Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Ab initio Kinetics of the $HOSO_2 + {}^3O_2 \rightarrow SO_3 + HO_2$ Reaction

Tam V.-T. Mai,[1,2] Minh v. Duong,[1] Hieu T. Nguyen[1] and Lam K. Huynh[3,*]

[1] Molecular Science and Nano-Materials Lab, Institute for Computational Science and Technology, SBI Building, Quang Trung Software City, Tan Chanh Hiep Ward, District 12, Ho Chi Minh City, Vietnam.
[2] University of Science, Vietnam National University – HCMC, 227 Nguyen Van Cu, Ward 4, District 5, Ho Chi Minh City, Vietnam.
[3] International University, Vietnam National University – HCMC, Quarter 6, Linh Trung Ward, Thu Duc District, Ho Chi Minh City, Vietnam.

[*]Corresponding author.

Contents

Table S1: The optimized geometries, electronic energies at 0 K ($E_{elec}^{0\,K}$), zero-point energy (ZPE) corrections and harmonic wavenumbers of the species involved, calculated at W1U level of theory for the title reaction.

Species	Cartesian coordinate (Å)				$E_{elec}^{0\,K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies (cm^{-1}) [a]
$HOSO_2$ (C_1)	S	0.133973000	0.069399000	0.252505000	-625.530878	0.022084	***281*** 419 429 530 751 1106 1114 1318 3744 [N/A; N/A; N/A; 538; 787; 1103; N/A; 1312; 3476][1-3] (278; 420; 429; 531; 759; 1112; 1147; 1317; 3865)[4] (284; 418; 428; 526; 745; 1009; 1112; 1309; 3734)[5] (257; 396; 411; 521; 725; 1045; 1129; 1317; 3582)[6,b] (282; 418; 431; 545; 783; 1103; 1147; 1378; 3600)[7,b]
	O	-1.169888000	-0.838173000	-0.109904000			
	H	-1.948695000	-0.260162000	-0.113307000			
	O	1.271870000	-0.693791000	-0.194507000			
	O	-0.126342000	1.425685000	-0.186435000			
O_2 (triplet) ($C_{\infty h}$)	O	0.000000000	0.000000000	0.602922000	-150.414422	0.003711	1629 [1580][8]; (1682)[4]; (1549)[6,b]
	O	0.000000000	0.000000000	-0.602922000			
$HOSO_4$ (Adduct) (C_1)	S	0.468967000	-0.038648000	0.085706000	-775.975287	0.030035	***101*** 216 ***327*** 346 387 458 503 574 656 866 1133 1155 1238 1489 3734 (95; 203; 313; 332; 363; 440; 484; 560; 637; 842; 1138; 1157; 1207; 1453; 3730)[4] (111; 226; 326; 348; 398; 453; 496; 561; 657; 839; 1121; 1175; 1211; 1467; 3768)[9] (99; 216; 315; 343; 372; 447; 495; 563; 655; 832; 1070; 1153; 1204; 1458; 3567)[6,b]
	O	0.316278000	1.188759000	-0.890097000			
	H	-0.238908000	1.869123000	-0.475917000			
	O	0.470797000	0.400500000	1.435544000			
	O	1.404683000	-0.935127000	-0.476815000			
	O	-2.050653000	0.009226000	0.008578000			
	O	-1.049175000	-0.819702000	-0.189132000			
Post-complex (C_s)	S	0.674689000	0.094604000	0.000004000	-775.969172	0.030106	***93*** 181 222 260 418 526 534 547 ***742*** 1051 1228 1329 1420 1546 3116 (93; 179; 213; 256; 284; 411; 511; 520; 532; 743; 1023; 1229; 1300; 1389; 1548; 3100)[4] (123; 273; 318; 474; 504; 605; 640; 715; 1025; 1041; 1077; 1265; 1402; 1885; >10^4)[9]
	O	0.016931000	1.384678000	0.000075000			
	H	-1.635843000	0.901172000	0.000038000			
	O	1.144782000	-0.426639000	1.238356000			
	O	1.144766000	-0.426508000	-1.238409000			
	O	-2.179831000	0.054889000	0.000001000			
	O	-1.271545000	-0.888274000	-0.000036000			
TS1	S	-0.555294000	-0.118998000	0.094636000	-775.945567	0.027206	-167 ***57*** 87

Species	Cartesian coordinate (Å)				$E_{elec}^{0\,K}$ (Hartree)	ZPE (Hartree)	Unscaled vibrational frequencies (cm^{-1}) [a]		
(C_1)	O	-1.085630000	0.791732000	-1.133674000			106	***293***	352
	H	-1.496348000	1.590801000	-0.768235000			431	441	542
	O	-0.378227000	-1.439734000	-0.433834000			769	1122	1141
	O	-1.347839000	0.177850000	1.262221000			1375	1482	3744
	O	2.456312000	-0.151613000	-0.102914000					
	O	1.653014000	0.660911000	0.314957000					
TS2 (C_s)	S	-0.579924000	0.000006000	0.055979000	-775.964104	0.026611	-920	133	276
	O	0.159804000	0.000116000	1.359026000			296	485	511
	H	1.298440000	0.000090000	0.955386000			598	624	762
	O	-1.154483000	1.242731000	-0.325045000			1055	1075	1237
	O	-1.154506000	-1.242775000	-0.324827000			1303	1437	1888
	O	2.045870000	0.000000000	-0.023483000			(-913; 132; 264; 284; 472; 497; 595; 609; 751; 1032; 1077; 1240; 1277; 1404; 1884)[4]		
	O	1.100857000	-0.000095000	-0.917052000			(-438; 114; 272; 340; 474; 480;540; 621; 879; 949; 1220; 1330; 1426; 1480; 2248)[9]		
TS_abs (C_1)	S	1.178164000	0.052368000	0.183279000	-775.896478	0.022470	-1706	***27***	38
	O	-0.132024000	-0.409442000	0.768446000			109	196	466
	H	-1.168108000	-0.442278000	0.175216000			480	544	578
	O	1.941549000	-0.962197000	-0.493415000			1017	1097	1206
	O	1.201437000	1.424937000	-0.248755000			1335	1343	1427
	O	-2.986827000	0.419253000	-0.033647000					
	O	-2.234451000	-0.522002000	-0.381089000					
SO_3 (D_{3h})	O	0.000000000	1.426051000	-0.000118000	-624.947038	0.012378	495	527	527
	O	1.234997000	-0.713026000	-0.000118000			1076	1404	1404
	S	0.000000000	0.000000000	0.000177000			[498; 530; 530; 1065; 1391;1391][10]		
	O	-1.234997000	-0.713026000	-0.000118000			(477; 512; 512; 1050; 1374; 1375)[4]		
HO_2 (C_1)	O	0.055357000	0.718609000	0.000000000	-151.001595	0.014117	1161	1432	3603
	O	0.055357000	-0.610398000	0.000000000			[1098; 1392; 3436][11]; (1160; 1432; 3602)[4]		
	H	-0.885712000	-0.865689000	0.000000000					

[a] Frequency modes in *italic* and **bold** corresponds to the internal rotations. Frequencies in square parentheses ("[ ]") are taken from experimental studies. [b] Anharmonic values.

Table S2: T1 diagnostics for the species involved in $HOSO_2 + O_2$ reaction computed at CCSD(T)/cc-pVTZ with the B3LYP/cc-pVTZ+d geometries.

No.	Species	*T1 diagnostics*
1	$HOSO_2$	0.02006765
2	$^3O_2$	0.01550560
3	SO_3	0.01807977
4	HO_2	0.02843197
5	$HOSO_4$ (adduct)	0.02387292
6	Post-complex	0.02523502
7	TS1	0.02756714
8	TS2	0.02179923
9	TS_abs	0.04249207

The T1 values of less than 0.02 and 0.04 (in some cases < 0.045[12] may be acceptable) for closed shell and radical species, respectively, suggest the non-dynamic correlation energy is small[13-17], thus there is no need to consider high-order methods for the title system.

Table S3: High-pressure rate constants for the $HOSO_2 + O_2$ system calculated at W1U method[a].

No.	Reaction	$k(T) = A \times T^n \times \exp(-E_a/RT)$			$k(T)$ at 298 K [b]
		A [b]	n	E_a/R (K)	
1	$HOSO_2 + O_2 \rightarrow HOSO_4$	5.62×10^{-18}	2.05	5.17×10^{1}	5.5×10^{-13} $(4.1\times10^{-13})^4$
	(reverse reaction)	4.29×10^{14}	0.20	8.71×10^{3}	2.7×10^{2} $(3.1\times10^{1})^4$
2	$HOSO_4 \rightarrow$ post-complex	6.87×10^{11}	-0.08	2.05×10^{3}	4.7×10^{8}
	(reverse reaction)	2.08×10^{12}	-0.03	3.31×10^{3}	5.7×10^{11}
3	$SO_3 + HO_2 \rightarrow$ post-complex[c]	5.62×10^{-18}	2.05	5.17×10^{1}	5.5×10^{-13}
	(reverse reaction)	1.83×10^{17}	-0.65	6.34×10^{3}	2.5×10^{6}

[a] Rate constants are valid for 200−1000 K. [b] Units of [s^{-1}] for first-order reactions and [cm^3 $molecule^{-1}$ s^{-1}] for second-order reactions. This work calculated at composite W1U method including Eckart tunneling, HIR treatments and symmetry reactions. [c] Assume equal to $HOSO_2 + O_2 \rightarrow HOSO_4$ reaction (see main text).

Table S4: Calculated the anharmonic and HIR factors for the addition step (via TS1).

T (K)	anharm/harm	hir factor
200	1.1	18.6
250	1.1	17.9
298	1.1	17.5
300	1.1	17.5
350	1.1	17.1
400	1.1	16.7
450	1.1	16.4
500	1.1	16.1
550	1.1	15.8
600	1.1	15.5
650	1.1	15.2
700	1.1	15.0
750	1.1	14.7
800	1.1	14.5
850	1.1	14.3
900	1.1	14.0
950	1.1	13.8
1000	1.1	13.6

Table S5: Parameters obtained from the modified Arrhenius expression[a] of the calculated values for the pressure-dependent rate coefficients over the temperature range of 200 – 1000 K for $HOSO_2 + O_2 \rightarrow SO_3 + HO_2$ reaction.

P (torr)	*A* (cm^3/molecule/s)	*n*	*Ea/R* (K)
10	2.59×10^{-7}	-1.75	9.72×10^{2}
50	5.51×10^{-7}	-1.85	1.03×10^{3}
100	1.17×10^{-6}	-1.95	1.09×10^{3}
300	6.77×10^{-6}	-2.18	1.25×10^{3}
760	5.82×10^{-5}	-2.47	1.44×10^{3}

Table S6: Rate constants and uncertainty for $HOSO_2 + O_2 \rightarrow$ products at T = 200 – 1000 K and P = 10 torr, using the stochastic approach with 10^8 trials.

P [torr]	T [K]	$HOSO_4$ (adduct) [cm^3/molecule/s]	unc. (%)	Post-complex [cm^3/molecule/s]	unc. (%)	$SO_3 + HO_2$ [cm^3/molecule/s]	unc. (%)
1.00E+01	200	3.90E-15	1.7E-04	3.41E-18	2.0E-01	1.97E-13	3.4E-06
1.00E+01	300	1.24E-15	1.4E-03	2.65E-18	6.3E-01	4.23E-13	4.0E-06
1.00E+01	400	3.84E-16	8.2E-03	2.46E-18	1.3E+00	6.18E-13	5.1E-06
1.00E+01	500	5.08E-17	1.0E-01	7.66E-19	6.7E+00	7.27E-13	7.0E-06
1.00E+01	600	3.02E-18	2.5E+00	7.55E-20	1.0E+02	7.49E-13	1.0E-05
1.00E+01	700	2.10E-19	5.0E+01	1.05E-19	1.0E+02	7.14E-13	1.5E-05
1.00E+01	800	1.39E-19	1.0E+02	1.39E-19	1.0E+02	6.52E-13	2.1E-05
1.00E+01	900	1.78E-19	1.0E+02	1.78E-19	1.0E+02	5.82E-13	3.1E-05
1.00E+01	1000	2.23E-19	1.0E+02	2.22E-19	1.0E+02	5.17E-13	4.3E-05

Table S7: Rate constants and uncertainty for $HOSO_4$ (adduct) $\rightarrow$ products at T = 200 – 1000 K and P = 10 torr, using the stochastic approach with 10^8 trials.

P [torr]	T [K]	$HOSO_2 + O_2$ [1/s]	unc. (%)	Post-complex [1/s]	unc. (%)	$SO_3 + HO_2$ [1/s]	unc. (%)
1.00E+01	200	1.32E-02	1.0E+02	4.64E+01	2.8E-02	1.32E-02	1.0E+02
1.00E+01	300	1.30E-01	1.0E+02	1.53E+02	8.5E-02	1.30E-01	1.0E+02
1.00E+01	400	3.75E-01	1.0E+02	1.67E+02	2.2E-01	3.75E-01	1.0E+02
1.00E+01	500	8.14E-01	1.0E+02	1.03E+02	7.9E-01	8.14E-01	1.0E+02
1.00E+01	600	8.28E+00	2.0E+01	5.79E+01	2.9E+00	2.48E+01	6.7E+00
1.00E+01	700	1.95E+02	1.8E+00	3.13E+01	1.1E+01	1.19E+03	2.9E-01
1.00E+01	800	5.75E+03	1.4E-01	5.74E+01	1.4E+01	2.00E+04	4.1E-02
1.00E+01	900	1.10E+05	2.2E-02	9.78E+01	2.5E+01	3.13E+05	7.8E-03
1.00E+01	1000	1.56E+06	4.6E-03	7.18E+01	1.0E+02	3.94E+06	2.1E-03

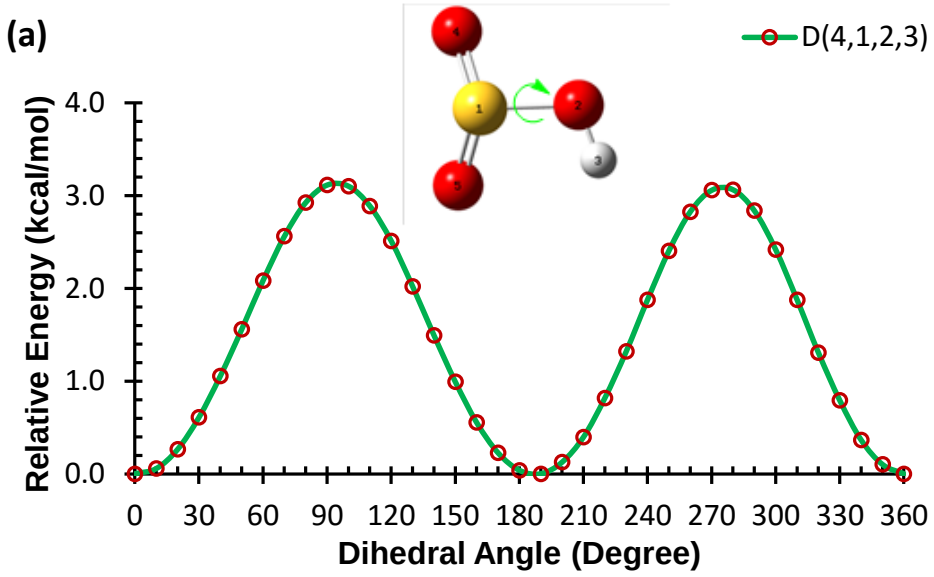
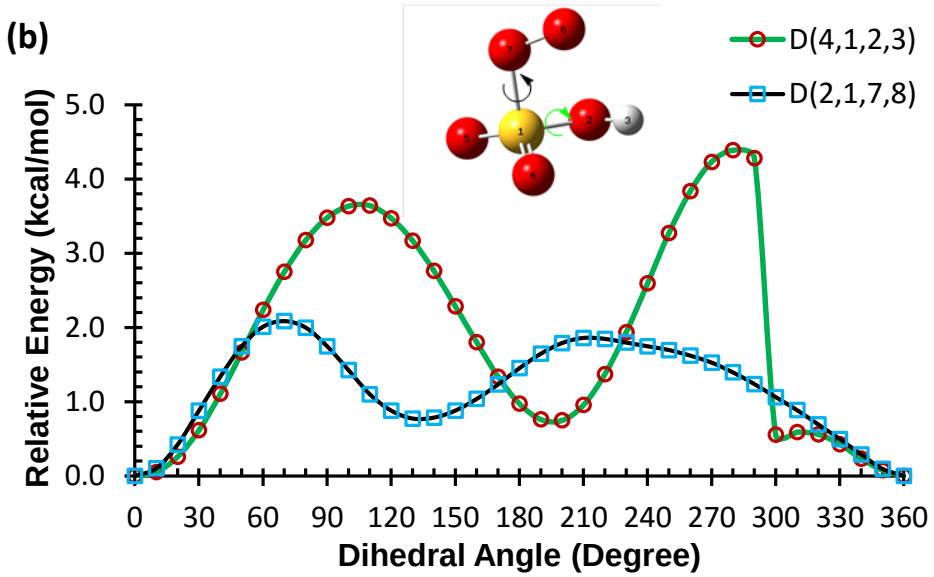
Table S8: Rate constants and uncertainty for post-complex → products at T = 200 – 1000 K and P = 10 torr, using the stochastic approach with 10^8 trials.

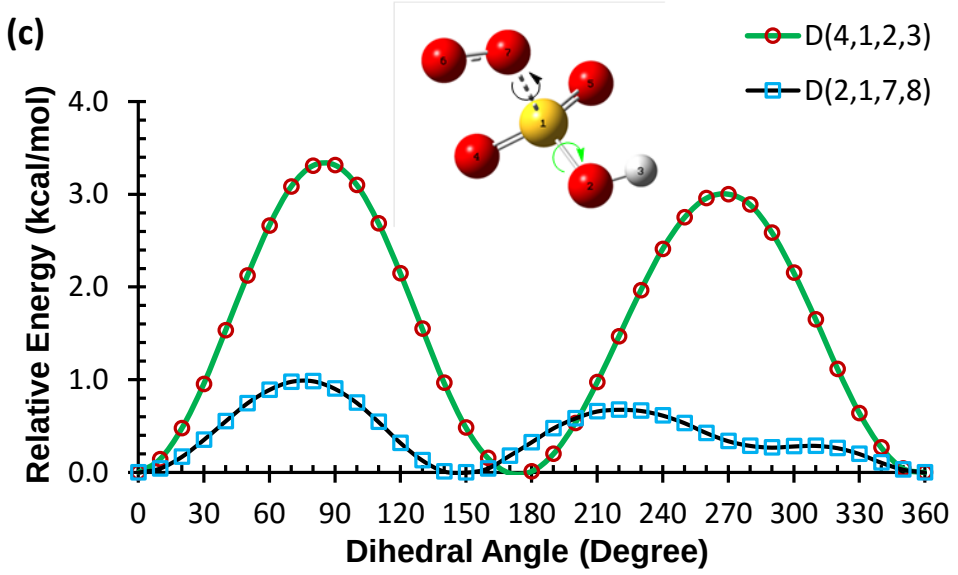
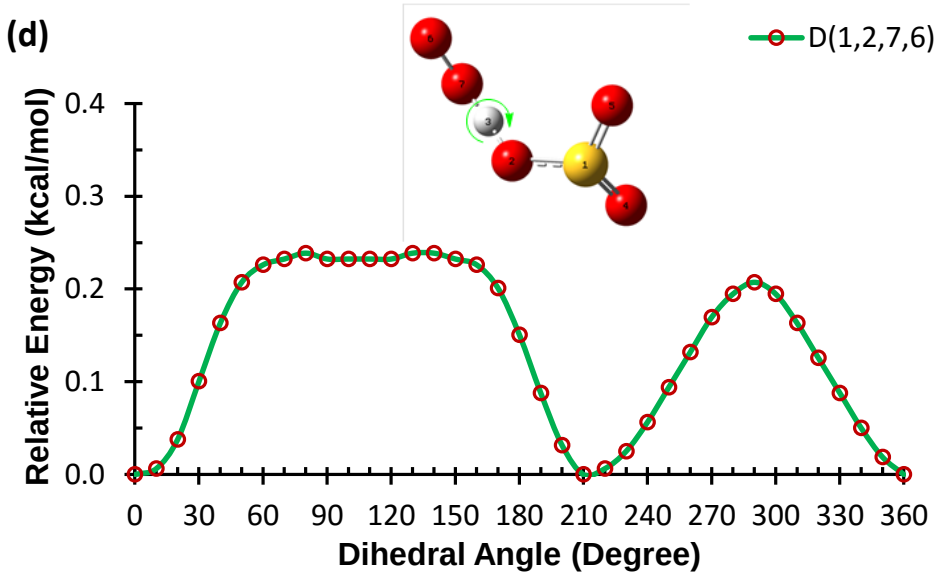
P [torr]	T [K]	$HOSO_4$ [1/s]	unc. (%)	$HOSO_2 + O_2$ [1/s]	unc. (%)	$SO_3 + HO_2$ [1/s]	unc. (%)
1.00E+01	200	2.41E+06	2.4E-05	5.87E-01	1.0E+02	5.87E-01	1.0E+02
1.00E+01	300	6.85E+05	1.7E-04	1.16E+00	1.0E+02	1.16E+00	1.0E+02
1.00E+01	400	1.90E+05	1.5E-03	2.84E+00	1.0E+02	2.84E+00	1.0E+02
1.00E+01	500	6.17E+04	1.0E-02	1.24E+01	5.0E+01	5.60E+01	1.1E+01
1.00E+01	600	1.59E+04	6.9E-02	4.41E+02	2.5E+00	2.87E+03	3.8E-01
1.00E+01	700	6.37E+03	2.8E-01	1.05E+04	1.7E-01	5.98E+04	3.0E-02
1.00E+01	800	4.39E+03	6.4E-01	1.29E+05	2.2E-02	6.39E+05	4.4E-03
1.00E+01	900	2.24E+03	2.0E+00	1.03E+06	4.2E-03	4.32E+06	1.0E-03
1.00E+01	1000	1.95E+03	3.4E+00	5.44E+06	1.2E-03	2.07E+07	3.3E-04

Table S9: Detailed kinetic submechanism in NASA format for the reaction $HOSO_2 + O_2$.

```
THERMO
   300.000  2500.000  1500.000
o2                O   2            G   300.000  2500.000 1500.000    1
8.43297122E+000-1.62395209E-0021.32352834E-005-4.71695080E-0096.20833224E-013    2
-2.89317271E+003-3.73564980E+0011.10448200E+000-7.85406683E-005-1.05590985E-007    3
2.92270364E-010-1.32453260E-013-2.62273670E+0022.32775248E+000                    4
hoso2             S   1O   3H   1    G   300.000  2500.000 1500.000    1
-2.84981961E+0017.11789201E-002-5.92051570E-0052.14614257E-008-2.86363137E-012    2
-1.93945190E+0021.83337614E+0022.73367116E+0003.15437893E-003-8.04459276E-006    3
7.57453027E-009-2.36932116E-012-1.12558918E+0041.44025696E+001                    4
hoso4             S   1O   5H   1    G   300.000  2500.000 1500.000    1
-6.16289220E+0001.08949836E-002-2.25545391E-008-2.96251786E-0097.81310105E-013    2
-7.18873210E+0038.49581414E+0012.64453600E+0001.17431701E-002-2.38431053E-005    3
1.88976548E-008-5.17693417E-012-1.32396431E+0042.89779628E+001                    4
post-complex      S   1O   5H   1    G   300.000  2500.000 1500.000    1
-1.07463499E+0022.17183010E-001-1.52316012E-0044.56431544E-008-4.91647256E-012    2
3.17394791E+0046.40074745E+0022.93138928E+0008.96400425E-003-1.66976089E-005    3
1.27897972E-008-3.37950936E-012-1.28845067E+0042.75358825E+001                    4
```

ts1 S 1O 5H 1 G 300.000 2500.000 1500.000 1
3.72902375E+002-7.04332098E-0014.97689114E-004-1.54432881E-0071.78162849E-011 2
-1.63829172E+005-2.02775883E+0038.43764394E+000-2.61464079E-0025.59805842E-005 3
-4.93910583E-0081.51874685E-011-1.19514957E+0042.56413807E+000 4
ts2 S 1O 5H 1 G 300.000 2500.000 1500.000 1
-2.61134980E+0025.62006312E-001-4.40597720E-0041.51419450E-007-1.92538876E-011 2
8.64209255E+0041.47223045E+0035.20507508E+000-6.51301433E-0031.49999148E-005 3
-1.34163479E-0084.08760422E-012-1.29544932E+0042.05068066E+001 4
so3 O 3S 1 G 300.000 2500.000 1500.000 1
1.47773814E+001-3.29997788E-0023.08079685E-005-1.21912159E-0081.74697537E-012 2
-1.50793980E+004-5.35975855E+0012.92825781E+000-3.60009684E-0037.33046251E-006 3
-5.66441893E-0091.45348661E-012-1.17851718E+0048.39774883E+000 4
ho2 O 2H 1 G 300.000 2500.000 1500.000 1
-5.36509260E+0011.13758079E-001-8.72004719E-0052.95346987E-008-3.72937254E-012 2
2.14211245E+0043.08587767E+0021.31176086E+0002.15680413E-003-4.33902987E-006 3
3.55108897E-009-1.00740206E-0126.98533618E+0016.60865839E+000 4
TS_abs S 1O 5H 1 G 300.000 2500.000 1500.000 1
9.23383030E+002-1.83936636E+0001.36733226E-003-4.47534479E-0075.44602023E-011 2
-3.72375242E+005-5.04349677E+0035.16461620E+000-8.09374819E-0032.08285083E-005 3
-2.01957457E-0086.66815816E-012-8.17617183E+0031.96097575E+001 4
post_complex S 1O 5H 1 G 300.000 2500.000 1500.000 1
-1.07463498E+0022.17183010E-001-1.52316011E-0044.56431546E-008-4.91647256E-012 2
3.17262491E+0046.40074741E+0022.93138928E+0008.96400425E-003-1.66976089E-005 3
1.27897972E-008-3.37950936E-012-1.28977367E+0042.75358825E+001 4

Species	Potential energy surfaces for the internal rotations
$HOSO_2$	
$HOSO_4$ (Adduct)	

Species	Potential energy surfaces for the internal rotations
TS1	
TS_abs	

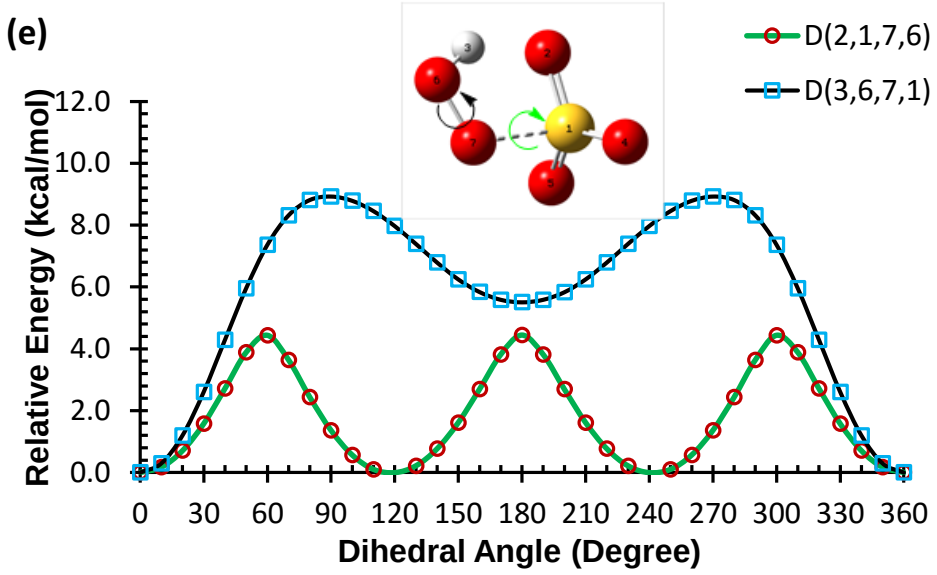
Species	Potential energy surfaces for the internal rotations
Post-complex	

Figure S1: Hindrance potentials for $HOSO_2$ (a), $HOSO_4$ (b), TS1 (c), TS_abs (d) and Post-complex (e) calculated at B3LYP/aug-cc-pVDZ level of theory.

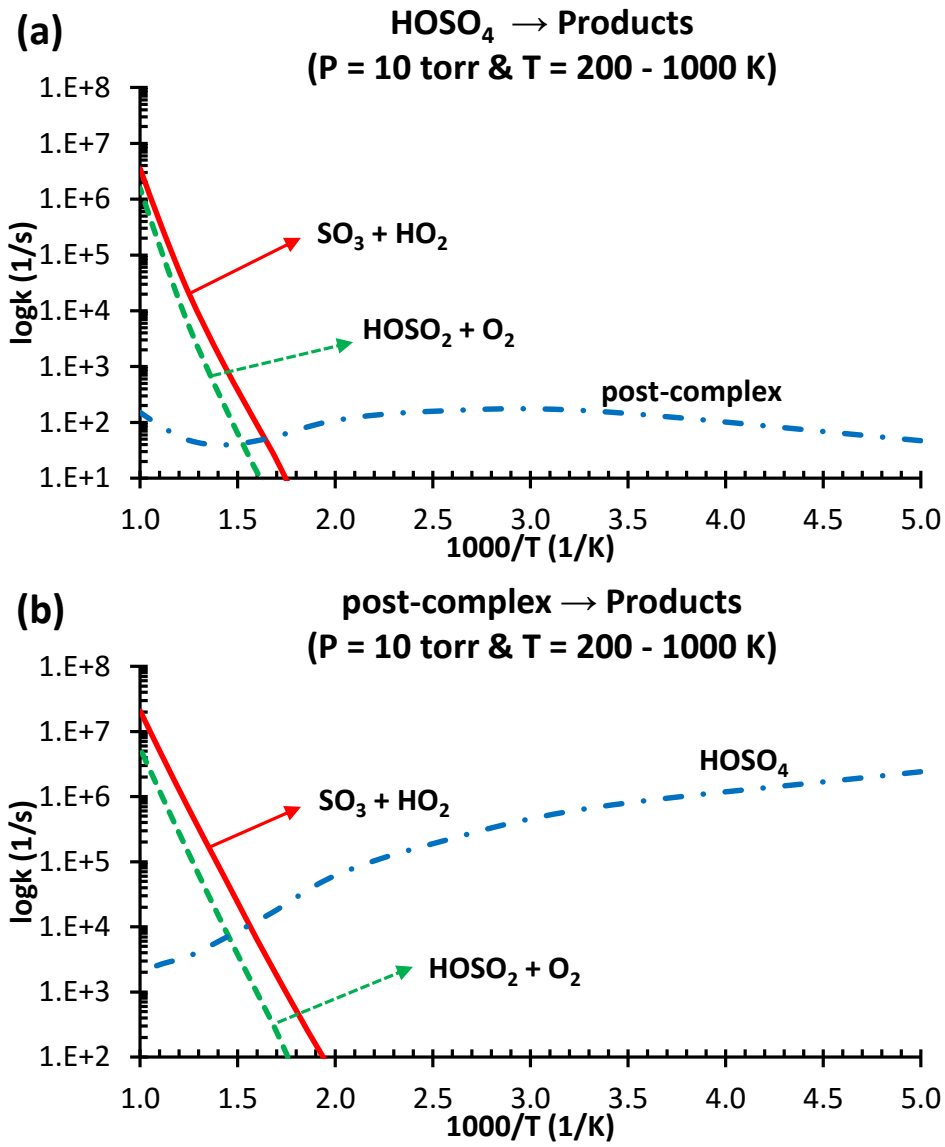


Figure S2: Calculated rate constants as a function of temperature at P = 10 torr for the $HOSO_4$ → products (a) and post-complex → products (b) reactions.

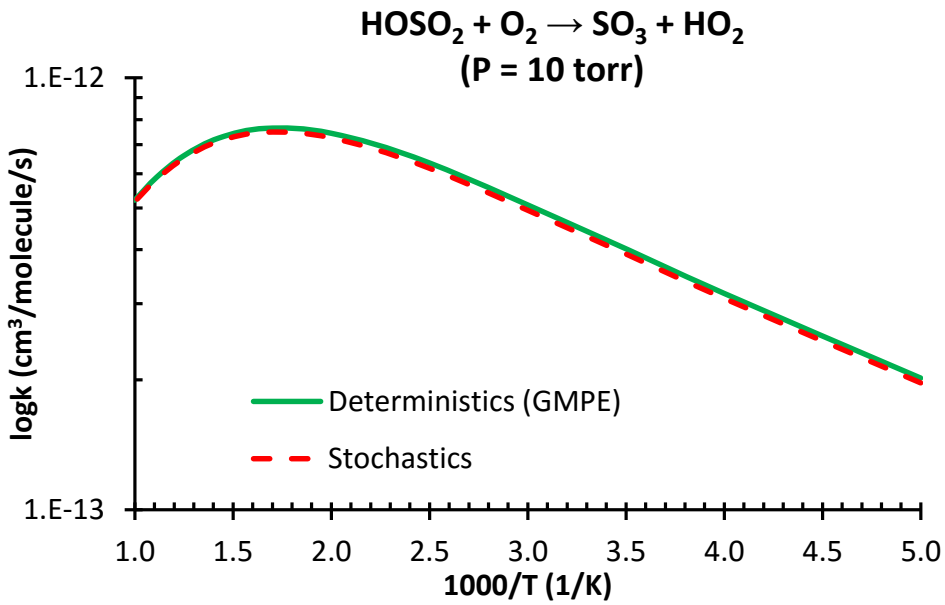


Figure S3: Comparison of the calculated rate constants between the deterministic (solid line) and stochastic (dashed line) models as a function of temperature (T = 200 – 1000 K) at P = 10 torr for the $HOSO_2 + O_2 \rightarrow SO_3 + HO_2$ reaction.

References

1. S. Nagase, S. Hashimoto and H. Akimoto, *J. Phys. Chem.*, 1988, **92**, 641-644.
2. S. Hashimoto, G. Iioue and H. Akimoto, *Chem. Phys. Lett.*, 1984, **107**, 198-202.
3. M. Wierzejewska and A. Olbert-Majkut, *J. Phys. Chem. A*, 2003, **107**, 10944-10952.
4. N. Gonzalez-Garcia and M. Olzmann, *Phys. Chem. Chem. Phys.*, 2010, **12**, 12290-12298.
5. H. Somnitz, *Phys. Chem. Chem. Phys.*, 2004, **6**, 3844.
6. N. González-García, W. Klopper and M. Olzmann, *Chem. Phys. Lett.*, 2009, **470**, 59-62.
7. W. Klopper, D. P. Tew, N. Gonzalez-Garcia and M. Olzmann, *J. Chem. Phys.*, 2008, **129**, 114308.
8. K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold Co, 1979.
9. D. Majumdar, G.-S. Kim, J. Kim, K. S. Oh, J. Y. Lee, K. S. Kim, W. Y. Choi, S.-H. Lee, M.-H. Kang and B. J. Mhin, *J. Chem. Phys.*, 2000, **112**, 723-730.
10. T. Shimanouchi, *Tables of Molecular Vibrational Frequencies, Consolidated Volume 1, NSRDS NBS-39*.
11. M. E. Jacox, *J. Phys. Chem.Ref. Data*, 1994, **Monograph 3**
12. I. M. Alecu and D. G. Truhlar, *J. Phys. Chem. A*, 2011, **115**, 2811-2829.
13. T. J. Lee and P. R. Taylor, *Int. J. Quantum Chem.*, 1989, **36**, 199-207.
14. D. Jayatilaka and T. J. Lee, *J Chem Phys*, 1993, **98**, 9734-9747.
15. J. C. Rienstra-Kiracofe, W. D. Allen and H. F. Schaefer, *J. Phys. Chem. A*, 2000, **104**, 9823-9840.
16. M. A. Ali, J. A. Sonk and J. R. Barker, *J. Phys. Chem. A*, 2016, **120**, 7060-7070.
17. M. Monge-Palacios and H. Rafatijo, *Phys Chem Chem Phys*, 2017, **19**, 2175-2185.