Catalytic effect of $(H_2O)_n$ (n = 1 - 3) on the $HO_2 + SO_2 \rightarrow HOSO + {}^3O_2$ reaction in tropospheric conditions†

Rui Wang[a,*], Qiuyue Yao [a,b,§], Mingjie Wen [a,§], Yan Wang[a, §], Shaobo Tian [a,§], Zhiyin Wang [a], Xiaohu Yu[a], Xianzhao Shao [a], and Long Chen[c,d]

[a] *Shaanxi Key Laboratory of Catalysis, School of Chemical & Environment Science, Shaanxi University of Technology, Hanzhong, Shaanxi, P. R. China*

[b] *Henan Key Laboratory of Boron Chemistry and Advanced Energy Materials, School of Chemisty and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China.*

[c] *Key Lab of Aerosol Chemistry & Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, Shaanxi, P. R. China*

[d] *State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, Shaanxi, P. R. China*

[*] Corresponding authors. Tel: +86-0916-2641083, Fax: +86-0916-2641083.
e-mail: wangrui830413@163.com(R. Wang).

[§]Qiuyue Yao, Mingjie Wen, Yan Wang and Shaobo Tian contributed equally to this work

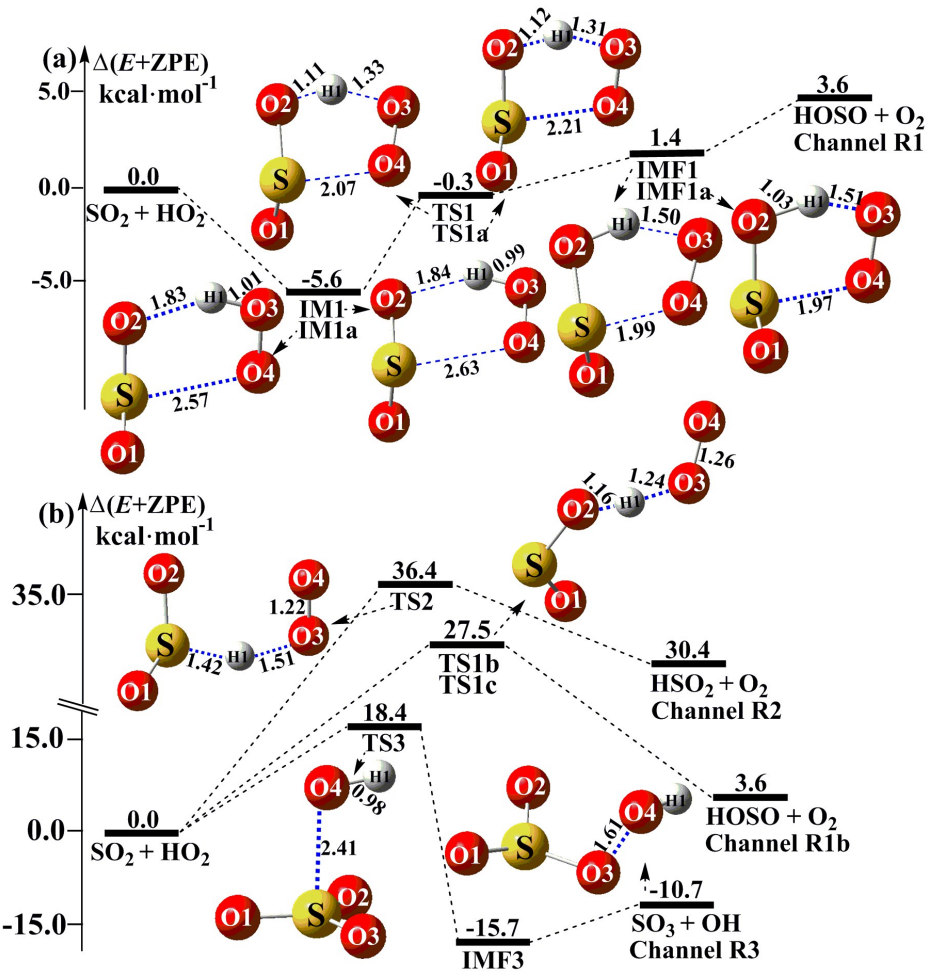
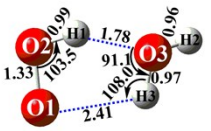
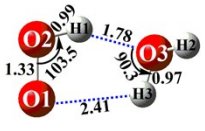


Fig. S1 Schematic energy diagram of the naked SO_2 + HO_2 reaction; energies (kcal·mol^{-1}) computed at the CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level include zero-point energy correction.



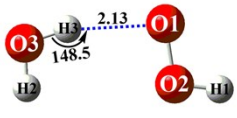
d O1-O2-O3-H2=-104.0

$H_2O\cdots HO_2$ (C_1,^{2}A)



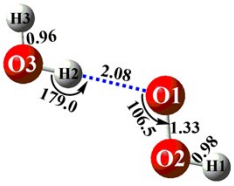
d O1-O2-O3-H2=104.3

$H_2O\cdots HO_2$a (C_1,^{2}A)



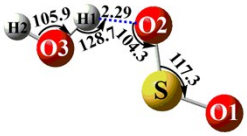
d H1-O2-O1-O3=-179.9

$HO_2\cdots H_2O$ (C_1,^{2}A)



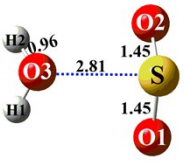
d H1-O2-O1-O3=-179.5

$HO_2\cdots H_2O$a (C_1,^{2}A)



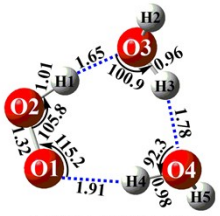
d O1-S-O2-O3=-179.5

$SO_2\cdots H_2O$ (C_1,^{1}A)



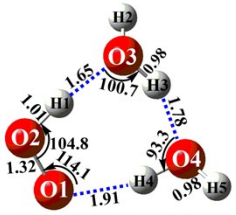
d O2-S-O3-H1=116.3

$H_2O\cdots SO_2$ (C_1,^{1}A)



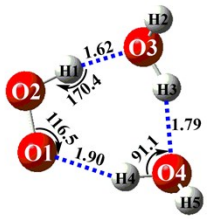
d H1-H3-O4-H2=124.9

$HO_2\cdots(H_2O)_2$ (C_1,^{2}A)



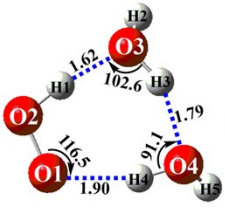
d H1-H3-O4-H2=-124.9

$HO_2\cdots(H_2O)_2$a (C_1,^{2}A)



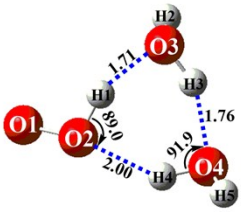
d H1-H3-O4-H2=-82.7

$HO_2\cdots(H_2O)_2$b (C_1,^{2}A)



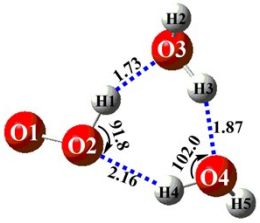
d H1-H3-O4-H2=82.7

$HO_2\cdots(H_2O)_2$c (C_1,^{2}A)



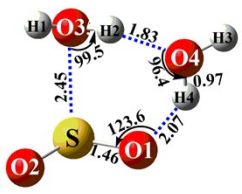
d O1-O2-H1-O4=-148.2

$HO_2\cdots(H_2O)_2$d (C_1,^{2}A)



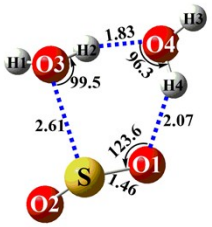
d O1-O2-H1-O4=148.2

$HO_2\cdots(H_2O)_2$e (C_1,^{2}A)



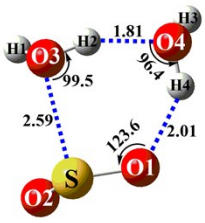
d H1-H2-O3-O1=-120.3

$SO_2\cdots(H_2O)_2$(C_1,^{1}A)



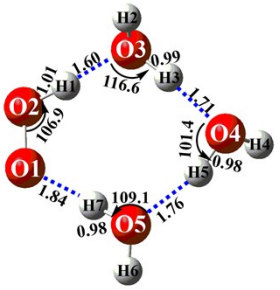
d H1-H2-O3-O1=120.3

$SO_2\cdots(H_2O)_2$a (C_1,^{1}A)



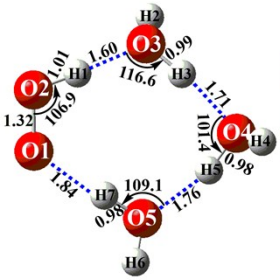
d H1-H2-O3-O1=120.3

$SO_2\cdots(H_2O)_2$b (C_1,^{1}A)



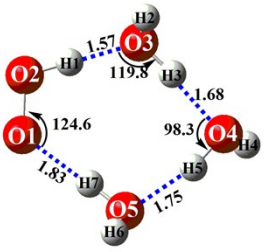
d O2-O4-O3-H2=120.1

$HO_2\cdots(H_2O)_3$(C_1,^{2}A)



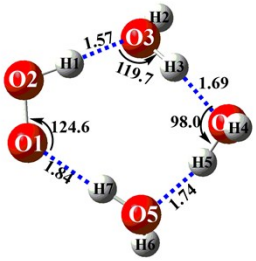
d O2-O4-O3-H2=-120.1

$HO_2\cdots(H_2O)_3$a(C_1,^{2}A)



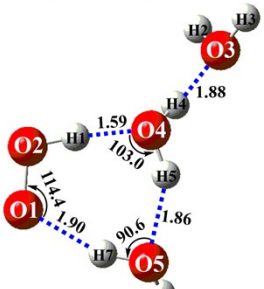
d O2-O4-O3-H2=129.9

$HO_2\cdots(H_2O)_3$b(C_1,^{2}A)



d O2-O4-O3-H2=-129.9

$HO_2\cdots(H_2O)_3$c(C_1,^{2}A)



d O1-O2-O4-H4=120.1

$HO_2\cdots(H_2O)_3$d(C_1,^{2}A)

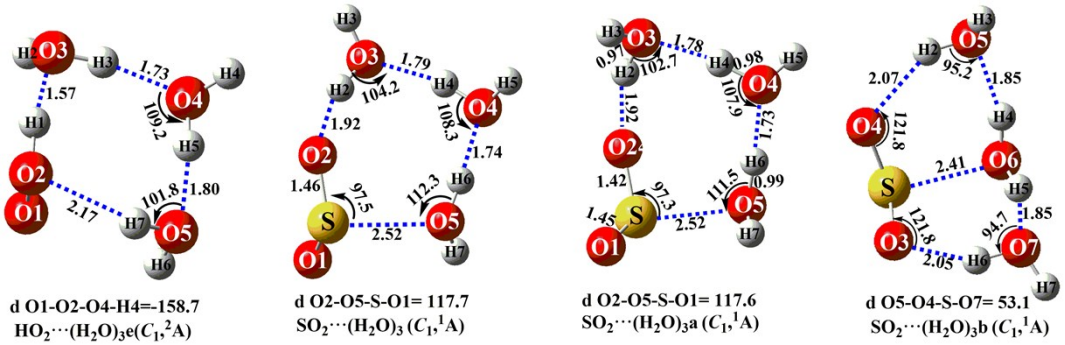


Fig. S2 The geometrical structures of the optimized of $H_2O\cdots HO_2$a, $HO_2\cdots H_2O$a, $HO_2\cdots(H_2O)_2$a, $SO_2\cdots(H_2O)_2$a , $SO_2\cdots(H_2O)_3$a, $HO_2\cdots(H_2O)_3$a at the M06-2X/aug-cc-pVTZ level of theory

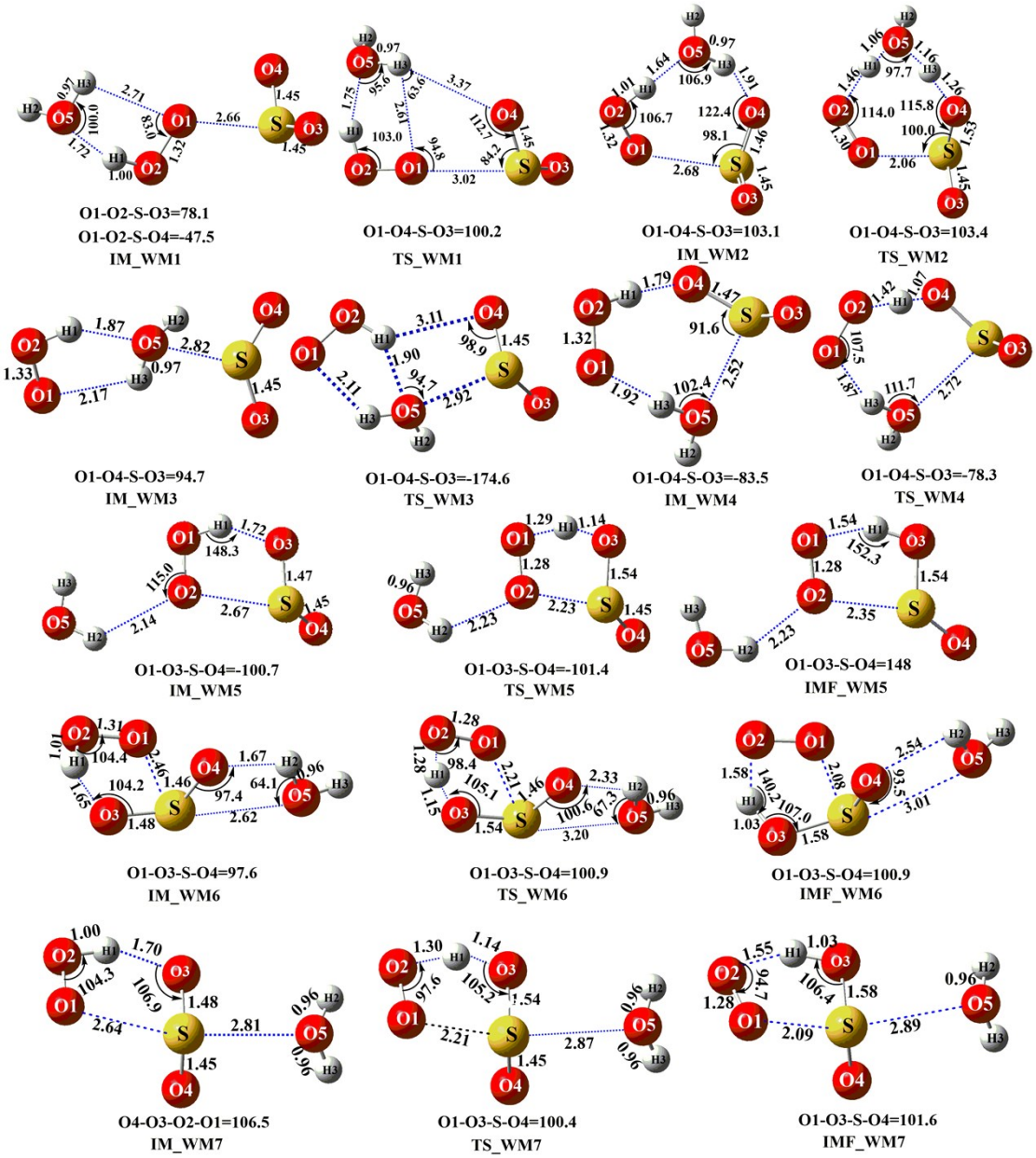


Fig. S3 The geometrical structures of the optimized transitions state, intermediates for water-assisted $HO_2 + SO_2 \rightarrow HOSO + {}^3O_2$ reaction at the M06-2X/aug-cc-pVTZ level of theory

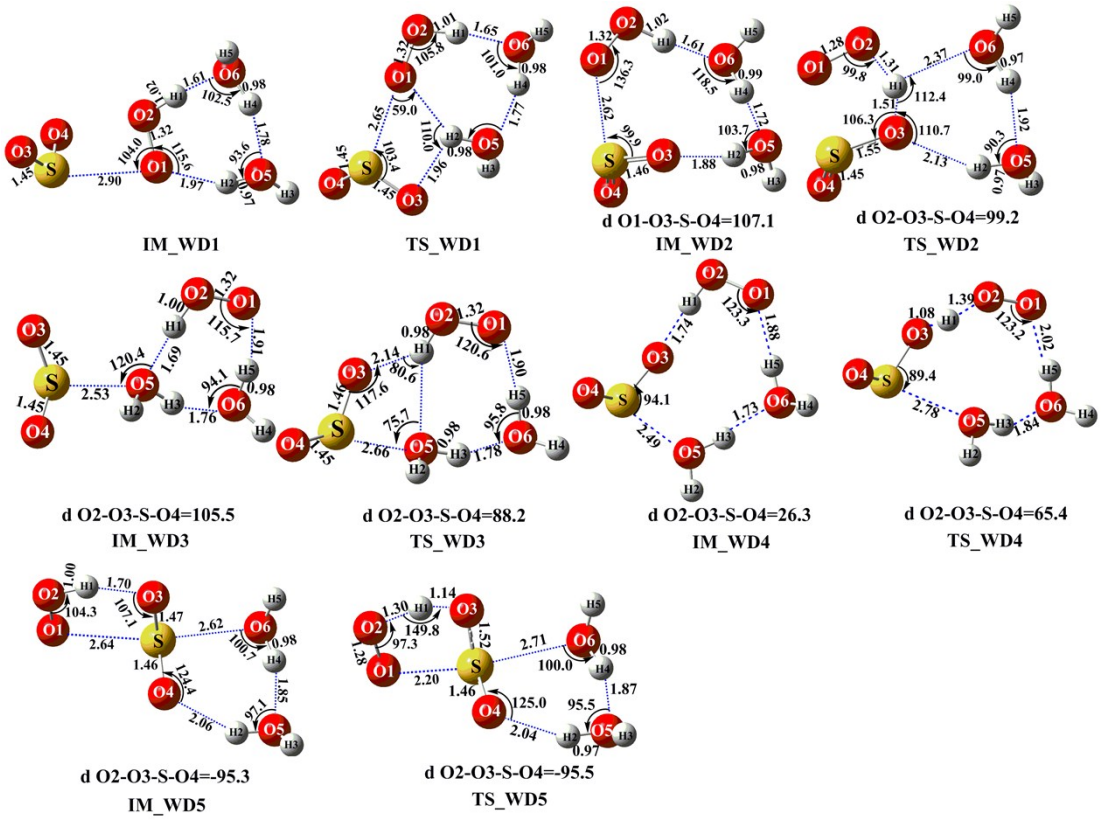


Fig. S4 The geometrical structures of the optimized transitions state, intermediates for water dimer-assisted $HO_2 + SO_2 \rightarrow HOSO + {}^3O_2$ reaction at the M06-2X/aug-cc-pVTZ level of theory

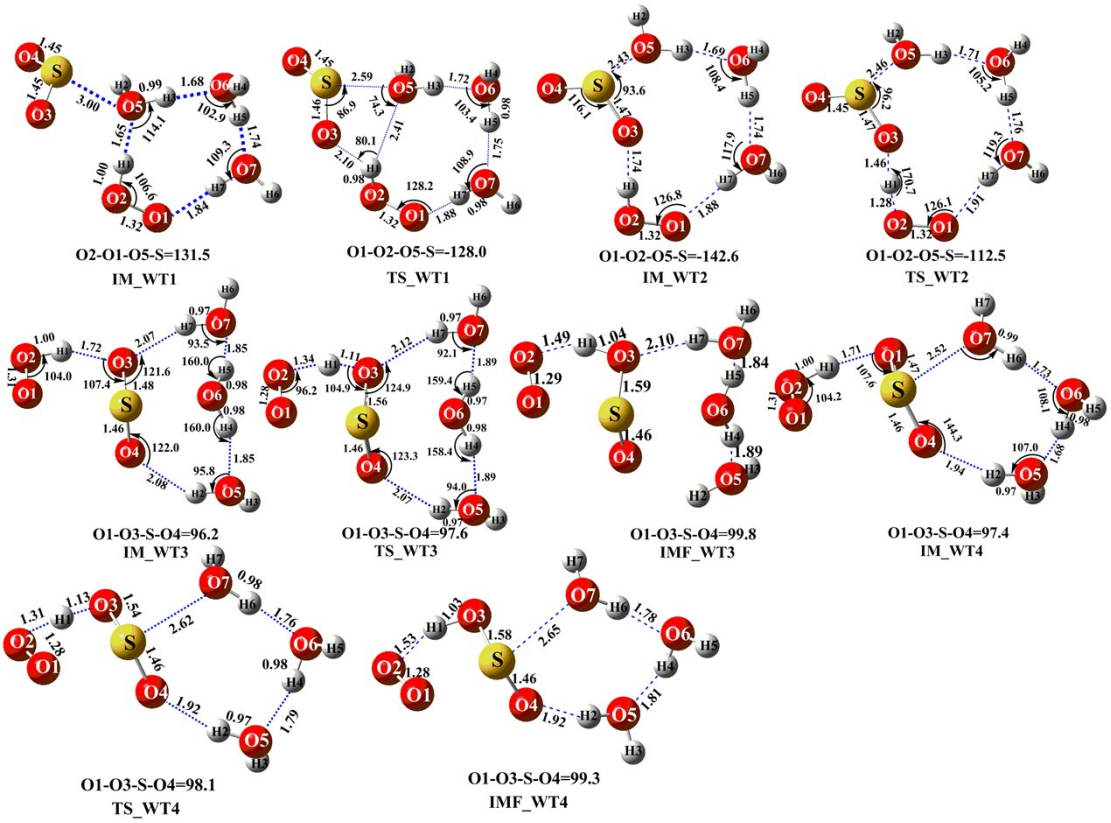


Fig. S5 The geometrical structures of the optimized transitions state, intermediates for water trimer-assisted $HO_2 + SO_2 \rightarrow HOSO + {}^3O_2$ reaction at the M06-2X/aug-cc-pVTZ level of theory

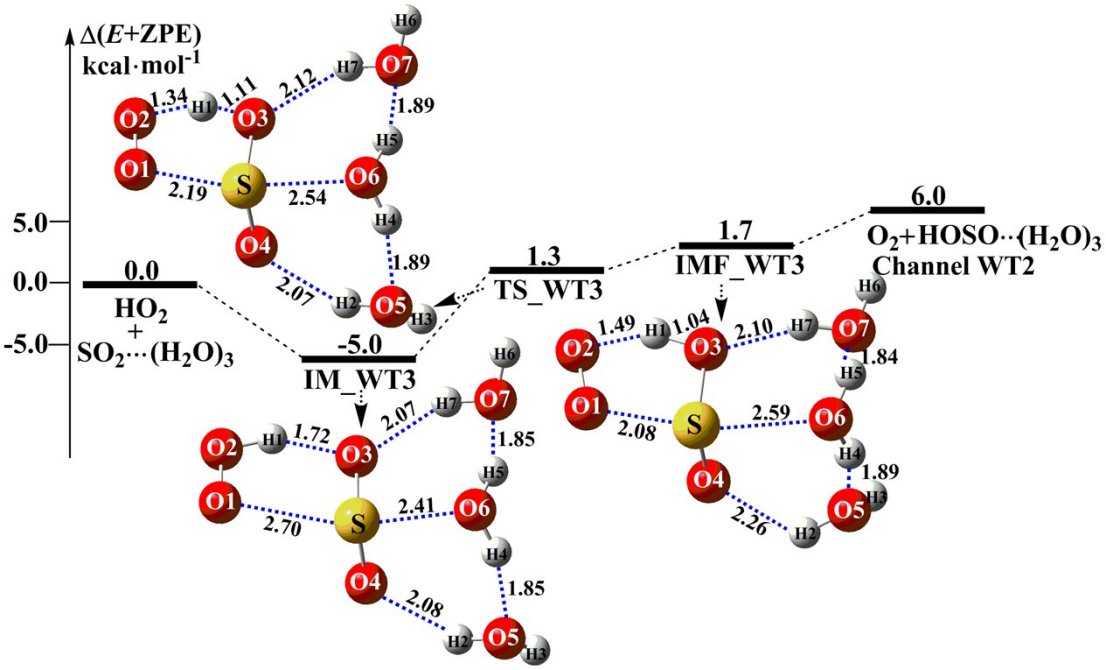


Fig. S6 Schematic energy diagram of water trimer-assisted the channel of HOSO + $^3O_2$ formations occurring through $HO_2 + SO_2\cdots(H_2O)_3$ reaction at the CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level of theory

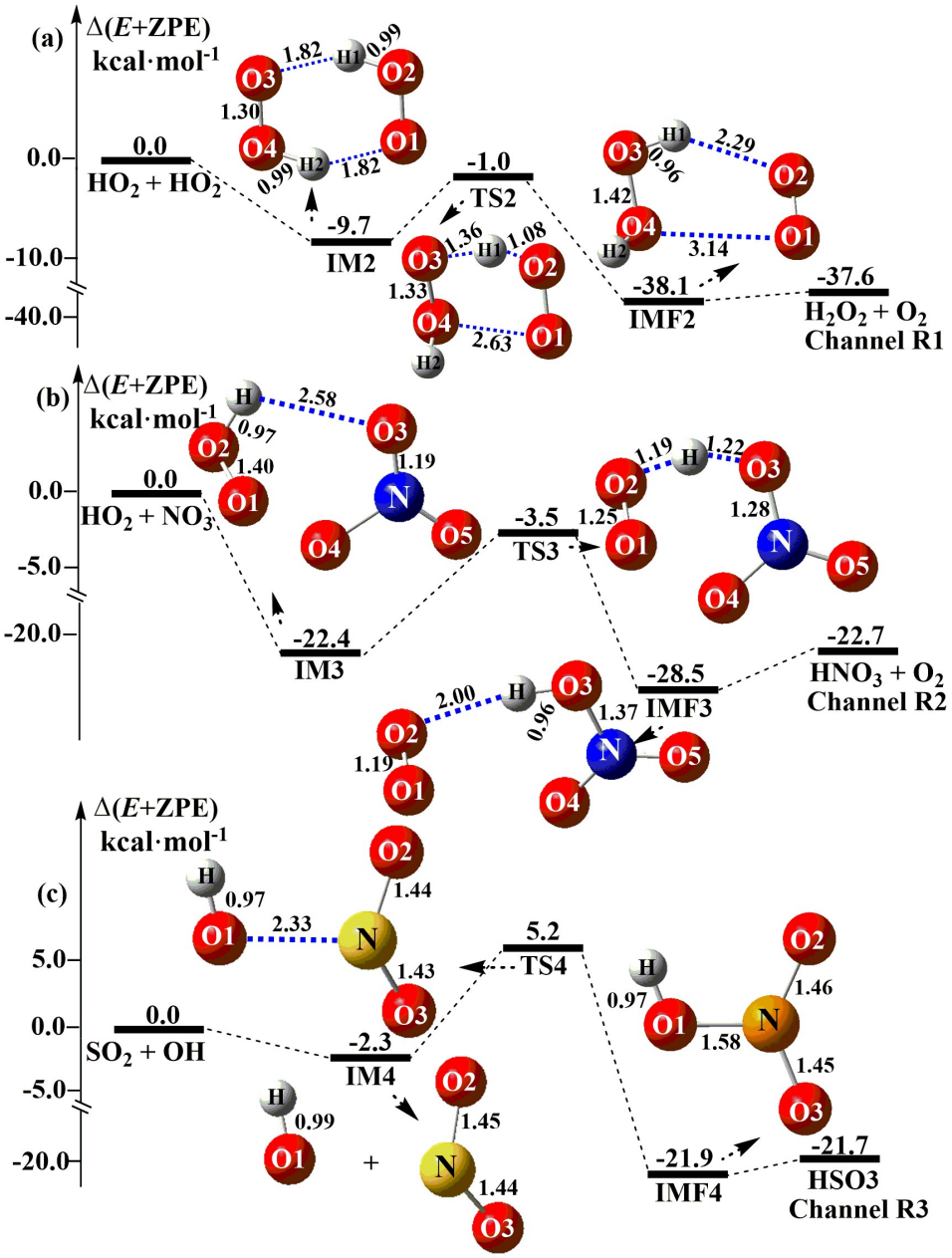


Fig. S7 Schematic energy diagram of the naked $HO_2 + HO_2$ reaction; $HO_2 + NO_3$ reaction; $SO_2 +$ OH reaction; energies (kcal·mol^{-1}) computed at the CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level include zero-point energy correction.

Table S1 The concentration of complexes H_2O (20%RH [H_2O], 40%RH [H_2O], 60%RH [H_2O], 80%RH [H_2O] , 100%RH [H_2O]), $(H_2O)_2$(100%RH [$(H_2O)_2$]), $(H_2O)_3$(100%RH [$(H_2O)_3$]) [1].

T(K)	20%RH [H_2O]	40%RH [H_2O]	60%RH [H_2O]	80%RH [H_2O]	100%RH [H_2O]	100%RH [$(H_2O)_2$]	100%RH [$(H_2O)_3$]
218.6	--	--	--	--	5.21E+12	3.58E+05	1.33E+01
223.7	--	--	--	--	2.62E+12	8.03E+04	1.01
229.7	--	--	--	--	4.92E+15	2.31E+11	3.25E+09
235.1	--	--	--	--	1.31E+12	1.50E+04	--
249.9	--	--	--	--	6.44E+12	2.12E+05	--
259.3	--	--	--	--	2.41E+16	2.67E+12	2.32E+10
275.0	3.78E+16	7.56E+16	1.13E+17	1.51E+17	1.89E+17	1.20E+14	3.29E+12
280.0	5.16E+16	1.03E+17	1.55E+17	2.07E+17	2.58E+17	2.04E+14	5.85E+12
290.0	9.56E+16	1.91E+17	2.87E+17	3.82E+17	4.78E+17	5.91E+14	1.89E+13
298.1	1.55E+17	3.09E+17	4.64E+17	6.18E+17	7.73E+17	1.36E+15	4.78E+13
300.0	1.72E+17	3.43E+17	5.15E+17	6.86E+17	8.58E+17	1.62E+15	5.82E+13
310.0	2.92E+17	5.84E+17	8.77E+17	1.17E+18	1.46E+18	4.06E+15	1.60E+14
320.0	4.70E+17	9.40E+17	1.41E+18	1.88E+18	2.35E+18	9.24E+15	3.91E+14

[H_2O], [$(H_2O)_2$] and [$(H_2O)_3$] are the concentration of the complexes $(H_2O)_2$, $(H_2O)_3$ and $(H_2O)_3$a. ([$(H_2O)_2$] = $K_{eq}((H_2O)_2) \times [H_2O]^2$; [$(H_2O)_3$] = $K_{eq}((H_2O)_3) \times [(H_2O)_2] \times [H_2O]$; [$(H_2O)_3$a] = $K_{eq}((H_2O)_3a) \times [(H_2O)_2] \times [H_2O]$)

[1] J. M. Anglada, G. J. Hoffman, L. V. Slipchenko, *J. Phys. Chem. A.*, 2013, 117, 10381-10396.

Table S2 The concentration and equilibrium constants of $SO_2\cdots(H_2O)_n$ (n = 1-3) and $HO_2\cdots(H_2O)_n$ (n = 1-3). [a,b,c]

T(K)	$H_2O\bullet\bullet\bullet HO_2$	$H_2O\bullet\bullet\bullet HO_2$a	$HO_2\bullet\bullet\bullet H_2O$	$HO_2\bullet\bullet\bullet H_2O$a	$SO_2\bullet\bullet\bullet H_2O$	$H_2O\bullet\bullet\bullet SO_2$
218.6	7.22E-18	6.95E-18	1.77E-22	9.78E-23	8.94E-24	1.05E-23
223.7	4.92E-18	4.74E-18	1.61E-22	8.91E-23	8.10E-24	9.72E-24
229.0	3.21E-19	3.09E-19	1.45E-22	8.05E-23	7.27E-24	8.95E-24
235.1	2.22E-18	2.14E-18	1.33E-22	7.39E-23	6.63E-24	8.35E-24
249.9	8.87E-18	8.54E-18	1.08E-22	5.98E-23	5.29E-24	7.06E-24
259.3	5.24E-19	5.04E-19	9.60E-23	5.31E-23	4.66E-24	6.45E-24
275.0	2.36E-19	2.28E-19	8.08E-23	4.47E-23	3.86E-24	5.67E-24
280.0	1.87E-19	1.80E-19	7.69E-23	4.26E-23	3.66E-24	5.47E-24
290.0	1.20E-19	1.16E-19	7.02E-23	3.89E-23	3.31E-24	5.12E-24
298.2	8.59E-19	8.28E-19	6.56E-23	3.63E-23	3.08E-24	4.88E-24
298.2	(1.99E+08)[c]	(1.92E+08)[c]	(1.52E+04)[c]	(8.42E+03)[c]	(2.38E+06)[c]	(3.77E+06)[c]
300.0	7.98E-19	7.69E-19	6.47E-23	3.58E-23	3.03E-24	4.84E-24
310.0	5.44E-19	5.25E-19	6.00E-23	3.32E-23	2.79E-24	4.60E-24
320.0	3.81E-20	3.68E-20	5.61E-23	3.10E-23	2.59E-24	4.40E-24

T(K)	$HO_2\bullet\bullet\bullet(H_2O)_2$	$HO_2\bullet\bullet\bullet(H_2O)_2$a	$HO_2\bullet\bullet\bullet(H_2O)_2$b	$HO_2\bullet\bullet\bullet(H_2O)_2$c	$HO_2\bullet\bullet\bullet(H_2O)_2$d	$HO_2\bullet\bullet\bullet(H_2O)_2$e
218.6	3.29E-15	3.28E-15	3.30E-17	3.35E-17	2.02E-24	2.41E-24
223.7	1.63E-15	1.62E-15	1.81E-17	1.83E-17	1.75E-24	2.21E-24
229.0	7.38E-16	7.37E-16	9.18E-18	9.30E-18	1.49E-24	2.02E-24
235.1	3.76E-16	3.75E-16	5.14E-18	5.21E-18	1.30E-24	1.75E-24
249.9	6.84E-17	6.83E-17	1.20E-18	1.21E-18	9.23E-25	1.49E-24
259.3	2.57E-17	2.57E-17	5.16E-19	5.23E-19	7.59E-25	1.30E-24
275.0	5.81E-18	5.80E-18	1.44E-19	1.46E-19	5.65E-25	9.23E-25
280.0	3.75E-18	3.74E-18	9.92E-20	1.00E-19	5.18E-25	7.57E-25
290.0	1.63E-18	1.63E-18	4.87E-20	4.92E-20	4.40E-25	5.64E-25
298.2	8.65E-18	8.60E-18	2.82E-20	2.86E-20	3.89E-25	5.16E-25
298.2	(3.53E+06)[c]	(3.51E+06)[c]	(1.15E+04)[c]	(1.17E+04)[c]	(1.59E-01)[c]	(1.57E-01)[c]
300.0	7.52E-19	7.51E-19	2.51E-20	2.54E-20	3.79E-25	3.79E-25
310.0	3.65E-19	3.64E-19	1.35E-20	1.36E-20	3.29E-25	3.29E-25
320.0	1.85E-19	1.85E-19	7.54E-21	7.63E-21	2.89E-25	2.89E-25

T(K)	$SO_2\bullet\bullet\bullet(H_2O)_2$	$SO_2\bullet\bullet\bullet(H_2O)_2$a	$SO_2\bullet\bullet\bullet(H_2O)_2$b	$HO_2\bullet\bullet\bullet(H_2O)_3$	$HO_2\bullet\bullet\bullet(H_2O)_3$a	$HO_2\bullet\bullet\bullet(H_2O)_3$b
218.6	2.46E-22	2.36E-22	2.46E-22	1.31E-15	1.28E-15	9.01E-17
223.7	1.73E-22	1.66E-22	1.67E-22	4.64E-15	4.56E-16	5.11E-17
229.7	1.17E-22	1.12E-22	1.32E-22	1.46E-16	1.44E-16	2.71E-17
235.1	8.33E-23	8.00E-23	8.53E-23	5.43E-16	5.34E-16	1.58E-17
249.9	3.57E-23	3.44E-23	3.64E-23	4.51E-16	4.43E-16	4.03E-18
259.3	2.20E-23	2.12E-23	2.17E-23	1.08E-16	1.06E-16	1.84E-18
275.0	1.06E-23	1.02E-23	1.32E-23	1.23E-17	1.21E-17	5.62E-19

T(K)	SO_2•••$(H_2O)_2$	SO_2•••$(H_2O)_2$a	SO_2•••$(H_2O)_2$b	HO_2•••$(H_2O)_3$	HO_2•••$(H_2O)_3$a	HO_2•••$(H_2O)_3$b
280.0	8.52E-24	8.20E-24	8.27E-24	6.48E-17	6.37E-17	3.96E-19
290.0	5.67E-24	5.46E-24	5.65E-24	1.93E-18	1.90E-18	2.04E-19
298.2	4.16E-24	4.01E-24	4.11E-24	5.89E-18	5.51E-18	1.23E-19
298.2	(5.66E+03)[c]	(5.45E+03)[c]	(5.52E+03)[c]	(8.45E+04)[c]	(7.90E+04)[c]	(1.77E+03)[c]
300.0	3.89E-24	3.74E-24	3.78E-24	6.23E-18	6.13E-18	1.10E-19
310.0	2.73E-24	2.63E-24	2.67E-24	2.17E-19	2.133E-19	6.20E-20
320.0	1.97E-24	1.90E-24	1.96E-24	8.08E-19	7.94E-19	3.62E-20
T(K)	HO_2•••$(H_2O)_3$c	HO_2•••$(H_2O)_3$d	HO_2•••$(H_2O)_3$e	SO_2•••$(H_2O)_3$	SO_2•••$(H_2O)_3$a	SO_2•••$(H_2O)_3$b
218.6	2.49E-17	6.20E-17	7.29E-19	5.68E-23	2.22E-23	2.60E-24
223.7	1.45E-17	3.81E-17	4.75E-19	2.42E-23	1.14E-23	1.44E-24
229.0	7.96E-18	2.21E-17	2.95E-19	1.23E-23	5.40E-23	7.50E-25
235.1	4.76E-18	1.39E-17	1.96E-19	4.93E-23	2.86E-23	4.29E-25
249.9	1.31E-18	4.34E-18	7.04E-20	1.65E-23	5.77E-23	1.05E-25
259.3	6.22E-19	2.22E-18	3.91E-20	1.25E-23	2.30E-23	4.72E-25
275.0	2.02E-19	8.10E-19	1.61E-20	2.71E-24	5.75E-24	1.41E-25
280.0	1.45E-19	6.02E-19	1.24E-20	6.71E-24	3.82E-24	9.86E-25
290.0	7.74E-20	3.44E-19	7.56E-21	3.76E-25	1.77E-25	5.04E-25
298.2	4.79E-20	2.24E-19	5.18E-21	1.41E-25	9.79E-25	3.02E-26
298.2	(6.87+02)[c]	(3.22E+03)[c]	(7.43E+01)[c]	(6.74E+00)[c]	(4.68E+01)[c]	(1.44E+00)[c]
300.0	4.31E-20	2.04E-19	4.77E-21	1.89E-25	8.61E-25	2.70E-26
310.0	2.50E-20	1.26E-19	3.11E-21	8.54E-25	4.41E-25	1.52E-26
320.0	1.50E-20	7.99E-20	2.09E-21	3.52E-25	2.36E-25	8.83E-26

[a] Equilibrium constants in units of $cm^3 \cdot molecule^{-1}$;

[b] All equilibrium constants were calculated by using energies computed at CCSD(T)/CBS level and partition functions obtained at M06-2X/aug-cc-pVTZ level about the relevant complexes H_2O•••HO_2, H_2O•••HO_2a, HO_2•••H_2O, HO_2•••H_2Oa, SO_2•••H_2O, H_2O•••SO_2, HO_2•••$(H_2O)_2$, HO_2•••$(H_2O)_2$a, SO_2•••$(H_2O)_2$, SO_2•••$(H_2O)_2$a, HO_2•••$(H_2O)_3$, HO_2•••$(H_2O)_3$a, SO_2•••$(H_2O)_3$, SO_2•••$(H_2O)_3$a at 218.6 - 320.0 K;

[c] The concentration of the corresponding complexes at 298 K.

Table S3 Zero point energy (ZPE/(kcal·mol^{-1})), entropies (S/(cal·mol^{-1}·K^{-1})), relative energies (ΔE and $\Delta(E$ + ZPE)/(kcal·mol^{-1})), enthalpies ($\Delta H(298)$/(kcal·mol^{-1})), and free energies ($\Delta G(298)$/(kcal·mol^{-1})) for $SO_2\cdots(H_2O)_n$ (n = 1-3) and $HO_2\cdots(H_2O)_n$ (n = 1-3) complexes

Species	ZPE	S	ΔE	ΔH	ΔG	$\Delta(E$ + ZPE)
$H_2O + HO_2$	0.0	101.1	0.0	0.0	0.0	0.0
$H_2O\bullet\bullet\bullet HO_2$	2.6	72.3	-9.5	-7.7	0.9	-6.9
$H_2O\bullet\bullet\bullet HO_2$a	2.6	72.2	-9.5	-7.7	0.9	-6.8
$HO_2\bullet\bullet\bullet H_2O$	1.5	75.2	-3.5	-2.6	5.1	-2.0
$H_2O + SO_2$	0.0	105.9	0.0	0.0	0.0	0.0
$SO_2\bullet\bullet\bullet H_2O$	1.1	88.7	-3.7	-2.4	2.7	-2.6
$H_2O\bullet\bullet\bullet SO_2$	1.2	83.4	-4.6	-3.3	3.4	-3.4
$H_2O + H_2O$	0.0	92.9	0.0	0.0	0.0	0.0
$(H_2O)_2$	2.1	69.5	-5.2	-3.6	3.4	-3.1
$(H_2O)_2 + HO_2$	0.0	124.2	0.0	0.0	0.0	0.0
$HO_2\bullet\bullet\bullet(H_2O)_2$	3.3	83.3	-15.9	-14.0	-1.8	-12.6
$HO_2\bullet\bullet\bullet(H_2O)_2$a	3.3	83.3	-15.9	-14.0	-1.8	-12.5
$HO_2\bullet\bullet\bullet(H_2O)_2$b	4.3	83.0	-15.0	-12.6	-1.4	-10.7
$HO_2\bullet\bullet\bullet(H_2O)_2$c	4.3	83.0	-15.0	-12.6	-1.4	-10.6
$HO_2\bullet\bullet\bullet(H_2O)_2$d	4.5	80.9	-9.7	-7.2	6.0	-5.2
$HO_2\bullet\bullet\bullet(H_2O)_2$e	4.4	80.8	-9.6	-7.0	6.0	-5.1
$(H_2O)_2 + SO_2$	0.0	128.9	0.0	0.0	0.0	0.0
$SO_2\bullet\bullet\bullet(H_2O)_2$	2.0	93.0	-8.9	-7.4	3.3	-6.9
$SO_2\bullet\bullet\bullet(H_2O)_2$a	2.0	92.9	-8.9	-7.4	3.3	-6.9
$SO_2\bullet\bullet\bullet(H_2O)_2$b	2.1	92.9	-8.8	-7.6	3.2	-6.3
$(H_2O)_2 + H_2O$	0.0	115.9	0.0	0.0	0.0	0.0
$(H_2O)_3$	3.3	79.5	-11.1	-9.1	1.8	-7.7
$(H_2O)_3 + HO_2$	0.0	134.2	0.0	0.0	0.0	0.0
$HO_2\bullet\bullet\bullet(H_2O)_3$	2.1	100.0	-14.3	-12.8	-2.6	-12.3
$HO_2\bullet\bullet\bullet(H_2O)_3$a	2.1	100.0	-14.3	-12.8	-2.6	-12.3
$HO_2\bullet\bullet\bullet(H_2O)_3$b	5.5	98.7	-14.1	28.8	31.5	-8.6
$HO_2\bullet\bullet\bullet(H_2O)_3$c	5.5	98.7	-13.5	29.3	32.0	-8.1
$HO_2\bullet\bullet\bullet(H_2O)_3$d	3.5	105.4	-11.0	31.0	31.1	-7.6
$HO_2\bullet\bullet\bullet(H_2O)_3$a	5.1	101.5	-11.3	30.9	33.3	-6.2
$(H_2O)_3 + SO_2$	0.0	138.9	0.0	0.0	0.0	0.0
$SO_2\bullet\bullet\bullet(H_2O)_3$	1.2	106.6	-7.7	-6.5	3.1	-6.5
$SO_2\bullet\bullet\bullet(H_2O)_3$a	1.2	106.9	-7.8	-6.5	3.0	-6.6
$SO_2\bullet\bullet\bullet(H_2O)_3$b	3.2	105.6	-6.3	-4.6	11.6	-3.0

ZPE and S values obtained at M06-2X/aug-cc-pVTZ level of theory; The energy values are obtained at CCSD(T)/CBS level whereas the H and G corrections are taken from the M06-2X/aug-cc-pVTZ level.

Table S4 Zero point energy (ZPE/(kcal·mol^{-1})), relative energies (ΔE and $\Delta(E + \text{ZPE})$/(kcal·mol^{-1})), enthalpies ($\Delta H(298)$/(kcal·mol^{-1})), and free energies ($\Delta G(298)$/(kcal·mol^{-1})) for water-assisted the formation of HOSO + O_2 from the SO_2 + HO_2 reaction

Species	ZPE	S	ΔE	ΔH	ΔG	$\Delta(E + \text{ZPE})$
H_2O•••HO_2 + SO_2	0.0	133.1	0.0	0.0	0.0	0.0
IM_WM1	0.7	108.9	-3.7	-2.5	4.4	-3.0
TS_WM1	0.4	105.4	-3.1	-2.5	5.3	-2.7
IM_WM2	1.2	99.3	-7.3	-6.1	3.6	-6.1
TS_WM2	-1.1	86.9	10.5	8.1	21.4	9.4
IM_WM3	3.4	103.3	-4.2	-1.0	7.9	-0.8
TS_WM3	3.3	97.3	-3.8	-1.1	9.6	-0.2
IM_WM4	3.6	97.5	-5.7	-2.4	8.2	-1.8
TS_WM4	-1.2	96.0	5.1	3.3	14.3	5.8
H_2O•••HOSO + O_2	-0.5	129.5	2.2	1.9	2.5	1.7
H_2O•••HO_2 + SO_2	0.0	133.1	0.0	0.0	0.0	0.0
IM_WM5	1.4	106.7	-7.2	-5.4	2.9	-5.8
TS_WM5	-1.1	97.0	1.0	-0.7	10.5	0.0
IMF_WM5	0.1	96.13	4.9	3.8	17.4	4.9
HOSO + H_2O + O_2	-2.0	162.8	7.6	6.5	-1.9	5.6
SO_2•••H_2O + HO_2	0.0	143.4	0.0	0.0	0.0	0.0
IM_WM6	1.9	106.4	-7.2	-5.9	5.1	-5.3
TS_WM6	-0.4	100.5	-0.6	-2.1	10.6	-1.0
IMF_WM6	1.39	99.9	-1.0	-0.5	12.4	0.4
HOSO•••H_2O + O_2	-0.5	144.6	3.9	3.1	3.3	3.4
H_2O•••SO_2 + HO_2	0.0	138.1	0.0	0.0	0.0	0.0
IM_WM7	1.7	102.6	-7.9	-6.5	4.0	-6.1
TS_WM7	-0.4	97.5	-0.3	-1.8	10.3	-0.7
IMF_WM7	1.3	99.3	-0.4	0.1	11.7	0.9
HOSO•••H_2O + O_2	-0.6	144.6	4.7	4.0	2.6	4.1

ZPE values obtained at M06-2X/aug-cc-pVTZ level of theory; The energy values are obtained at CCSD(T)/CBS level whereas
the H and G corrections are taken from the M06-2X/aug-cc-pVTZ level

Table S5 Zero point energy (ZPE/(kcal·mol^{-1})), entropies (S/ (cal·mol^{-1}·K^{-1})), relative energies (ΔE and $\Delta(E$+ZPE)/(kcal·mol^{-1})), enthalpies ($\Delta H(298)$/(kcal·mol^{-1})), and free energies ($\Delta G(298)$/(kcal·mol^{-1})) for the SO_2 + HO_2 with dimer water molecule reaction

Species	ZPE	S	ΔE	ΔH	ΔG	$\Delta(E$ + ZPE)
HO_2•••$(H_2O)_2$ + SO_2	0.0	142.7	0.0	0.0	0.0	0.0
IM_WD1	0.4	120.6	-4.8	-2.2	4.4	-4.4
TS_WD1	0.1	113.9	-3.0	-4.0	4.6	-2.9
IM_WD2	0.6	114.9	-4.7	-3.6	4.7	-4.0
TS_WD2	-2.5	113.4	9.2	7.0	15.7	6.6
$(H_2O)_2$•••HOSO + O_2	-0.9	142.4	2.2	1.7	1.8	1.3
HO_2•••$(H_2O)_2$ + SO_2	0.0	144.1	0.0	0.0	0.0	0.0
IM_WD3	0.5	120.3	-3.2	-2.0	5.1	-2.7
TS_WD3	-0.2	115.0	-1.3	-1.0	7.7	-1.5
IM_WD4	0.2	112.5	-2.6	-1.5	8.0	-1.8
TS_WD4	-4.1	116.9	3.3	0.3	8.5	-0.4
$(H_2O)_2$•••HOSO + O_2	-0.9	142.4	2.2	1.7	2.2	1.3
SO_2•••$(H_2O)_2$ + HO_2	0.0	147.7	0.0	0.0	0.0	0.0
IM_WD5	1.6	113.4	-7.7	-6.4	3.9	-6.1
TS_WD5	-0.5	107.7	-0.3	-1.8	10.1	-0.9
IMF_WD5	1.1	109.2	-0.6	-0.2	11.3	0.5
IM_WD6	2.4	110.6	-10.5	-8.7	2.3	-8.1
TS_WD6	-1.3	104.9	16.0	13.6	26.4	14.7
HOSO•••$(H_2O)_2$ + O_2	-0.9	151.5	4.9	4.6	3.5	4.0

[a] ZPE and S values obtained at M06-2X/aug-cc-pVTZ level of theory; The energy values are obtained at CCSD(T)/CBS level whereas the H and G corrections are taken from the M06-2X/aug-cc-pVTZ level.

Table S6 Zero point energy (ZPE/(kcal·mol^{-1})), entropies (S/ (cal·mol^{-1}·K^{-1})), relative energies (ΔE and $\Delta(E + \text{ZPE})$/(kcal·mol^{-1})), enthalpies ($\Delta H(298)$/(kcal·mol^{-1})), and free energies ($\Delta G(298)$/(kcal·mol^{-1})) for the $SO_2 + HO_2$ with water trimer

Species	ZPE	S	ΔE	ΔH	ΔG	$\Delta(E + \text{ZPE})$
$HO_2\cdots(H_2O)_3 + SO_2$	60.7	160.8	0.0	0.0	0.0	0.0
IM_WT1	61.0	126.2	-3.4	-2.9	7.4	-3.0
TS_WT1	57.5	121.4	2.5	-0.9	10.8	-0.7
IM_WT2	61.4	130.6	-1.7	-0.5	8.6	-1.0
TS_WT2	58.1	123.0	18.6	16.0	27.2	16.0
$HOSO\cdots(H_2O)_3 + O_2$	56.4	167.1	13.6	11.7	11.2	11.7
$SO_2\cdots(H_2O)_3 + HO_2$	0.0	162.7	0.0	0.0	0.0	0.0
IM_WT3	1.5	125.8	-6.4	-5.1	5.6	-4.8
TS_WT3	-0.6	120.9	1.8	0.5	12.7	1.3
IMF_WT3	1.4	118.1	0.3	0.8	13.5	1.7
$HOSO\cdots(H_2O)_3 + O_2$	-1.4	167.1	7.1	6.7	5.1	6.0

ZPE and S values obtained at M06-2X/aug-cc-pVTZ level of theory; The energy values are obtained at CCSD(T)/CBS level whereas the H and G corrections are taken from the M06-2X/aug-cc-pVTZ level.

Table S7 Rate constants ($cm^3 \cdot molecules^{-1} \cdot s^{-1}$) for the HOSO + O_2 formations from the SO_2 + HO_2 reaction without and with $(H_2O)_n$ (n = 1-3) within the temperature range of 218.6 - 320.0K

T(K)	k_R	k_a(TS_WM1)	k_a(TS_WM2)	k_a(WM1a)	k_a(TS_WM3)	k_a(TS_WM4)
218.6	9.09E-18	8.52E-15	1.35E-04	8.52E-15	5.75E-13	4.61E-02
223.7	1.02E-17	8.08E-15	3.00E-04	8.08E-15	5.30E-13	9.46E-02
229.7	1.08E-17	7.64E-15	7.33E-04	7.64E-15	4.85E-13	2.12E-01
235.1	1.31E-17	7.29E-15	1.58E-03	7.29E-15	4.50E-13	4.23E-01
249.9	1.75E-17	6.53E-15	1.81E-02	6.53E-15	3.76E-13	2.40E+00
259.3	1.76E-17	6.17E-15	3.27E-02	6.17E-15	3.41E-13	6.54E+00
275.0	2.72E-17	5.71E-15	1.74E-01	5.71E-15	2.96E-13	2.99E+01
280.0	2.95E-17	5.60E-15	2.84E-01	5.60E-15	2.85E-13	4.67E+01
290.0	3.44E-17	5.41E-15	7.21E-01	5.41E-15	2.65E-13	1.09E+02
298.2	3.87E-17	5.27E-15	1.47E+00	5.27E-15	2.52E-13	2.09E+02
300.0	3.98E-17	5.25E-15	1.72E+00	5.25E-15	2.49E-13	2.41E+02
310.0	4.57E-17	5.13E-15	3.84E+00	5.13E-15	2.36E-13	5.06E+02
320.0	5.22E-17	5.04E-15	8.17E+00	5.04E-15	2.25E-13	1.01E+03
375.0	9.95E-17	--	--	--	--	--
400.0	1.28E-16	--	--	--	--	

T(K)	k_a(WM1b)	k_a(WM1)	k_a(WM2)	k_b(WM3)	k_b(WM4)	k_b(WM4)
218.6	5.75E-13	5.84E-13	1.04E-24	2.16E-16	2.89E-16	2.89E-16
223.7	5.30E-13	5.38E-13	1.82E-24	2.18E-16	3.01E-16	3.01E-16
229.7	4.85E-13	4.93E-13	3.17E-24	2.19E-16	3.14E-16	3.14E-16
235.1	4.50E-13	4.57E-13	5.53E-24	2.21E-16	3.27E-16	3.27E-16
249.9	3.76E-13	3.83E-13	1.92E-24	2.27E-16	3.62E-16	3.62E-16
259.3	3.41E-13	3.47E-13	1.95E-24	2.31E-16	3.84E-16	3.84E-16
275.0	2.96E-13	3.02E-13	3.57E-24	2.37E-16	4.23E-16	4.23E-16
280.0	2.85E-13	2.90E-13	3.69E-24	2.40E-16	4.36E-16	4.36E-16
290.0	2.65E-13	2.71E-13	6.75E-24	2.45E-16	4.62E-16	4.62E-16
298.2	2.52E-13	2.57E-13	1.08E-23	2.49E-16	4.83E-16	4.83E-16
300.0	2.49E-13	2.54E-13	1.29E-23	2.50E-16	4.88E-16	4.88E-16
310.0	2.36E-13	2.41E-13	2.46E-23	2.55E-16	5.15E-16	5.15E-16
320.0	2.25E-13	2.30E-13	4.72E-23	2.61E-16	5.43E-16	5.43E-16

k_a(TS_WM1) is the rate constant for the process of $H_2O \bullet\bullet\bullet HO_2 + SO_2 \rightarrow$IM_WM1 $\rightarrow$TS_WM1 $\rightarrow$IM_WM2, k_a(TS_WM2) is the rate constant for the process of IM_WM2 $\rightarrow$TS_WM2 $\rightarrow$ $H_2O \bullet\bullet\bullet HOSO + O_2$. k_a(WM1a) is the rate constant for the process of $H_2O \bullet\bullet\bullet HO_2 + SO_2 \rightarrow H_2O \bullet\bullet\bullet HOSO + O_2$. k_a(TS_WM3) and k_a(TS_WM4) are the rate constant for the process of $H_2O \bullet\bullet\bullet HO_2 + SO_2 \rightarrow$IM_WM3 $\rightarrow$TS_WM3 $\rightarrow$ IM_WM4. k_a(WM1a), k_a(WM1b), k_a(WM2), k_b(WM3) and k_b(WM4) are the rate constant occurring through Channel WM1, Channel WM2, Channel WM3 and Channel WM4.(k_a(WM1a)= $1/[(1/k_a(\text{TS\_WM1})) + (1/k_a(\text{TS\_WM2}))]$; k_a(WM1b) = $1/[(1/k_a(\text{TS\_WM3})) + (1/k_a(\text{TS\_WM4}))]$. The letter "a" "b" was used to distinguish the complexes，"a"is the complex of $HO_2 \cdots (H_2O)_n$ (n = 1-3), "b"is the complex of $SO_2 \cdots (H_2O)_n$ (n = 1-3).

Table S8 Rate constants ($cm^3 \cdot molecules^{-1} \cdot s^{-1}$) for the $HOSO + O_2$ formations from the $SO_2 + HO_2$ reaction without and with $(H_2O)_n$ (n = 1-3) within the temperature range of 218.6~ 320.0 K

T(K)	k_a(TS_WD1)	k_a(TS_WD2)	k_a(WD1a)	k_a(TS_WD3)	k_a(TS_WD4)
218.6	1.91E-14	1.35E+02	1.91E-14	6.24E-15	3.19E+05
223.7	2.02E-14	2.28E+02	2.02E-14	7.11E-15	4.78E+05
229.7	2.15E-14	4.11E+02	2.15E-14	8.24E-15	7.53E+05
235.1	2.27E-14	6.81E+02	2.27E-14	9.38E-15	1.11E+06
249.9	2.64E-14	2.46E+03	2.64E-14	1.31E-14	3.00E+06
259.3	2.90E-14	5.20E+03	2.90E-14	1.61E-14	5.33E+06
275.0	3.37E-14	1.63E+04	3.37E-14	2.22E-14	1.28E+07
280.0	3.53E-14	2.28E+04	3.53E-14	2.44E-14	1.66E+07
290.0	3.88E-14	4.35E+04	3.88E-14	2.95E-14	2.72E+07
298.2	4.18E-14	7.14E+04	4.18E-14	3.43E-14	3.98E+07
300.0	4.25E-14	7.96E+04	4.25E-14	3.54E-14	4.32E+07
310.0	4.65E-14	1.40E+05	4.65E-14	4.23E-14	6.67E+07
320.0	5.08E-14	2.40E+05	5.08E-14	5.01E-14	1.00E+08
T(K)	k_a(WD1b)	k_a(WD1)	k_b(WD2a)	k_b(WD2b)	k_b(WD2)
218.6	6.24E-15	2.54E-14	6.80E-16	6.80E-16	6.80E-16
223.7	7.11E-15	2.73E-14	6.97E-16	6.97E-16	6.97E-16
229.7	8.24E-15	4.51E-14	7.18E-16	7.18E-16	7.18E-16
235.1	9.38E-15	3.21E-14	7.37E-16	7.37E-16	7.37E-16
249.9	1.31E-14	3.95E-14	7.89E-16	7.89E-16	7.89E-16
259.3	1.61E-14	1.01E-13	2.90E-14	2.90E-14	2.90E-14
275.0	2.22E-14	5.59E-14	8.82E-16	8.82E-16	8.82E-16
280.0	2.44E-14	5.98E-14	9.01E-16	9.01E-16	9.01E-16
290.0	2.95E-14	6.83E-14	9.40E-16	9.40E-16	9.40E-16
298.2	3.43E-14	7.61E-14	9.73E-16	9.73E-16	9.73E-16
300.0	3.54E-14	7.80E-14	9.81E-16	9.81E-16	9.81E-16
310.0	4.23E-14	8.88E-14	1.02E-15	1.02E-15	1.02E-15
320.0	5.01E-14	5.59E-14	1.06E-15	1.06E-15	1.06E-15

k_a(TS_WD1) is the rate constant for the process of $HO_2 \bullet\bullet\bullet (H_2O)_2 + SO_2 \rightarrow$ IM_WD1 $\rightarrow$ TS_WD1 $\rightarrow$ IM_WD2, k_a(TS_WD2) is the rate constant for the process of IM_WD2 $\rightarrow$ TS_WD2 $\rightarrow (H_2O)_2 \bullet\bullet\bullet HOSO + O_2$. k_a(TS_WD3) is the rate constant for the process of $HO_2 \bullet\bullet\bullet (H_2O)_2 + SO_2 \rightarrow$ IM_WD3 $\rightarrow$ TS_WD3 $\rightarrow$ IM_WD4; k_a(TS_WD4) is the rate constant for the process of IM_WD4 $\rightarrow$ TS_WD4 $\rightarrow (H_2O)_2 \bullet\bullet\bullet HOSO + O_2$; k_a(WD1a), k_a(WD1b), k_b(WD2a) and k_b(WD2b) is the rate constant of the Channel WD1a, WD1b, WD2a and Channel WD2b; k_a(WD1a) and k_a(WD1b) are the rate constant for the process of $HO_2 \bullet\bullet\bullet (H_2O)_2 + SO_2 \rightarrow (H_2O)_2 \bullet\bullet\bullet HOSO + O_2$; k_b(WD2) is the rate constant for the process of $SO_2 \bullet\bullet\bullet (H_2O)_2 + HO_2 \rightarrow HOSO \bullet\bullet\bullet (H_2O)_2 + O_2$. $k_a(WD1a) = 1/[(1/k_a(TS\_WD1)) + (1/k_a(TS\_WD2))]$; $k_a(WD1b) = 1/[(1/k_a(TS\_WD3)) + (1/k_a(TS\_WD4))]$; $k_a(WD1) = k_a(WD1a) + k_a(WD1b)$; $k_b(WD2) = k_b(WD2a) + k_b(WD2b)$. The letter "a" "b" was used to distinguish the complexes，"a"is the complex of $HO_2 \cdots (H_2O)_n$ (n = 1-3), "b"is the complex of $SO_2 \cdots (H_2O)_n$ (n = 1-3).

Table S9 Rate constants ($cm^3 \cdot molecules^{-1} \cdot s^{-1}$) for the HOSO + O_2 formations from the SO_2 + HO_2 reaction without and with $(H_2O)_n$ (n = 1-3) within the temperature range of 218.6 - 320.0 K

T(K)	k_a(TS_WT1)	k_a(TS_WT2)	k_a(WT1)
218.6	3.44E-15	1.51E-05	4.02E-15
223.7	3.48E-15	3.51E-05	4.08E-15
229.7	3.53E-15	8.99E-05	3.53E-15
235.1	3.58E-15	2.02E-04	3.58E-15
249.9	3.73E-15	1.55E-03	3.73E-15
259.3	3.83E-15	5.03E-03	3.83E-15
275.0	4.02E-15	3.01E-02	4.02E-15
280.0	4.08E-15	5.11E-02	4.08E-15
290.0	4.22E-15	1.39E-01	4.22E-15
298.2	4.35E-15	3.01E-01	4.34E-15
300.0	4.37E-15	3.56E-01	4.37E-15
310.0	4.52E-15	8.58E-01	4.52E-15
320.0	4.69E-15	1.96E-00	4.69E-15

k_a(TS_WT1) is the rate constant for the process of $HO_2 \bullet\bullet\bullet (H_2O)_3 + SO_2 \rightarrow$ IM_WT1 $\rightarrow$ TS_WT1 $\rightarrow$ IM_WT2, k_a(TS_WT2) is the rate constant for the process of IM_WT2 $\rightarrow$ TS_WT2 $\rightarrow (H_2O)_3 \bullet\bullet\bullet HOSO + O_2$. $k_a(WT1) = 1/[(1/k_a(TS\_WT1)) + (1/k_a(TS\_WT2))]$

Table S10 Rate constants ($cm^3 \cdot molecules^{-1} \cdot s^{-1}$) and Experimental values for the $H_2O_2 + O_2$ formations from the $HO_2 + HO_2$ reaction (R1), the $HNO_3 + O_2$ formations from the $NO_3 + HO_2$ reaction (R2) and the HSO_3 formations from the SO_2 + OH reaction (R3) within the temperature range of 218.6 -325.0 K

T(K)	k_{R1}	k_{R2}	k_{R3}
218.6	1.38E-10	5.06E-10	2.06E-12
223.7	8.29E-11	2.55E-10	2.09E-12
225.0	--	--	(2.42E-12)
229.7	4.69E-11	1.22E-10	2.14E-12
235.1	2.88E-11	6.72E-11	2.20E-12
236.0	(1.04E-11)	--	--
249.9	8.50E-11	1.68E-11	2.32E-12
250.0	(7.26E-12)	--	(2.84E-12)
259.3	4.22E-11	8.20E-12	2.37E-12
263.0	--	(4.41E-12)	--
275.0	(4.21E-12)	(4.28E-12)	(3.24E-12)
280.0	1.08E-11	2.32E-12	2.53E-12
290.0	6.01E-12	1.42E-12	2.64E-12
298.2	3.85E-12	9.96E-13	2.70E-12
300.0	3.49E-12	9.23E-13	2.71E-12
300.0	(2.67E-12)	(4.07E-12)	(3.61E-12)
309.0	(2.31E-12)	--	--
310.0	2.11E-12	6.29E-13	2.79E-12
320.0	1.32E-12	4.46E-13	2.90E-12
325.0	--	(3.89E-12)	(3.96E-12)

The values in parentheses are k_{R1}, k_{R2} and k_{R3} experimental values. k_{R1} is the rate constant for the process of $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$. k_{R2} is the rate constant for the process of $HO_2 + NO_3 \rightarrow HNO_3 + O_2$. k_{R3} is the rate constant for the process of $SO_2 + OH \rightarrow HSO_3$.