455393 O 1.1968183345 -0.0006376395 -0.7865867996 O -0.8511032141 -1.2700578522 -0.4973010186 H -1.4913831920 -1.4854263382 0.1964792294
	CCSD(T)-F12a/DZF	S 0.0012651531 -0.0013833590 0.0017895656 O -0.0003331832 0.0009567940 1.4428915547 O 1.1976173132 -0.0001470897 -0.7871547314 O -0.8522594347 -1.2707420587 -0.4981627953 H -1.4912766284 -1.4855197066 0.1970619264
	CCSD(T)/aTZ	S 0.0011695704 0.0022079264 0.0021858715 O 0.0007104686 0.0033270529 1.4524480086 O 1.2039036026 0.0020390917 -0.7935195470 O -0.8538066653 -1.2775654825 -0.5005076481 H -1.4969637563 -1.4868440085 0.1958188350
	M08-HX/MG3S	S -0.12494700 0.07800900 0.25138200 O 0.27097800 1.39135600 -0.18348800 O -1.32515600 -0.55986700 -0.19562700 O 1.06678700 -0.93220300 -0.10585900 H 1.89828600 -0.44242800 -0.14230600
	QCISD/STZ	S -0.12475000 0.07925100 0.24876400 O 0.27386300 1.39952100 -0.18252900 O -1.33287900 -0.56189000 -0.19215100 O 1.07178400 -0.94164200 -0.10777200 H 1.89385500 -0.43593100 -0.12060700
	M08-HX/maTZ	S -0.12530200 0.07596700 0.25148800 O 0.25038000 1.39615600 -0.18389700 O -1.31863300 -0.57741000 -0.19473800 O 1.08071400 -0.91865000 -0.10815800 H 1.90514500 -0.41623900 -0.12946500
	M08-HX/aTZ	S -0.12504900 0.07624000 0.25171200 O 0.25579100 1.39528200 -0.18365400 O -1.32088000 -0.57255900 -0.19547300 O 1.07746600 -0.92259200 -0.10690200 H 1.90176700 -0.42089000 -0.13916400
	M06-2X/MG3S	S -0.12495400 0.07623700 0.25011600 O 0.24623200 1.39625700 -0.18296800 O -1.31538500 -0.58079900 -0.19372700 O 1.08067400 -0.91625400 -0.10688400 H 1.90710500 -0.41341900 -0.13322600
	M06-2X/maTZ	S -0.12493200 0.07566500 0.25013000 O 0.24544100 1.39756600 -0.18292600 O -1.31704800 -0.58147000 -0.19349000

		O 1.08289600 -0.91617400 -0.10769900 H 1.90860100 -0.41000800 -0.12915300
	M06-2X/aTZ	S -0.12487000 0.07563400 0.25028000 O 0.24625700 1.39770400 -0.18271800 O -1.31759800 -0.58073500 -0.19403600 O 1.08270000 -0.91707700 -0.10668000 H 1.90704900 -0.40927200 -0.13700700
TS1	CCSD(T)-F12a/TZF	S -0.3763806742 -0.0183999348 0.2982645747 O -0.7508807861 1.2605473056 -0.2315844983 O -0.9652475821 -1.2062308201 -0.2390247388 O 2.0604501591 -0.1614920281 -0.0914524962 H 2.3262598835 0.7422364775 0.1510281585
	CCSD(T)-F12a/DZF	S -0.3762115117 -0.0184393107 0.2977858498 O -0.7506934102 1.2614193328 -0.2313860377 O -0.9653292912 -1.2070494410 -0.2388196549 O 2.0604374538 -0.1615725757 -0.0913770181 H 2.3259977594 0.7423029946 0.1510278608
	CCSD(T)/aTZ	S -0.3417128143 -0.0037698818 0.2654856243 O -0.7913746012 1.2738394689 -0.2328771924 O -0.9595600494 -1.2129528057 -0.2135348379 O 2.0605124288 -0.1634727430 -0.1200822067 H 2.3263360361 0.7230169616 0.1882396126
	M08-HX/MG3S	S -0.31127100 0.00584300 0.28998200 O -0.64411000 1.28608800 -0.24005600 O -0.94366400 -1.15237400 -0.23626800 O 1.93124000 -0.22956600 -0.11392100 H 2.23261600 0.67333600 0.08225000
	QCISD/STZ	S -0.31582500 0.00455900 0.28813600 O -0.65702800 1.29720200 -0.23729800 O -0.96278200 -1.16095200 -0.23580000 O 1.97022800 -0.23064200 -0.11155100 H 2.24985700 0.68218500 0.06701500
	M08-HX/maTZ	S -0.31373300 0.00565700 0.29011300 O -0.64201400 1.28827600 -0.23987600 O -0.95162300 -1.15043600 -0.23702100 O 1.94072900 -0.23295200 -0.11328700 H 2.24297700 0.67038000 0.07967200
	M08-HX/aTZ	S -0.31650600 0.00564300 0.29302300 O -0.63318500 1.28993000 -0.24110600 O -0.95594600 -1.14648100 -0.24184100 O 1.94233100 -0.23884400 -0.10947400 H 2.23849200 0.67287200 0.05099500
	M06-2X/MG3S	S -0.31965800 0.00469900 0.28840400 O -0.64146500 1.28920800 -0.23722100 O -0.96550700 -1.14566600 -0.23801400 O 1.96478600 -0.23764200 -0.10844800 H 2.25201900 0.67762500 0.05500900
	M06-2X/maTZ	S -0.32275200 0.00444800 0.28897600

		O -0.62114100 1.29684500 -0.23559000 O -0.98784900 -1.13490000 -0.24130900 O 1.97177000 -0.25410100 -0.10476200 H 2.26177700 0.66607600 0.02967600
	M06-2X/aTZ	S -0.32498200 0.00434800 0.29126900 O -0.61569800 1.29771400 -0.23650500 O -0.99078800 -1.13234100 -0.24505500 O 1.97435900 -0.25761000 -0.10193300 H 2.25672100 0.66833900 0.00763400

Table S9. Absolute energies in hartrees.

Methods	Species			
	OH	SO_2	TS1	$HOSO_2$
MW3.2//CCSD(T)-F12a/TZF	-75.79421151	-549.8021775	-625.5982935	-625.6456752
W3X-L//CCSD(T)-F12a/TZF	-75.79399865	-549.8014140	-625.5974131	-625.6448092
M08-HX/MG3S	-75.72715708	-548.6021208	-624.3312600	-624.3782680
W3X//CCSD(T)-F12a/TZF	-75.77673679	-549.5832442	-625.3620352	-625.4088677
CCSD(T)-F12a/TZF	-75.67409900	-548.0938420	-623.7694280	-623.8173670
W3X-L//QCISD/STZ	-75.79399936	-549.8013890	-625.5982086	-625.6447014
W2X//CCSD(T)-F12a/TZF	-75.79353781	-549.7991471	-625.5941439	-625.6424224
CCSD(T)-F12a/DZF	-75.66380000	-548.0639980	-623.7290890	-623.7765840
CCSD(T)-F12b/VQZ-F12//CCSD(T)-F12a/TZF	-75.67392067	-548.0932588	-623.7686299	-623.8173276
CCSD(T)-F12b/VQZ-F12//CCSD(T)-F12a/DZF	-75.67392054	-548.0932550	-623.7686191	-623.8173195
M08-HX/maTZ	-75.73346734	-548.6182246	-624.3528246	-624.4011812
M08-HX/aTZ	-75.73398003	-548.6197711	-624.3555288	-624.4040975
M06-2X/maTZ	-75.73338632	-548.6340144	-624.3699276	-624.4189573
M06-2X/aTZ	-75.73381017	-548.6351094	-624.3719801	-624.4210654
CCSD(T)/aTZ	-75.64554700	-548.0062710	-623.6530330	-623.6969750
M06-2X/MG3S	-75.72913496	-548.6206904	-624.3528654	-624.4007039

Table S10. Parameters used to fit $k(T,p)$.[a]

	$k_\infty(T)$	$k_0(T)$		$p_{1/2}$
A	3.275×10^{-12}	3.8735×10^{107}	a_1	-2.81111
n	0.1966	219.980	a_2	4.88071
E	0.6022	103.4219	a_3	0.61832
T_0	259.802	243.8243	l_1	191.8051
			l_2	425.2390
			T_1	15.1164
			T_2	31.0877

[a]Units are given in text.

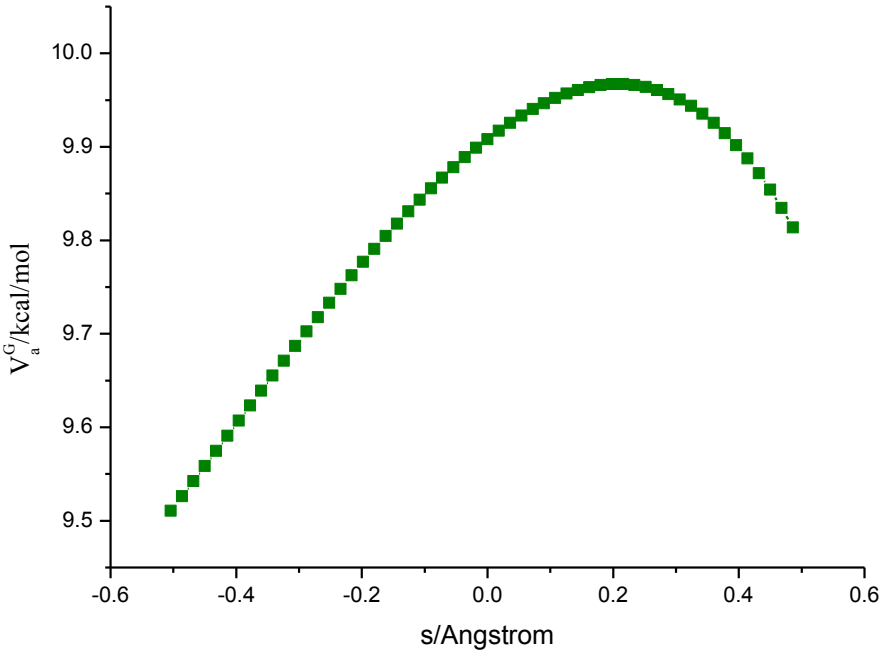

Figure S1. Vibrationally adiabatic potential energy along the minimum energy path for the OH + SO_2 reaction.

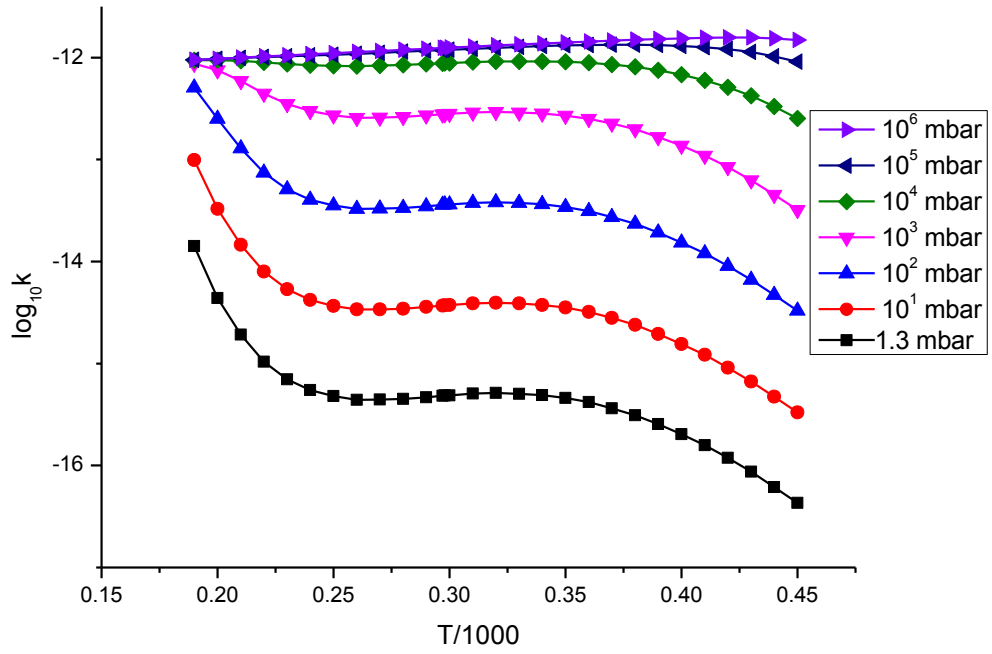

Figure S2. The rate constant of the OH + SO_2 reaction at the different temperatures and pressures (bath gas: Ar).

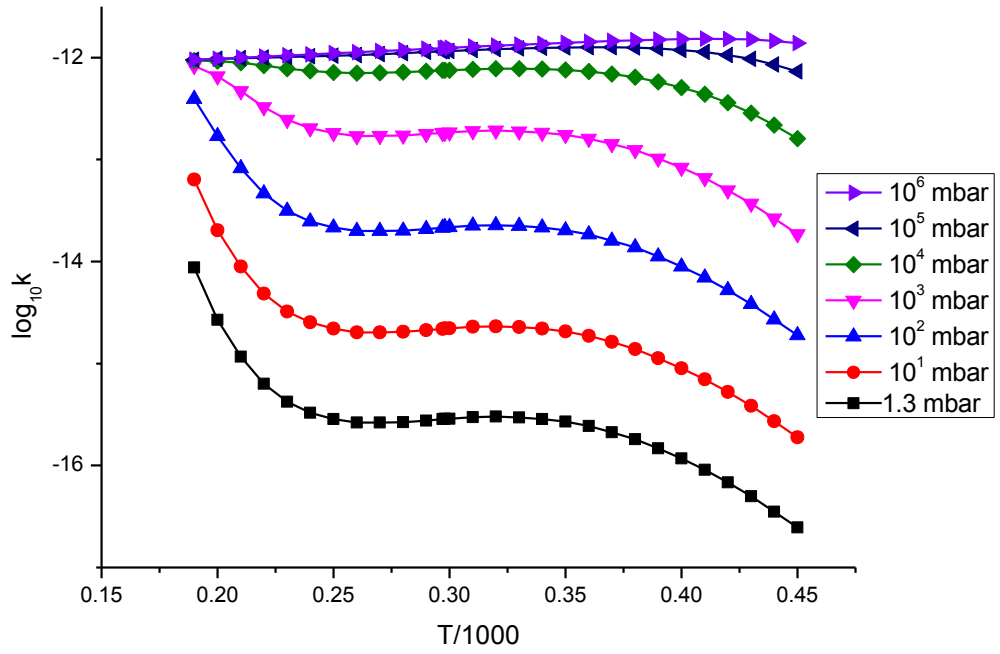

Figure S3. The rate constant of the OH + SO2 reaction at the different temperatures and pressures (bath gas: He).