A computational study of the $HO_2 + SO_3 \rightarrow HOSO_2 + {}^3O_2$

reaction catalyzed by water monomer, water dimer and small

clusters of sulfuric acid: kinetics and atmospheric implications

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S. NO	Caption
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S2	Table S1 The energy barriers (ΔE) and unsigned error (UE) (kcal·mol ⁻¹) for the HO ₂ + SO ₃ \rightarrow HOSO ₂ + ³ O ₂ reaction at different theoretical methods with zero-point energy (ZPE) correction
S3	Fig. S2 Optimized geometries and binding energies of the reactant complexes $HO_2 \cdots X$ ($X = H_2O$, $(H_2O)_2$, H_2SO_4 , $H_2SO_4 \cdots H_2O$ and $(H_2SO_4)_2$) and $SO_3 \cdots X$ at the CCSD(T)/aug-cc-pVTZ//M06-2X/6-311+G(2 <i>df</i> ,2 <i>pd</i>) level of theory
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\$9-\$10	$SO_3 \cdots (H_2O)_2$, $c-HO_2 \cdots H_2SO_4$, $c-SO_3 \cdots H_2SO_4$, $t-HO_2 \cdots H_2SO_4$, $t-SO_3 \cdots H_2SO_4$, $c-SO_3 \cdots H_2SO_4$, $c-SO_$
	$H_2SO_4\cdots H_2O, c-HO_2\cdots H_2SO_4\cdots H_2O, c-SO_3\cdots H_2SO_4\cdots H_2O, t-H_2SO_4\cdots H_2O, t$

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	$HO_2 \cdots H_2 SO_4 \cdots H_2 O$, $t-SO_3 \cdots H_2 SO_4 \cdots H_2 O$, $(H_2 SO_4)_2$, $HO_2 \cdots (H_2 SO_4)_2$ and									
	SO_3 ···(H ₂ SO ₄) ₂ within the temperature range of 280-320 K									
S 11	Table S3 Zero point energy (ZPE/(kcal·mol ⁻¹)), entropies (S/(cal·mol ⁻¹ ·K ⁻¹)), relative									
S11- S12	energies (ΔE and $\Delta (E + ZPE)/(\text{kcal·mol}^{-1})$), enthalpies ($\Delta H(298)/(\text{kcal·mol}^{-1})$) and									
512	free energies ($\Delta G(298)/(\text{kcal·mol}^{-1})$) for the HO ₂ + SO ₃ reaction without and w									
	catalyst $X (X = H_2O, (H_2O)_2, H_2SO_4, H_2SO_4 \dots H_2O \text{ and } (H_2SO_4)_2)$									
C12	Fig. S8 Hindrance potentials for HO ₂ SO ₃ , HOSO ₄ and HOSO ₂ calculated at the									
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C1 4	Part A Hindered internal rotation analysis for the HO ₂ + SO ₃ reaction without									
514	and with $X (X = H_2O, (H_2O)_2, H_2SO_4, H_2SO_4 \dots H_2O$ and $(H_2SO_4)_2)$									
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515	$HO_2 \cdots SO_3 \cdots X \rightarrow HO_2 \cdots X + SO_3$, path 3) yielding from $HO_2 \cdots SO_3 \cdots X$ adduct within									
	the pressure range of 10-300 Torr (at 298 K)									
	Part B Bimolecular rate constants (cm ³ ·molecules ⁻¹ ·s ⁻¹) for the SO ₃ + HO ₂ ···X									
S16	$(X = H_2O, (H_2O)_2, H_2SO_4, H_2SO_4 \cdots H_2O \text{ and } (H_2SO_4)_2) \text{ and } HO_2 + SO_3 \cdots X$									
	reaction									
	reactionTable S6 Bimolecular rate constants (cm^3 ·molecules ⁻¹ ·s ⁻¹) for the HO ₂ + SO ₃ ····X (X)									
S17	reactionTable S6 Bimolecular rate constants (cm^3 ·molecules ⁻¹ ·s ⁻¹) for the HO ₂ + SO ₃ ···X (X= H ₂ O, (H ₂ O) ₂ , H ₂ SO ₄ , H ₂ SO ₄ ···H ₂ O and (H ₂ SO ₄) ₂) reaction calculated by master									
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S17 S18 S19 S20 S21- S25	reactionTable S6 Bimolecular rate constants (cm ³ ·molecules ⁻¹ ·s ⁻¹) for the HO ₂ + SO ₃ ···X (X= H ₂ O, (H ₂ O) ₂ , H ₂ SO ₄ , H ₂ SO ₄ ····H ₂ O and (H ₂ SO ₄) ₂) reaction calculated by masterequation within the temperature range of 280-320 K (at 760 Torr)Table S7 The calculated rate constants (cm ³ ·molecules ⁻¹ ·s ⁻¹) for the HO ₂ + SO ₃ reaction without and with H ₂ O, (H ₂ O) ₂ and H ₂ SO ₄ within the temperature range of280-320 K and the pressure range of 10-760 TorrTable S8 Effective rate constants (k') for the HO ₂ + SO ₃ reaction with X (X = H ₂ O,(H ₂ O) ₂ , H ₂ SO ₄ , H ₂ SO ₄ ····H ₂ O and (H ₂ SO ₄) ₂) within the temperature range of 280-320 K (at 0 km altitude)Table S9 Equilibrium constants (K _{eq} , cm ³ ·molecules ⁻¹) for the formation ofHO ₂ ····(H ₂ O) ₂ , c-HO ₂ ····H ₂ SO ₄ and c-HO ₂ ····H ₂ SO ₄ ····H ₂ O, and rateconcentrations (molecules·cm ⁻³) of H ₂ O, (H ₂ O) ₂ , H ₂ SO ₄ and H ₂ SO ₄ ····H ₂ O, and rateconstants (cm ³ ·molecules ⁻¹ ·s ⁻¹) of the HO ₂ + SO ₃ reaction with H ₂ O, (H ₂ O) ₂ , H ₂ SO ₄ and H ₂ SO ₄ ····H ₂ O at different altitudes in troposphereTable S10 Coordinates stationary points for the HO ₂ + SO ₃ reaction without and withX (X = H ₂ O, (H ₂ O) ₂ , H ₂ SO ₄ , H ₂ SO ₄ ····H ₂ O and (H ₂ SO ₄) ₂) at the M06-2X/6-									



Fig. S1 The optimized geometries for the species involved in the $HO_2 + SO_3$ reaction at several different levels of theory

^{a, b, c and d} respectively represent the values obtained at the M06-2X/6-311+G(2df,2pd), M06-2X/aug-cc-pVTZ, M06-2X/aug-cc-pV(T+d)Z and M06-2X/6-311++G(2df,2pd) level of theory. (The values in parentheses were the experimental values; bond length is in angstrom and angle is in degree.)

In order to check whether the geometric parameters of the reactants, pre-reactive complexes, transition states and products for the $HO_2 + SO_3$ reaction can give good and reliable results at the M06-2X/6-311+G(2df,2pd) level, we have re-optimized all equilibrium structures at the M06-2X/aug-cc-pVTZ and M06-2X/aug-cc-pV(T+d)Z levels. As shown in Fig. S1, for the calculated geometrical parameters of the above species, the mean absolute deviation of calculated bond distances and bond angles between the M06-2X/6-311+G(2df,2pd) level and the M06-2X/aug-ccpVTZ level were 0.005 Å and 0.1°, respectively. Meanwhile, when comparing the M06-2X/6-311+G(2df,2pd) and M06-2X/aug-cc-pV(T+d)Z levels, it was found that the calculated the mean absolute deviation of calculated bond distances and bond angles were found to be 0.006 Å and 0.23°. Therefore, the bond lengths and angles for the reactants, pre-reactive complexes, transition states and products at the M06-2X/6-311+G(2df,2pd) level are close to those from the M06-2X/aug-ccpVTZ and M06-2X/aug-cc-pV(T+d)Z method. In addition, the calculated bond distances and bond angles for the M06-2X/6-311+G(2df,2pd) level agree well with the corresponding experimental values (From the NIST chemistry webbook, http://webbook.nist.gov/chemistry.). Therefore, due to its efficiency, the M06-2X/6-311+G(2df,2pd) was adopted to optimize the geometries of all stationary points for the $HO_2 + SO_3$ reactions.

Methods	$\Delta E^{ m a}$	ΔE^{b}	ΔE^{c}	UE
W3X-L//M06-2X/6-311+G(2df,2pd)	-10.6	-9.7	-14.4	0.00
W2X//M06-2X/6-311+G(2 <i>df</i> ,2 <i>pd</i>)	-10.7	-10.0	-14.8	0.38
CCSD(T)/aug-cc-pVTZ//M06-2X/6-311+G(2df,2pd)	-10.5(-10.48) ^d	-9.8(-9.68) ^d	-14.2(-13.81) ^d	0.13
CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G(2 <i>df</i> ,2 <i>pd</i>)	-10.5(-10.48) ^d	-9.8(-9.68) ^d	-14.2(-13.81) ^d	0.13
CCSD(T)/aug-cc-pVTZ//M06-2X//aug-cc-pVTZ	-10.4	-9.8	-14.1	0.20
CCSD(T)/aug-cc-pV(T+d)Z//M06-2X//aug-cc- pV(T+d)Z	10.8	10.1	14.8	0.33
DLPNO-CCSD(T)-F12/cc-pVDZ-F12//M06-2X/6- 311+G(2df,2pd)	-10.6	-9.9	-14.8	0.20
CCSD(T)-F12a/cc-pVDZ-F12//M06-2X/6- 311+G(2df,2pd)	-11.7	-11.0	-15.8	1.27
CCSD(T)/cc-pVTZ//M06-2X/6-311+G(2 <i>df</i> ,2 <i>pd</i>)	-9.4(-9.44) ^d	-8.9(-8.67) ^d	-12.4(-12.64) ^d	1.33
CCSD(T)/aug-cc-pVDZ//M06-2X/6-311+G(2df,2pd)	-9.1	-7.3	-11.7	2.17
CCSD(T)/cc-pVDZ//M06-2X/6-311+G(2df,2pd)	-7.5	-5.4	-7.1	4.9

Table S1 The energy barriers (ΔE) and unsigned error (UE) (kcal·mol⁻¹) for the HO₂ + SO₃ \rightarrow HOSO₂ + ³O₂ reaction at different theoretical methods with zero-point energy (ZPE) correction

^{a, b} and ^c respectively denote the species of pre-reactive complexes, transition states and post-reactive complexes involved in $HO_2 + SO_3$ reaction. ^d The value taken from reference 1.

To further confirm the reliability of the M06-2X/6-311+G(2df,2pd) method, the CCSD(T)/augcc-pVTZ single point energies based on the M06-2X/6-311+G(2df,2pd) optimized geometries were redefined. As presented in Table S1, the relative energy of pre-reactive complexes, transition states and products to the reactants at the CCSD(T)/aug-cc-pVTZ//M06-2X/6-311+G(2df,2pd) level was respectively -10.5 kcal·mol⁻¹, -9.8 kcal·mol⁻¹ and -14.2 kcal·mol⁻¹, which were consistent with the corresponding predicted values at the CCSD(T)/aug-cc-pVTZ//M06-2X//aug-cc-pVTZ level. Similarly, the energies difference at the CCSD(T)/aug-cc-pVTZ//M06-2X//aug-cc-pVTZ, CCSD(T)/aug-cc-pVTZ//M06-2X/6-311+G(2df,2pd) and CCSD(T)/aug-cc-pV(T+d)Z//M06-2X// aug-cc-pV(T+d)Z levels compared to the relative energies calculated at the W3X-L//M06-2X/6-311+G(2df,2pd) level, were less than 0.33 kcal·mol⁻¹. This suggests that the relative energies obtained at the CCSD(T)/aug-cc-pVTZ//M06-2X/6-311+G(2df,2pd) level are also reasonable. Considering the computational accuracy and cost, the CCSD(T)/aug-cc-pVTZ//M06-2X/6-311+G(2df,2pd) method was chosen to calculate the single point energies of all species for the HO₂ + SO₃ reactions.



Fig. S2 Optimized geometries and binding energies of the reactant complexes $HO_2 \cdots X$ ($X = H_2O$, $(H_2O)_2$, H_2SO_4 , $H_2SO_4 \cdots H_2O$ and $(H_2SO_4)_2$) and $SO_3 \cdots X$ at the CCSD(T)/aug-cc-pVTZ//M06-2X/6-311+G(2*df*,2*pd*) level of theory (bond distance in Angstroms and angles in degrees)



Fig. S3 The optimized geometries and electric energies (in Hartree-Fock) of $HO_2\cdots SO_3\cdots H_2SO_4$ at the M06-2X/6-311+G(2df,2pd) level of theory (Bond distances in
Angstroms and angles in degrees)



Fig. S4 The optimized geometries and electric energies (in Hartree-Fock) of $HO_2\cdots SO_3\cdots H_2SO_4\cdots H_2O$ at the M06-2X/6-311+G(2df,2pd) level of theory (Bond
distances in Angstroms and angles in degrees)



Fig. S5 The optimized geometries and electric energies (in Hartree-Fock) of $HO_2 \cdots SO_3 \cdots (H_2SO_4)_2$ at the M06-2X/6-311+G(2df,2pd) level of theory (Bond distances in Angstroms and angles in degrees)



Fig. S6 The results of IRC calculations for all the transition states involved in the $HO_2 + SO_3$ reactions without and with catalyst X ($X = H_2O$, (H_2O)₂, H_2SO_4 , H_2SO_4 , H_2SO_4 , H_2SO_4 , H_2SO_4)₂)



Fig. S7 Potential energy surface for the unfavorable routes in the $HO_2 + SO_3$ reaction with H_2O at the CCSD(T)/aug-cc-pVTZ//M06-2X/6-311+G(2*df*,2*pd*) level of theory

<i>T</i> /K	K _{eq1A}	[HO ₂ …H ₂ O]	K _{eq1B}	[SO ₃ …H ₂ O]	K _{eq1C}	[H ₂ O…HO ₂]
280	1.53 × 10 ⁻²⁰	$1.18 imes 10^6$	1.73 × 10 ⁻²⁰	4.46	1.88 × 10 ⁻²³	1.45×10^{3}
290	9.42 × 10 ⁻²¹	$1.35 imes 10^6$	1.07×10^{-20}	5.12	1.68 × 10 ⁻²³	2.41×10^{3}
298	6.55 × 10 ⁻²¹	1.52×10^{6}	7.50×10^{-21}	5.80	1.54 × 10 ⁻²³	3.58×10^3
300	6.00 × 10 ⁻²¹	$1.55 imes 10^6$	6.88 × 10 ⁻²¹	5.90	1.51 × 10 ⁻²³	3.90×10^{3}
310	3.94 × 10 ⁻²¹	$1.73 imes 10^{6}$	4.55 × 10 ⁻²¹	6.65	1.38 × 10 ⁻²³	6.03×10^{3}
320	2.66 × 10 ⁻²¹	$1.87 imes 10^6$	$3.10 imes 10^{-21}$	7.28	1.26×10^{-23}	$8.89 imes 10^3$
<i>T</i> /K	K _{eq2A}	$[HO_2 \cdots (H_2O)_2]$	K _{eq2B}	$[SO_3 \cdots (H_2O)_2]$	K _{eq3A}	$[c-HO_2\cdots H_2SO_4]$
280	3.45×10^{-18}	2.11×10^{5}	1.10×10^{-17}	2.25	8.24 × 10 ⁻¹⁸	9.64 × 10 ⁻¹
290	1.47×10^{-18}	2.60×10^{5}	4.80×10^{-18}	2.83	3.90 × 10 ⁻¹⁸	4.45×10^{-1}
298	7.72 × 10 ⁻¹⁹	3.15×10^5	2.57 × 10 ⁻¹⁸	3.49	2.23 × 10 ⁻¹⁸	2.47×10^{-1}
300	6.61 × 10 ⁻¹⁹	3.21×10^{5}	2.21 × 10 ⁻¹⁸	3.58	1.95×10^{-18}	2.10×10^{-1}
310	3.14 × 10 ⁻¹⁹	3.82×10^5	1.07×10^{-18}	4.35	1.02×10^{-18}	1.07×10^{-1}
320	1.56×10^{-19}	4.32×10^5	5.44 × 10 ⁻¹⁹	5.03	4.55×10^{-19}	4.64 × 10 ⁻²
<i>T</i> /K	K _{eq3B}	$[c-SO_3\cdots H_2SO_4]$	K _{eq4A}	$[t-HO_2\cdots H_2SO_4]$	K _{eq4B}	$[t-SO_3\cdots H_2SO_4]$
280	1.09 × 10 ⁻¹⁸	4.25×10^{-7}	2.85 × 10 ⁻¹⁶	3.33×10^{1}	3.09 × 10 ⁻¹⁹	1.21 × 10 ⁻⁷
290	5.13 × 10 ⁻¹⁹	1.95×10^{-7}	1.19 × 10 ⁻¹⁶	1.36×10^{1}	1.62 × 10 ⁻¹⁹	6.17×10^{-8}
298	2.91 × 10 ⁻¹⁹	1.08×10^{-7}	$6.20 imes 10^{-17}$	6.89	$1.00 imes 10^{-19}$	3.71×10^{-8}
300	2.54 × 10 ⁻¹⁹	9.15 × 10 ⁻⁸	5.30 × 10 ⁻¹⁷	5.72	8.92×10^{-20}	3.21 × 10 ⁻⁸
310	$1.32 imes 10^{-19}$	4.62×10^{-8}	2.49×10^{-17}	2.61	5.11 × 10 ⁻²⁰	1.79×10^{-8}
320	7.16×10^{-20}	2.43×10^{-8}	1.22×10^{-17}	1.25	3.04×10^{-20}	1.03×10^{-8}
T/K	K _{eq(c-SW)}	$[c-H_2SO_4\cdots H_2O]$	K _{eq5A}	$[c-HO_2\cdots H_2SO_4$ $\cdots H_2O]$	K_{eq5B}	$\begin{matrix} [c\text{-}\mathrm{SO}_3\cdots\mathrm{H}_2\mathrm{SO}_4\\\cdots\mathrm{H}_2\mathrm{O}] \end{matrix}$
280	2.03 × 10 ⁻¹⁹	2.04×10^7	3.02 × 10 ⁻¹⁶	1.85	5.30 × 10 ⁻¹⁹	1.08×10^{-8}
290	$1.20 imes 10^{-19}$	2.18×10^7	$1.30 imes 10^{-16}$	8.53×10^{-1}	2.44×10^{-19}	5.33 × 10 ⁻⁹
298	8.10 × 10 ⁻²⁰	2.31×10^7 $(2.40 \times 10^7)^{b}$	6.94×10^{-17}	4.80×10^{-1}	1.37 × 10 ⁻¹⁹	3.16 × 10 ⁻⁹
300	$7.36 imes 10^{-20}$	2.27×10^{7}	5.96 × 10 ⁻¹⁷	4.07×10^{-1}	1.19 × 10 ⁻¹⁹	2.71 × 10 ⁻⁹
310	4.67×10^{-20}	2.39×10^7	2.87×10^{-17}	2.05×10^{-1}	6.08×10^{-20}	1.45×10^{-9}
320	$3.05 imes 10^{-20}$	2.44×10^{7}	1.45×10^{-17}	1.06×10^{-1}	3.24×10^{-20}	7.91×10^{-10}
T/K	K _{eq(t-SW)}	$[t-H_2SO_4\cdots H_2O]$	K _{eq6A}	$\begin{bmatrix} t-HO_2\cdots H_2SO_4\\\cdots H_2O\end{bmatrix}$	K _{eq6B}	$\begin{bmatrix} t-SO_3\cdots H_2SO_4\\\cdots H_2O\end{bmatrix}$
280	$4.05 imes 10^{-19}$	4.08×10^7	$2.20 imes 10^{-15}$	2.69×10^{1}	$1.68 imes 10^{-18}$	3.43 × 10 ⁻⁸
290	2.24×10^{-19}	4.07×10^7	9.24 ×10 ⁻¹⁶	1.13×10^{1}	$8.58 imes 10^{-19}$	1.87×10^{-8}
298	1.44×10^{-19}	4.09×10^{7}	4.82 ×10 ⁻¹⁶	5.92	5.18 × 10 ⁻¹⁹	1.20×10^{-8}
300	$1.29 imes 10^{-19}$	3.99×10^7	4.12×10^{-16}	4.93	$4.59\times10^{\text{-19}}$	1.04×10^{-8}
310	7.71×10^{-20}	3.94×10^7	$1.94 imes 10^{-16}$	2.29	2.56×10^{-19}	6.11 × 10 ⁻⁹
320	4.77×10^{-20}	3.81 ×10 ⁷	9.58 × 10 ⁻¹⁷	1.10	1.49 × 10 ⁻¹⁹	3.63 × 10 ⁻⁹

<i>T</i> /K	K _{eq(SD)}	$[(\mathrm{H}_2\mathrm{SO}_4)_2]$	K _{eq7A}	$[\mathrm{HO}_2 \cdots (\mathrm{H}_2 \mathrm{SO}_4)_2]$	K _{eq7B}	$[\mathrm{SO}_3 \cdots (\mathrm{H}_2 \mathrm{SO}_4)_2]$
280	$4.88\times10^{\text{-}17}$	7.42	1.03×10^{-16}	2.29×10^{-7}	$1.55 imes 10^{-17}$	1.15×10^{-13}
290	1.84×10^{-17}	2.65	4.36×10^{-17}	3.46×10^{-8}	$6.96 imes 10^{-18}$	1.84×10^{-14}
298	$8.82 imes 10^{-18}$	1.21	$2.29 imes 10^{-17}$	8.31×10^{-9}	$3.83 imes 10^{-18}$	4.63×10^{-15}
300	$7.38 imes 10^{-18}$	1.01	1.96×10^{-17}	5.94×10^{-9}	$3.31 imes 10^{-18}$	3.35×10^{-15}
310	3.15×10^{-18}	4.09×10^{-1}	9.30 × 10 ⁻¹⁸	1.14 × 10 ⁻⁹	1.66×10^{-18}	6.78×10^{-16}
320	1.42×10^{-18}	1.64×10^{-1}	4.63 × 10 ⁻¹⁸	2.28×10^{-10}	8.69 × 10 ⁻¹⁹	1.42×10^{-16}

^a K_{eq1A} , K_{eq1B} and K_{eq1C} represented the equilibrium constant of HO₂···H₂O, SO₃···H₂O and H₂O···HO₂; K_{eq2A} and K_{eq2B} denoted the equilibrium constant of HO₂···(H₂O)₂ and SO₃···(H₂O)₂; K_{eq3A} and K_{eq3B} represented the equilibrium constant of c-HO₂···H₂SO₄ and c-SO₃···H₂SO₄; K_{eq4A} and K_{eq4B} denoted the equilibrium constant of t-HO₂···H₂SO₄; K_{eq4A} and K_{eq4B} denoted the equilibrium constant of t-HO₂····H₂SO₄; $K_{eq(c-SW)}$, K_{eq5A} and K_{eq5B} denoted the equilibrium constant of c-H₂SO₄···H₂O, c-HO₂····H₂SO₄····H₂O and c-SO₃····H₂SO₄····H₂O; $K_{eq(c-SW)}$, K_{eq6A} and K_{eq6B} represented the equilibrium constant of t-H₂SO₄····H₂O, t-HO₂····H₂SO₄····H₂O and t-SO₃····H₂SO₄····H₂O; $K_{eq(r-SW)}$, K_{eq6A} and K_{eq6B} represented the equilibrium constant of t-H₂SO₄····H₂O, t-HO₂····H₂SO₄····H₂O and t-SO₃·····H₂O₄····H₂O; $K_{eq(r-SW)}$, K_{eq6A} and K_{eq7B} denoted the equilibrium constant of t-H₂SO₄····H₂O, t-HO₂····H₂SO₄····H₂O and t-SO₃····H₂SO₄····H₂O; $K_{eq(r-SD)}$, K_{eq7A} and K_{eq7B} denoted the equilibrium constant of (H₂SO₄)₂, HO₂····(H₂SO₄)₂ and SO₃···(H₂SO₄)₂.

^b The concentrations of HO₂···H₂O, SO₃···H₂O and H₂O···HO₂ were respectively expressed as $[HO_2^{...}H_2O] = K_{eq1A} \times [H_2O] \times [HO_2]$, $[SO_3^{...}H_2O] = K_{eq1B} \times [H_2O] \times [SO_3]$ and $[H_2O^{...}HO_2] = K_{eq1C} \times [H_2O] \times [HO_2]$; the concentrations of HO₂···(H₂O)₂ and SO₃···(H₂O)₂ were respectively expressed as $[HO_2^{...}(H_2O)_2] = K_{eq2A} \times [(H_2O)_2] \times [HO_2]$ and $[SO_3^{...}(H_2O)_2] = K_{eq2B} \times [(H_2O)_2] \times [SO_3]$; the concentrations of *c*-HO₂····H₂SO₄ and *c*-SO₃····H₂SO₄ were respectively expressed as $[c-HO_2^{...}H_2SO_4] = K_{eq3A} \times [H_2SO_4] \times [HO_2]$ and $[c-SO_3^{...}H_2SO_4] = K_{eq3B} \times [H_2SO_4] \times [SO_3]$; the concentrations of *t*-HO₂····H₂SO₄ and *t*-SO₃····H₂SO₄ and *t*-SO₃····H₂SO₄ and *t*-SO₃····H₂SO₄ and *t*-SO₃····H₂SO₄ and *t*-SO₃····H₂SO₄ are respectively expressed as $[t-HO_2^{...}H_2SO_4] = K_{eq3A} \times [H_2SO_4] \times [HO_2]$ and $[t-SO_3^{...}H_2SO_4] = K_{eq3B} \times [H_2SO_4] \times [HO_2]$ and $[t-SO_3^{...}H_2SO_4] = K_{eq4A} \times [H_2SO_4] \times [HO_2]$ and $[t-SO_3^{...}H_2SO_4] = K_{eq4A} \times [H_2SO_4] \times [H_2O_3] \times [HO_2]$ and $[t-SO_3^{...}H_2SO_4] = K_{eq4A} \times [SO_3]$; the concentrations of *c*-H₂SO₄····H₂O and *c*-SO₃····H₂O were respectively expressed as $[t-H_2SO_4^{...}H_2O] = K_{eq(c-SW)} \times [H_2SO_4] \times [H_2O]$, $[c-HO_2^{...}H_2SO_4^{...}H_2O]$ and $[t-SO_3^{...}H_2SO_4^{...}H_2O] = K_{eq(c-SW)} \times [H_2SO_4] \times [H_2O]$, $[c-HO_2^{...}H_2SO_4^{...}H_2O] = K_{eq6A} \times [H_2SO_4^{...}H_2O] \times [HO_2]$ and $[c-SO_3^{...}H_2SO_4^{...}H_2O] = K_{eq6B} \times [H_2SO_4^{...}H_2O] = K_{eq(t-SW)} \times [H_2SO_4] \times [H_2SO_4] \times [H_2SO_4^{...}H_2O] = K_{eq(t-SW)} \times [H_2SO_4] \times [H_2SO_4] \times [H_2SO_4^{...}H_2O] = K_{eq(t-SW)} \times [H_2SO_4] \times [H_2SO_4] \times [H_2O_4] = K_{eq(t-SW)} \times [H_2SO_4] \times [H_2SO_4] \times [H_2O_4] = K_{eq(t-SW)} \times [H_$

^c The typical tropospheric concentrations ^{2,3} of $2.60 \times 10^{17} - 2.30 \times 10^{18}$ molecules cm⁻³ for H₂O, $2.04 \times 10^{14} - 9.24 \times 10^{15}$ molecules cm⁻³ for (H₂O)₂ and 5.0×10^7 molecules cm⁻³ of H₂SO₄ were respectively taken from reference. Besides, the concentrations of H₂SO₄…H₂O and (H₂SO₄)₂ were respectively calculated to be $2.04 \times 10^7 - 2.44 \times 10^7$ molecules cm⁻³ and $7.42 \times 10^9 - 1.64 \times 10^{-1}$ molecules cm⁻³.

As for HO₂… $X(X = H_2O, (H_2O)_2, H_2SO_4, H_2SO_4 \dots H_2O$ and $(H_2SO_4)_2)$ and SO₃…X complexes, their corresponding equilibrium constants and concentrations within the temperature range of 280-320 K have been listed in Table S2. However, due to the concentration ^{1,4} of SO₃ (1.0 × 10³ molecules cm⁻³) is much lower than that of HO₂ (3.0 × 10⁸ molecules cm⁻³), the concentrations of HO₂…X complexes shown in Table S2 are larger than those of SO₃…X complexes. Thus, we predict that the HO₂ + SO₃ rection in the presence of X mainly occurs through the HO₂…X + SO₃ reaction.

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 the HO₂ + SO₃ reaction without and with catalyst $X (X = H_2O, (H_2O)_2, H_2SO_4, H_2SO_4, H_2SO_4, \dots H_2SO_4)$

Species	ZPE	ΔE	S	ΔG	$\Delta(E + \text{ZPE})$	ΔH	T_1
$HO_2 + SO_3$	16.3	0.0	115.8	0.0	0.0	0.0	0.0256; 0.0177
IM	18.6	-12.9	79.6	-9.8	-10.5	-11.2	0.0231
TS	16.5	-10.0	75.8	-8.6	-9.8	-11.1	0.0197
HOSO ₄	18.6	-16.5	78.1	-13.1	-14.2	-15.0	0.0227
$HOSO_2 + {}^3O_2$	15.9	-2.6	48.9	12.8	-3.0	-2.9	0.0204, 0.0168
$HO_2 + H_2O + SO_3$	29.2	0.0	160.8	0.0	0.0	0.0	0.0256, 0.0106, 0.0177
$HO_2 \cdots H_2O + SO_3$	31.6	-9.2	132.3	1.0	-6.8	-7.5	0.0239, 0.0177
SO_3 ···H ₂ O + HO ₂	31.5	-9.4	132.5	1.9	-7.2	-7.6	0.0163, 0.0256
IM_WM1	33.6	-23.9	90.2	0.2	-19.5	-20.9	0.0226
TS_WM1	32.6	-22.0	84.6	1.9	-18.5	-20.8	0.0245
IMF_WM1	33.7	-30.8	90.2	-6.7	-26.3	-27.8	0.0224
$\mathrm{HOSO}_4 + \mathrm{H}_2\mathrm{O}$	31.5	-16.5	123.1	-3.7	-14.2	-15.0	0.0227, 0.0106
$HO_2 + H_2O + SO_3$	29.2	0.0	160.8	0.0	0.0	0.0	0.0256, 0.0106, 0.0177
H_2O ··· $HO_2 + SO_3$	30.7	-3.3	142.6	4.3	-1.8	-1.8	0.0235, 0.0177
IM_WM2	32.3	-13.9	104.3	5.9	-10.7	-11.0	0.0222
TS_WM2	30.8	-3.4	92.4	16.7	-1.8	-3.7	0.0242
IMF_WM2	32.8	-18.7	101.3	2.1	-15.1	-15.7	0.0222
$\mathrm{HOSO}_4 + \mathrm{H}_2\mathrm{O}$	31.5	-16.5	123.2	-3.8	-14.2	-15.0	0.0227, 0.0106
$HO_2 + H_2O + SO_3$	29.2	0.0	160.8	0.0	0.0	29.2	0.0256, 0.0106, 0.0177
SO_3 ···H ₂ O + HO ₂	31.5	-9.4	132.5	0.9	-7.0	31.5	0.0163, 0.0177
IM_WM3	32.8	-18.9	98.1	2.9	-15.2	32.8	0.0222
TS_WM3	30.7	-14.5	93.4	5.9	-12.9	30.7	0.0186
IMF_WM3	33.6	-29.4	91.9	-5.8	-25.0	33.6	0.0215
$HOSO_4 + H_2O$	31.5	-16.5	123.2	-3.8	-14.2	31.5	0.0227, 0.0106
$\mathrm{HO}_2 + (\mathrm{H}_2\mathrm{O})_2 + \mathrm{SO}_3$	45.5	0.0	187.7	0.0	0.0	0.0	0.0256, 0.0123, 0.0177
HO_2 ···($H_2O)_2 + SO_3$	48.8	-15.9	147.1	-1.9	-12.6	-14.0	0.0240, 0.0256
SO_3 ···(H ₂ O) ₂ + HO ₂	48.4	-16.5	146.6	-2.3	-13.6	-14.6	0.0233, 0.0177
IM_WD1	49.4	-28.6	108.0	-2.5	-24.6	-26.2	0.0224
TS_WD1	48.3	-27.9	91.5	-1.9	-25.2	-27.5	0.0240
IMF_WD1	50.3	-35.0	106.9	-7.5	-30.2	-32.2	0.0212
$HOSO_4 + (H_2O)_2$	31.5	-16.5	123.2	-3.8	-14.2	31.5	0.0227, 0.0123
$HO_2 + c-H_2SO_4 + SO_3$	40.0	0.0	188.2	0.0	0.0	0.0	0.0256, 0.0161, 0.0177
c-HO ₂ ····H ₂ SO ₄ + SO ₃	41.8	-15.1	152.1	-3.1	-13.4	-13.9	0.0225, 0.0177

c- SO ₃ ····H ₂ SO ₄ + HO ₂	41.5	-13.6	148.5	-0.8	-12.2	-12.6	0.0169, 0.0256
c-IM_SA1	42.6	-26.4	109.0	-1.2	-23.8	-24.8	0.0175
c-TS_SA1	41.5	-24.9	105.2	-0.4	-23.5	-25.1	0.0205
c-IMF_SA1	43.3	-32.8	108.1	-6.7	-29.5	-30.6	0.0219
$HOSO_4 + c-H_2SO_4$	42.4	-16.5	150.6	-3.8	-14.2	-15.0	0.0227, 0.0161
$\mathrm{HO}_2 + t - \mathrm{H}_2 \mathrm{SO}_4 + \mathrm{SO}_3$	40.3	0.0	189.5	0.0	0.0	0.0	0.0256, 0.0162, 0.0177
t-HO ₂ ····H ₂ SO ₄ + SO ₃	41.7	-15.5	153.9	-3.9	-14.1	-14.5	0.0225, 0.0177
t-SO ₃ ····H ₂ SO ₄ + HO ₂	41.3	-12.1	154.6	-0.4	-11.1	-10.8	0.0169, 0.0256
t-IM_SA1	42.8	-23.8	111.1	1.5	-21.3	-21.9	0.0198
t-TS_SA1	40.2	-18.3	106.6	4.9	-18.4	-19.8	0.0207
t-IMF_SA1	42.8	-27.1	111.8	-7.1	-24.6	-30.3	0.0222
$HOSO_4 + t-H_2SO_4$	42.4	-16.5	149.7	-3.8	-14.2	-15.0	0.0227, 0.0162
$\frac{\mathrm{HO}_{2} + c \cdot \mathrm{H}_{2} \mathrm{SO}_{4} \cdots \mathrm{H}_{2} \mathrm{O}}{+ \mathrm{SO}_{3}}$	55.2	0.0	202.5	0.0	0.0	0.0	0.0256, 0.0148, 0.0177
$c-HO_2\cdots H_2SO_4\cdots H_2O$ + SO ₃	56.5	-15.0	166.6	-3.3	-13.6	-14.1	0.0213, 0.0177
$c-SO_3\cdots H_2SO_4\cdots H_2O + HO_2$	59.6	-17.0	156.8	-2.3	-12.5	-13.3	0.0162, 0.0256
c-IM_SW1	57.6	-28.0	119.8	-2.0	-25.6	-26.6	0.0192
c-TS_SW1	56.3	-26.5	117.6	-1.5	-25.3	-26.8	0.0174
c-IMF_SW1	57.8	-33.4	122.3	-7.9	-30.8	-31.8	0.0209
$ \begin{array}{c} HOSO_4 + c - \\ H_2SO_4 \cdots H_2O \end{array} $	57.5	-16.5	164.9	-3.8	-14.2	-15.0	0.0227, 0.0148
$\frac{\text{HO}_2 + t - \text{H}_2 \text{SO}_4 \cdots \text{H}_2 \text{O}}{+ \text{SO}_3}$	55.4	0.0	200.6	0.0	0.0	0.0	0.0256, 0.0153, 0.0177
t-HO ₂ ····H ₂ SO ₄ ····H ₂ O + SO ₃	56.5	-15.3	167.2	-4.5	-14.2	-14.4	0.0213; 0.0177
$t-SO_3\cdots H_2SO_4\cdots H_2O + HO_2$	55.8	-11.9	166.5	-1.1	-11.5	-11.3	0.0162, 0.0256
t-IM_SW1	57.3	-24.8	125.8	-1.2	-22.9	-23.5	0.0192
t-TS_SW1	54.9	-21.4	118.6	1.2	-21.8	-23.3	0.0174
t-IMF_SW1	57.4	-32.6	124.3	-8.7	-30.6	-31.4	0.0209
$\frac{\text{HOSO}_4 + t}{\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O}}$	57.7	-16.5	162.9	-3.8	-14.2	-15.0	0.0227, 0.0153
$\mathrm{HO}_{2} + (\mathrm{H}_{2}\mathrm{SO}_{4})_{2} + \mathrm{SO}_{3}$	65.1	0.0	224.0	0.0	0.0	0.0	0.0256, 0.0181, 0.0177
HO_2 ···(H_2SO_4) ₂ + SO_3	66.7	-15.7	184.0	-2.5	-14.0	-14.4	0.0218, 0.0177
SO_3 ···(H ₂ SO ₄) ₂ + HO ₂	57.2	-14.1	126.8	-0.8	-13.2	-13.4	0.0157, 0.0256
IM_SD1	67.7	-31.8	140.0	-5.0	-26.0	-30.0	0.0183
TS_SD1	65.8	-32.0	136.2	-6.4	-27.0	-32.7	0.0205
IMF_SD1	67.5	-36.3	139.5	-9.6	-31.3	-34.7	0.0215
$HOSO_4 + (H_2SO_4)_2$	67.4	-16.5	184.1	-3.8	-14.2	-15.0	0.0227, 0.0181



Fig. S8 Hindrance potentials for HO_2 ···SO₃, $HOSO_4$ and $HOSO_2$ calculated at the M06-2X/6-311+G(2*df*,2*pd*) level of theory

For hindered internal rotation (HIR) treatment, the hindrance potentials, $V(\theta)$, as a function of torsional angle, θ , along with the single bonds (i.e., S1-O4 and O4-O5, Fig. S8) were explicitly obtained at the M06-2X/6-311+G(2*df*,2*pd*) level via relaxed surface scans with the step size of 10° for the dihedral angles corresponding to the rotations. As seen in Fig. S8, the single bond of O4-O5 and S1-O4 in HO₂···SO₃, the single bond of S1-O4 in HOSO₄ and the single bond of S1-O4 in HOSO₂ need to treated by hindered internal rotators. The parameters of the HIR are automatically determined using the Graphical User Interface (GUI) in Mesmer software, and the procedural details of the hindered internal rotation (HIR) correction can be found in the works of Le et al.^{5,6} and Mai et

Part A Hindered internal rotation analysis for the $HO_2 + SO_3$ reaction without and with $X(X = H_2O, (H_2O)_2, H_2SO_4, H_2SO_4, \dots H_2O$ and $(H_2SO_4)_2)$

Within the temperature range of 280-320 K, the rate constants (k_{R1}) for the HO₂ + SO₃ reaction without and with HIR treatments at 760 Torr has been listed in Table S4. It should be noted that, at 760 Torr, the HIR correction just plays a minor role in the $HO_2 + SO_3$ reaction, e.g., HIR treatment listed in Table S4 enhanced the rate constants by a factor of 1.14 to 1.15 within the temperature range of 280-320 K. Besides, the hindered internal rotation analysis for the pre- and post-reactive complexes and transition states involved in the $HO_2 + SO_3$ reaction with X have been calculated in the Gaussian 09 program with the keywords of "freq = hindrot" and "integral = ultrafine". The calculations reveal that no frequencies need to be corrected. So, we predict that the HIR correction just plays a minor role in the $HO_2 + SO_3$ reaction with X. This can be explained by two reasons as follows. On the one hand, the pre- and post-reactive complexes and transition states involved in the $HO_2 + SO_3$ reaction with X were shown the quasi-planar ring structures and cage-like ring structures. As compared with the naked reaction (Fig. 3(a)), these ring structures reduce the ring tension obviously and increase the stability of the pre- and post-reactive complex and transition state greatly. On the other hand, the numbers of hydrogen bonds in X-assisted pre- and post-reactive complexes and transition states were increased, which hinder the rotation bonds of S-O4 and O4-O5 (Fig. 3-6) in X-assisted pre- and post-reactive complex and transition state. The detail information for the rate constants (k_{R1}) for the HO₂ + SO₃ reaction without and with HIR treatments has been displayed in Table S4.

with HIR treatments	without HIR treatments	Factor
2.11 × 10 ⁻¹¹	1.85×10^{-11}	1.14
1.95×10^{-11}	1.71×10^{-11}	1.14
1.83×10^{-11}	1.60×10^{-11}	1.14
1.80×10^{-11}	1.57×10^{-11}	1.14
1.66×10^{-11}	1.45×10^{-11}	1.15
1.53 × 10 ⁻¹¹	1.33 × 10 ⁻¹¹	1.15

Table S4 The rate constants (k_{R1}) for the HO₂ + SO₃ reaction without and with HIR treatments within the temperature range of 280-320 K (at 760 Torr)

Table S5 The calculated branching ratio (β)^a for the three pathways (HO₂···SO₃···X \rightarrow HOSO₂ + O₂ + X, path 1, HO₂···SO₃···X \rightarrow HO₂ + SO₃···X, path 2, and HO₂···SO₃···X \rightarrow HO₂···X + SO₃, path 3) yielding from HO₂···SO₃···X adduct within the pressure range of 10-300 Torr (at 298 K)

_					Bi	ranching Ratio	• (%) for HO ₂ •	\cdots SO ₃ \cdots X com	plex			
P (Torr)	HO ₂ ••	··SO ₃	HO ₂ ····S	O₃····H₂O	HO ₂ ···SO	3 ··· (H₂O)₂	HO ₂ ····SC	O ₃ ····H₂SO₄	HO ₂ ···SO ₃ ···	∙H ₂ SO ₄ •••H ₂ O	HO ₂ ···SO ₃	•••(H ₂ SO ₄) ₂
(1011)	β_1	$\beta_2 + \beta_3$	β_1	$\beta_2 + \beta_3$	β_1	$\beta_2 + \beta_3$	eta_1	$\beta_2 + \beta_3$	β_1	$\beta_2 + \beta_3$	β_1	$\beta_2 + \beta_3$
300	99.89%	0.11%	99.85%	0.15%	99.97%	0.03%	99.93%	0.07%	99.93%	0.07%	99.88%	0.12%
100	99.84%	0.16%	99.86%	0.14%	99.98%	0.02%	99.95%	0.05%	99.95%	0.05%	99.95%	0.05%
50	99.80%	0.20%	99.87%	0.13%	99.98%	0.02%	99.96%	0.04%	99.96%	0.04%	99.96%	0.04%
10	99.76%	0.24%	99.87%	0.13%	99.99%	0.01%	99.97%	0.03%	99.97%	0.03%	99.98%	0.02%

 $a\beta_1, \beta_2$ and β_3 were the branching ratio for the path 1, path 2 and path 3. The calculated β_1, β_2 and β_3 can be respectively expressed as $\beta_1 = k_{\text{path }1}/(k_{\text{path }1} + k_{\text{path }2} + k_{\text{path }3})$, $\beta_2 = k_{\text{path }2}/(k_{\text{path }1} + k_{\text{path }2} + k_{\text{path }3})$ and $\beta_3 = k_{\text{path }3}/(k_{\text{path }1} + k_{\text{path }2} + k_{\text{path }3})$.

The pressure dependent rate constant for the three pathways (HO₂···SO₃···X \rightarrow HOSO₂ + O₂ + X, path 1, HO₂···SO₃···X \rightarrow HO₂ + SO₃···X, path 2, and HO₂···SO₃···X \rightarrow HO₂···X + SO₃, path 3) yielding from HO₂···SO₃···X adduct as given below,

$$HO_2 \cdots SO_3 \cdots X \to HOSO_2 + O_2 + X$$
 (path 1)

$$\text{HO}_2 \cdots \text{SO}_3 \cdots X \to \text{HO}_2 + \text{SO}_3 \cdots X$$
 (path 2)

$$HO_2 \cdots SO_3 \cdots X \rightarrow HO_2 \cdots X + SO_3$$
 (path 3)

The pressure dependent rate constant at 298 K for the above-mentioned pathways were calculated within the pressure range of 10-300 Torr. Their corresponding branching ratios were given in Table S5. As can be seen from Table S5, one can easily conclude that path 1 was the major pathway, whereas paths 2 and 3 were the minor channels within the pressure range of 10-300 Torr. Since the branching ratios of path 1 were more than 99%, the paths 2 and 3 can be conveniently avoided for further discussion. The result and discussion will be based on the kinetics of path 1 only unless otherwise stated.

Part B Bimolecular rate constants (cm³·molecules⁻¹·s⁻¹) for the SO₃ + HO₂···X ($X = H_2O$, (H₂O)₂, H₂SO₄, H₂SO₄···H₂O and (H₂SO₄)₂) and HO₂ + SO₃···X reactions

As for the HO₂ + SO₃ + $X(X = H_2O, (H_2O)_2, H_2SO_4, H_2SO_4, \dots H_2O \text{ and } (H_2SO_4)_2)$ reaction, two entry channels HO₂...X + SO₃ (Channel A) and SO₃...X + HO₂ (Channel B) have been considered for the rate constants calculations as follows.

Channel A

Step 1A:
$$HO_2 + X \xleftarrow{k_{1A}} HO_2 \cdots X$$
 (S1)

Step 2A: HO₂ggX + SO₃
$$\ddagger \frac{k_{2A}}{k_{-2A}}$$
 products (S2)

Channel B

Step 1B:
$$SO_3 + X \xleftarrow{k_{\rm IB}} SO_3 \cdots X$$
 (S3)

Step 2B: SO₃ ggpX + HO₂
$$\ddagger \frac{k_{2B}}{k_{-2B}} \dagger$$
 products (S4)

As for the HO₂ + SO₃ + X reaction, two entry channels HO₂...X + SO₃ (Channel A) and SO₃...X + HO₂ (Channel B) have been respectively considered for the rate constants calculations involved in Table S6 and Table S7. Due to the fact that both of the HO₂...X + SO₃ and SO₃...X + HO₂ reactions proceed through the same pre-reactive trimolecular complex HO₂...SO₃...X, so the product of $K_{eq1A} \times k_{2A}$ is equal to the product of $K_{eq1B} \times k_{2B}$. Based on two facts above, the effective rate constant for the HO₂...X + SO₃ reaction was equal to the SO₃...X + HO₂ reaction. These results have been reported in our previous work ^{15,16}. The detail information of bimolecular rate constants (cm³·molecules⁻¹·s⁻¹) for the SO₃ + HO₂...X (X = H₂O, (H₂O)₂, H₂SO₄, H₂SO₄...H₂O and (H₂SO₄)₂) and HO₂ + SO₃...X reaction have been respectively listed in Table 1 and Table S6.

8	(-						
Reaction	<i>T</i> (K)	280	290	298	300	310	320
Channel WM1	k _{WM1_b}	1.61 × 10 ⁻¹¹	1.34 × 10 ⁻¹¹	1.16 × 10 ⁻¹¹	1.12 × 10 ⁻¹¹	9.25 × 10 ⁻¹²	7.65 × 10 ⁻¹²
Channel WD1	$k_{\rm WD1_b}$	1.15 × 10 ⁻¹¹	8.75 × 10 ⁻¹²	7.01 × 10 ⁻¹²	6.63 × 10 ⁻¹²	5.01 × 10 ⁻¹²	3.77×10^{-12}
Channel <i>c</i> -SA	k_{c-SA_b}	2.05×10^{-11}	1.57 × 10 ⁻¹¹	1.26 × 10 ⁻¹¹	1.20 × 10 ⁻¹¹	9.06 × 10 ⁻¹¹	6.84 × 10 ⁻¹¹
Channel <i>t</i> -SA	k_{t-SA_b}	1.77×10^{-13}	1.25 × 10 ⁻¹³	9.41 × 10 ⁻¹⁴	8.77×10^{-14}	6.18 × 10 ⁻¹⁴	4.37×10^{-14}
Channel <i>c</i> -SW	$k_{c\text{-}SW_b}$	6.06 × 10 ⁻¹¹	5.09 × 10 ⁻¹¹	4.38 × 10 ⁻¹¹	4.21 × 10 ⁻¹¹	3.45 × 10 ⁻¹¹	2.79×10^{-11}
Channel <i>t</i> -SW	k_{t-SW_b}	7.18×10^{-12}	5.61 × 10 ⁻¹²	4.60 × 10 ⁻¹²	4.37 × 10 ⁻¹²	3.39×10^{12}	2.62×10^{-12}
Channel SD	$k_{\rm SD_b}$	6.59 × 10 ⁻¹¹	5.40 × 10 ⁻¹¹	4.55 × 10 ⁻¹¹	4.35 × 10 ⁻¹¹	3.44 × 10 ⁻¹¹	2.68 × 10 ⁻¹¹

Table S6 Bimolecular rate constants (cm³·molecules⁻¹·s⁻¹) for the HO₂ + SO₃···X ($X = H_2O$, (H₂O)₂, H_2SO_4 , H_2SO_4 ... H_2O and $(H_2SO_4)_2$) reaction calculated by master equation within the temperature range of 280-320 K (at 760 Torr) ^a

 $k_{WM1_b}, k_{WD1_b}, k_{c-SA_b}, k_{t-SA_b}, k_{c-SW_b}, k_{t-SW_b}$ and k_{SD_b} was respectively denoted the rate constants for the HO₂ + SO₃···H₂O, HO₂ $+ SO_{3} \cdots (H_{2}O)_{2}, HO_{2} + c - SO_{3} \cdots H_{2}SO_{4}, HO_{2} + t - SO_{3} \cdots H_{2}SO_{4}, HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O, HO_{2} + t - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}SO_{4} \cdots H_{2}O \text{ and } HO_{2} + c - SO_{3} \cdots H_{2}O \text{ a$ $SO_3 \cdots (H_2SO_4)_2$ reactions.

	<i>T</i> (K)	10 Torr	50 Torr	100 Torr	300 Torr	760 Torr
	280	2.11 × 10 ⁻¹¹				
	290	1.95×10^{-11}	1.95×10^{-11}	1.95 × 10 ⁻¹¹	1.95×10^{-11}	1.95×10^{-11}
$k_{\rm P1}$	298	1.8×10^{-11}	1.83×10^{-11}	1.83×10^{-11}	1.83×10^{-11}	1.83×10^{-11}
$\kappa_{\rm R1}$	300	1.80×10^{-11}	$1.80 imes 10^{-11}$	1.80×10^{-11}	$1.80 imes 10^{-11}$	1.80×10^{-11}
	310	1.66×10^{-11}	1.66 × 10 ⁻¹¹	1.66×10^{-11}	1.66 × 10 ⁻¹¹	1.66 × 10 ⁻¹¹
	320	1.53 × 10 ⁻¹¹	1.53 × 10 ⁻¹¹	1.53×10^{-11}	1.53 × 10 ⁻¹¹	1.53 × 10 ⁻¹¹
	280	1.63×10^{-11}	1.64×10^{-11}	1.64×10^{-11}	1.64×10^{-11}	1.65×10^{-11}
	290	1.39×10^{-11}	1.40×10^{-11}	1.40×10^{-11}	1.40×10^{-11}	1.40×10^{-11}
L	298	1.21×10^{-11}	1.22×10^{-11}	1.22×10^{-11}	1.22×10^{-11}	1.22×10^{-11}
K _{WM1}	300	1.17×10^{-11}	$1.18 imes 10^{-11}$	1.18×10^{-11}	1.18×10^{-11}	1.18×10^{-11}
	310	9.82×10^{-12}	$9.95 imes 10^{-12}$	$9.97 imes 10^{-12}$	$9.98 imes 10^{-12}$	9.99 × 10 ⁻¹²
	320	8.22×10^{-12}	$8.38 imes 10^{-12}$	8.40×10^{-12}	8.41×10^{-12}	8.42 × 10 ⁻¹²
	280	4.77×10^{-11}	4.81 × 10 ⁻¹¹	4.81×10^{-11}	4.82×10^{-11}	4.82×10^{-11}
	290	4.18 × 10 ⁻¹¹	4.23 × 10 ⁻¹¹	4.23 × 10 ⁻¹¹	4.24×10^{-11}	4.24×10^{-11}
,	298	3.74×10^{-11}	$3.79 imes 10^{-11}$	3.79 × 10 ⁻¹¹	3.80×10^{-11}	3.80×10^{-11}
$\kappa_{\rm WD}$	300	3.63 × 10 ⁻¹¹	3.68 × 10 ⁻¹¹	3.68 × 10 ⁻¹¹	3.69 × 10 ⁻¹¹	3.69 × 10 ⁻¹¹
	310	3.13×10^{-11}	3.18×10^{-11}	3.18×10^{-11}	$3.19 imes 10^{-11}$	3.19 × 10 ⁻¹¹
	320	2.76×10^{-11}	$2.80 imes 10^{-11}$	$2.80 imes 10^{-11}$	2.84×10^{-11}	2.84×10^{-11}
	280	1.48 × 10 ⁻¹¹	1.60×10^{-11}	1.62×10^{-11}	1.63 × 10 ⁻¹¹	1.64×10^{-11}
	290	1.19×10^{-11}	$1.28 imes 10^{-11}$	1.30×10^{-11}	1.31×10^{-11}	1.31×10^{-11}
L	298	8.50×10^{-12}	1.03×10^{-11}	1.06×10^{-11}	1.08×10^{-11}	1.09×10^{-11}
κ_{c-SA}	300	$7.89 imes 10^{-12}$	$9.76 imes 10^{-12}$	1.01×10^{-11}	1.03×10^{-11}	1.04×10^{-11}
	310	5.13 × 10 ⁻¹²	7.22×10^{-12}	7.66×10^{-12}	8.00×10^{-12}	8.18×10^{-12}
	320	3.69×10^{-12}	4.50×10^{-12}	5.47×10^{-12}	5.66 × 10 ⁻¹²	6.40×10^{-12}

Table S7 The calculated rate constants (cm³·molecules⁻¹·s⁻¹) for the HO₂ + SO₃ reaction without and with H₂O, (H₂O)₂ and H₂SO₄ within the temperature range of 280-320 K and the pressure range of 10-760 Torr

Channels	<i>T</i> (K)	280	290	298	300	310	320			
Channel WM1	$k'_{\rm WM1}$	6.48×10^{-14}	6.28×10^{-14}	6.10 × 10 ⁻¹⁴	6.09×10^{-14}	5.75×10^{-14}	5.26×10^{-14}			
Channel WM2	$k'_{\rm WM2}$	5.92 × 10 ⁻²¹	8.51 × 10 ⁻²¹	1.13 × 10 ⁻²⁰	1.20×10^{-20}	1.65 × 10 ⁻²⁰	2.16 × 10 ⁻²⁰			
Channel WM3	$k'_{\rm WM3}$	3.33 × 10 ⁻¹⁴	3.09×10^{-14}	2.96×10^{-14}	2.89 × 10 ⁻¹⁴	2.62×10^{-14}	2.32×10^{-14}			
Channel WD1	$k'_{\rm WD1}$	3.39×10^{-14}	3.68 × 10 ⁻¹⁴	3.80×10^{-14}	3.96 × 10 ⁻¹⁴	4.06×10^{-14}	4.11 × 10 ⁻¹⁴			
Channel <i>c</i> -SA	$k'_{c-\mathrm{SA}}$	5.27 × 10 ⁻²⁰	1.94×10^{-20}	8.98 × 10 ⁻²¹	7.29 × 10 ⁻²¹	2.92 × 10 ⁻²¹	9.91 × 10 ⁻²²			
Channel <i>t</i> -SA	k'_{t-SA}	1.23 × 10 ⁻²⁰	3.49 × 10 ⁻²¹	1.53 × 10 ⁻²¹	1.21 × 10 ⁻²¹	4.89 × 10 ⁻²²	1.53 × 10 ⁻²²			
Channel <i>c</i> -SW	k'_{c-SW}	1.05×10^{-19}	4.00×10^{-20}	1.92×10^{-20}	1.56 × 10 ⁻²⁰	6.38 × 10 ⁻²¹	2.63 × 10 ⁻²¹			
Channel <i>t</i> -SW	k'_{t-SW}	5.02×10^{-19}	1.68 × 10 ⁻¹⁹	7.38 × 10 ⁻²⁰	5.87 × 10 ⁻²⁰	2.18 × 10 ⁻²⁰	8.30 × 10 ⁻²¹			
Channel SD	$k'_{\rm SD}$	2.85×10^{-26}	3.82×10^{-27}	8.20×10^{-28}	5.69 × 10 ⁻²⁸	9.36 × 10 ⁻²⁹	1.57×10^{-29}			
$k'_{\rm WM1}/k_{\rm tot}$ (%	6)	0.31%	0.32%	0.33%	0.34%	0.34%	0.34%			
$k'_{\rm WD1}/k_{\rm tot}$ (%)		0.16%	0.19%	0.21%	0.22%	0.24%	0.27%			

Table S8 Effective rate constants (*k*') for the HO₂ + SO₃ reaction with $X (X = H_2O, (H_2O)_2, H_2SO_4, H_2SO_4 \cdots H_2O \text{ and } (H_2SO_4)_2)$ within the temperature range of 280-320 K (at 0 km altitude)

Table S9 Equilibrium constants (K_{eq} , cm³·molecules⁻¹) for the formation of HO₂···H₂O, HO₂···H₂O)₂, *c*-HO₂···H₂SO₄ and *c*-HO₂···H₂SO₄···H₂O complexes, concentrations (molecules·cm⁻³) of H₂O, (H₂O)₂, H₂SO₄ and H₂SO₄···H₂O, and rate constants (cm³·molecules⁻¹·s⁻¹) of the HO₂ + SO₃ reaction with H₂O, (H₂O)₂, H₂SO₄ and H₂SO₄···H₂O at different altitudes in troposphere

Altitude	<i>T</i> (K)	P(atm)	$k_{ m WM1}$	$K_{eq}(HO_2 \cdots H_2O)$	[H ₂ O]
5 km	259.3	0.535	1.22×10^{-11}	3.26×10^{-20}	2.41×10^{16}
10 km	229.7	0.266	2.85×10^{-11}	2.83×10^{-19}	$4.92 imes 10^{15}$
15 km	212.6	0.120	2.26×10^{-11}	1.18×10^{-18}	$1.96 imes 10^{13}$
Altitude	<i>T</i> (K)	P(atm)	$k_{ m WD1}$	$K_{eq}(HO_2 \cdots (H_2O)_2)$	[(H ₂ O) ₂]
5 km	259.3	0.535	6.64 × 10 ⁻¹²	2.56×10^{-17}	2.70×10^{12}
10 km	229.7	0.266	4.20×10^{-11}	$7.39 imes 10^{-16}$	2.30×10^{11}
15 km	212.6	0.120	6.02×10^{-11}	8.06×10^{-15}	6.30×10^{6}
Altitude	<i>T</i> (K)	P(atm)	$k_{c-{ m SA}}$	$K_{eq}(c-HO_2\cdots H_2SO_4)$	[H ₂ SO ₄]
5 km	259.3	0.535	2.68×10^{-11}	4.81×10^{-17}	6.00×10^{7}
10 km	229.7	0.266	2.63×10^{-11}	9.49×10^{-16}	$8.30 imes 10^6$
15 km	212.6	0.120	$1.90 imes 10^{-11}$	$8.03 imes 10^{-15}$	2.40×10^5
Altitude	<i>T</i> (K)	P(atm)	k_{c-SW}	$K_{eq}(c-HO_2\cdots H_2SO_4$ $\cdots H_2O)$	$[H_2SO_4\cdots H_2O]^a$
5 km	259.3	0.535	3.45 × 10 ⁻¹¹	9.79×10^{-17}	1.02×10^{6}
10 km	229.7	0.266	3.54×10^{-11}	1.88×10^{-15}	2.34×10^5
15 km	212.6	0.120	2.42×10^{-11}	1.56×10^{-14}	1.21×10^{2}

^a The concentrations of $H_2SO_4\cdots H_2O$ at 5, 10 and 15 km altitudes were respectively calculated to be 1.02×10^5 , 2.34×10^5 and 1.21×10^2 molecules cm⁻³ by using the above concentration of H_2SO_4 and H_2O .

The average concentration^{2,17} of H₂SO₄ at 5, 10 and 15 km altitudes were known to be 6.00×10^7 , 8.30×10^6 and 2.40×10^5 molecules·cm⁻³, respectively. Meanwhile, the concentration for H₂O was respectively found to be 2.41×10^{16} , 4.92×10^{15} and 1.96×10^{13} molecules·cm⁻³, whereas the concentration of (H₂O)₂ was respectively found to be 2.70×10^{12} , 2.30×10^{11} and 6.30×10^6 molecules·cm³, in the same order considering temperatures (259 K, 230 K and 213 K, respectively) and pressures (0.533, 0.266 and 0.120 atm, respectively) at those altitudes (Table S9). Using the above concentrations of H₂SO₄ and H₂O along with the equilibrium constants for the H₂SO₄…H₂O complex formation, the concentrations of H₂SO₄…H₂O complex were calculated to be 1.2×10^6 , 2.34×10^5 and 1.21×10^2 molecules·cm⁻³ at 5, 10 and 15 km altitudes, respectively.

<u>(11</u>	120	$j_2, 11_2, 50, 4, 11_2$	504 H ₂ 0 and	(112504)(2) at the	1110	0-277/0-311+0	(<i>2uj</i> , <i>2pu</i>) ieve	1 of theory
			HO.				SO ₃	
	`	0.05495900	0 70602200	0.0000000	S	0.00000000	0.00000000	0.00004200
))	0.05495900	0.70092200	0.00000000	0	0.00000000	1.22894800	-0.70957800
L	, 1	0.03493900	0.86666200	0.00000000	0	0.00000000	-1.22894800	-0.70957800
1	1	-0.8/934000	-0.80000200	0.00000000	0	0.00000000	0.00000000	1.41907300
			IM				TS	
S	5 -	0.65103500	0.09510600	-0.00000300	S	-0.56835000	0.00037700	0.06110100
0) -	1.12311500	-0.41905700	1.23336900	0	-1.13555000	-1.24032700	-0.31712500
0) -	1.12315800	-0.41921800	-1.23329100	0	-1.13538100	1.23659100	-0.33185300
0)	0.00168700	1.38229700	-0.00009700	0	0.16647700	0.00813500	1.35484800
0)	2.13179700	0.02563700	0.00000200	0	2.01351200	-0.00009100	-0.04412500
H	ł	1.62474200	0.89379400	-0.00004500	Н	1.31450400	0.00606100	0.93812100
0)	1.21176700	-0.87159600	0.00003000	0	1.06333000	-0.00582000	-0.90121400
			HOSO ₄				н.оно.	
	S	0.45817600	-0.03289000	0.08694800	0	1.06875500	0.66141400	0.01171800
	0	0.30730800	1.14735200	-0.92649700		0.07010600	0.63876500	0.00812200
	Н	-0.22081500	1.85697100	-0.53058500	ц	0.00081000	-0.03870500	0.00812200
	0	0.42856000	0.45974200	1.41365000		1 61563500	0.02251500	0.08822100
	0	1.40805100	-0.94165100	-0.41900500	Ц	2 207/3800	-0.02231300	0.58550700
	0	-2.01578900	-0.01185900	0.00414500		-2.29743800	-0.01048500	0.38539700
	0	-1.01688000	-0.81992500	-0.17986600	п	-1.1/018200	0.83118700	-0.03332000
			IM_WM1				TS_WM1	
S	5	0.84128700	-0.27789400	0.00003400	S	0.78614400	-0.24277500	0.02292800
0)	0.27117000	-0.76843600	-1.21913900	0	2.14203000	0.13895600	-0.11285700
0)	0.27136100	-0.76822600	1.21935000	0	0.01771000	1.45151600	-0.08795400
0)	2.15628900	0.24655900	-0.00016300	0	-1.26219800	1.46036700	0.00451100
H	ł	-1.85551700	-1.27871600	-0.76258100	0	0.26120700	-0.64710200	1.29556000
0)	-2.27583700	-0.85682300	-0.00020000	0	0.13418400	-0.87229400	-1.11362500
H	ł	-1.85793200	-1.27845000	0.76360600	H	-1.43929500	-1.13997000	-0.61478400
H	ł	-1.71652500	0.45822900	-0.00001400	0	-2.19846000	-0.78781300	-0.06024600
0)	-1.35554200	1.46470300	-0.00000800	H	-1.80870600	0.27444700	0.03480400
0)	-0.07126800	1.50037700	-0.00003700	H	-2.08608300	-1.19912500	0.81002200
			IMF_WM1			1	HO(H2O)2	
S	5	0.70762400	-0.29202900	0.07272100	н	0 96147100	2 13177900	0 63004000
0)	2.06630600	-0.51595600	-0.23279600	0	0.69884900	1 54744000	-0.08606200
0)	0.56536600	1.40799600	-0.10103400	н	1 28314500	0.76015200	-0.04311900
0)	-0.66345900	1.79447300	0.00416100	0	1 62710600	-0.98756500	0.07946800
0)	0.11893800	-0.59163700	1.33280000	Н	0.67954700	-1 21924300	0.06195200
)	-0.19801700	-0.75394700	-1.07129400	Н	2 05172900	-1 51245200	-0.60385200
H	ł	-1.17567100	-0.74675600	-0.75352700	0	-1.22190200	-0.97042700	0.04321700
0)	-2.52983000	-0.56791900	-0.09738200		-1 62729500	0.28482600	-0.03710900
H	ł	-2.46339300	0.34331600	0.21494700	Н	-0 78995100	0.84556600	-0.04113500
ŀ	ł	-2.55735600	-1.10817800	0.69939800		0.70552100	0.01220000	0.011122000
			IM_WD1				TS_WD1	
	Н	-3.00639900	1.43058400	-0.04638800	H	-2.95846900	1.36812500	-0.12597400
	0	-2.26708100	0.99072600	0.38472500	0	-2.25225900	0.93424900	0.36583500
	Η	-2.36411200	0.01607300	0.20550100	H	-2.30565000	-0.06564900	0.17809400
	0	-2.39950600	-1.56507300	-0.30322400	0	-2.29574600	-1.54691000	-0.28606500
	Η	-1.48892100	-1.64268600	-0.63691900	H	-1.38094900	-1.60097300	-0.63099000
	Η	-2.49279900	-2.23560800	0.37971400	H	-2.35456400	-2.19377200	0.42380400
	0	-0.17953800	2.15482400	-0.27571300	0	-0.21673600	2.07201600	-0.27045400
	Η	-0.99995600	1.53911900	0.04937500	H	-1.15589000	1.41019300	0.08669200
	0	0.92813000	1.49505500	-0.46284500	0	0.91284100	1.45737100	-0.45595700
	S	1.04201500	-0.49497600	0.11159500	S	1.02594300	-0.43762300	0.10508800
	0	0.30852500	-1.07493500	-0.99527800	0	0.32238600	-1.05374100	-1.01007200

Table S10 Coordinates stationary points for the HO₂ + SO₃ reaction without and with $X (X = H_2O, (H_2O)_2, H_2SO_4, H_2SO_4, \dots H_2O)$ and $(H_2SO_4)_2$ at the M06-2X/6-311+G(2*df*,2*pd*) level of theory

0	0.34936300	-0.38021100	1.36590900	0	0.29290600	-0.35633000	1.34324800
	2.47010000	-0.3188/000	0.00932700		2.45410200	-0.49014800	0.11185500
		IMF_WD1					
Н	-2.97400100	1.57263500	0.60601700			11011 SO	
0	-2.72452300	0.69442700	0.90787600	G	<i>c</i> -	0.05005800	0 11922700
Н	-2.46852500	-0.50261200	-0.25498400		0.80332900	-0.03993800	-0.11832/00
0	-2.10214700	-1.20102900	-0.85703600		-0.08301400	-1.13400900	0.09080400
Н	-0.67323700	-1.20733200	-0.74367900	0	1 68049500	-0.04915700	-1 26888200
Н	-2.53432000	-2.03093000	-0.63479100	0	1.84003100	-0.02503700	1 11109800
0	0.08313000	1.65186700	-1.14737700	н	-0.90156600	1 09729300	0.04687500
Н	-1.81496600	0.76998800	1.23712400	н	1 35788200	-0 17442100	1 93504400
0	1.22524100	1.16881200	-0.73762100	0	-2 64478700	-0.60725900	-0 02748700
S	1.00929700	-0.23944800	0.29475300	н	-1 73331000	-1 01138800	-0.02578800
0	0.38371900	-1.23141000	-0.69072600	0	-2 45147400	0.67315900	0.04267400
0	0.07244300	0.16593500	1.30966300		2.1011/100	0.07515900	0.01207100
0	2.35167300	-0.59492400	0.59950400				
	1 00505000	c-IM_SA	0.000.00700		1 00 101 (00	c-TS_SA1	0.00100000
8	1.80/3/200	-0.51138300	0.00060/00	8	-1.80491600	-0.48149200	0.00180900
	0.99691000	-0.61240900	1.18438400	0	-3.15560300	-0.88/49100	0.04342100
	3.16063400	-0.90880800	0.04465200		-0.9885/200	-0.60/26400	1.18315100
	1.080/9400	-0.58005900	-1.24480000		-1.07084200	-0.58621700	-1.24208100
	0.12170600	2.09332000	-0.00707200		-1.02120000	2.03931200	-0.00339000
	2 11//7300	1.34234000	-0.03201000		-0.00382300	1.49023000	-0.03730800
s	-2.02253800	0.00463000	-0.01800300	s	2.08243400	-0.01424500	-0.01906100
0	-1 71700800	-0.67505200	1 34241800		1 48615700	-1.01229000	-1.06783800
0	-3 41437500	0.17672500	-0 12452900		3 39978800	0 13097400	-0.13210900
0	-1 17481000	1 18941100	-0 12947000	0	1 20661800	1 21580600	-0 14758000
0	-1 54321900	-1.00913500	-1 08399400	0	1.67872400	-0.65053600	1 35092900
н	-0.74691900	-0.74053500	1.47989900	Н	0.50364700	-0.90391000	-1.22553100
Н	-0.57311500	-0.91314100	-1.25651700	Н	0.70202300	-0.72605700	1.46827800
		c-IMF_SA1		1			
S	-1.88461100	-0.39379400	-0.06357400				
0	-3.17887800	-0.93045200	-0.18791400		t-	HO ₂ …H ₂ SO ₄	
0	-1.29789100	-0.62414400	1.31756300	S	-0.87225200	-0.07063300	-0.11654600
0	-0.87620200	-0.54185000	-1.06998400	0	0.06468000	-1.14580700	-0.30637300
0	-1.09358400	1.98081600	-0.00125600	0	-1.23478000	-0.13395700	1.41776000
Н	0.66920700	1.41080400	-0.49069400	0	-2.06980600	-0.00092100	-0.87004800
0	-2.18323500	1.29155000	-0.00462100	0	-0.11377400	1.26925900	-0.25306100
S	2.07510800	-0.06567200	0.09050200	H	-2.06234800	0.33982400	1.57606600
	1.83296100	-1.16851900	-0.98233500	H	0.87071300	1.11957400	-0.09540900
	3.45909700	-0.00258400	0.33451900		2.61864700	-0.59087800	-0.01361900
	1.62469800	1.24858500	-0.61594500	H	1.717/0800	-0.9947/8200	-0.14704200
	1.17164800	-0.29524300	1.20439000	0	2.4137/800	0.68549400	0.091/3100
	0.88448600	-1.22341600	-1.20433600				
Н	-0.2/055300	-0.50119800	1.30884100				

t-IM_SA1 S -1.85438500 -0.55024600 0.03784300 O -1.12156200 -0.68421500 -1.20222500 O -3.21691500 -0.92518800 0.05174600 O -1.06537600 -0.53904800 1.22279800 O -1.13762200 2.12011300 0.01354900 H -0.26014700 1.56180500 0.06127300	t-TS_SA1 S 1.84564300 -0.47141800 -0.04303900 O 1.12965200 -0.64618400 1.22547300 O 3.19822200 -0.87852800 -0.06742300 O 0.99905500 -0.56051500 -1.18810100 O 1.02720300 2.02289500 -0.02163500 H -0.06080600 1.42628100 -0.07994100
O -2.18038200 1.38108500 -0.08111600 S 2.04783200 0.03119900 -0.05891000 O 1.95670900 -0.60690900 1.37262800 O 1.44454600 -1.03371700 -0.99137500 O 1.15964300 1.16786000 -0.00621100	O 2.10554100 1.33881800 0.04318900 S -1.99982700 -0.01242400 0.07020600 O -1.93019100 -0.66786200 -1.34821700 O -1.28249600 -0.95283500 1.00046100 O -1.21697700 1.22621300 -0.99002900
O 3.40744400 0.22292400 -0.40198400 H 2.74227200 -1.14635600 1.53841500 H 0.45082400 -0.93393200 -1.08508100	O -3.34870300 0.16582500 0.45137600 H -2.70097100 -1.23671300 -1.48553700 H -0.22173900 -0.83069500 1.09006500
<i>t</i> -IMF_SA1	c-HO₂…H₂SO₄…H₂O
O -1.30041100 -0.41325400 -0.07704000 O -1.22053400 -0.65080700 -1.26518200 O -3.20690300 -0.90321300 0.09858300 O -0.95669700 -0.55531800 1.14865400 O -1.09721600 1.98877500 0.01926800 H 0.37734400 1.30876700 0.20987600 O -2.17290500 1.29315300 -0.03599800 S 2.04605200 -0.05279500 -0.10265900 O 1.95969100 -0.77547200 1.29257000 O 1.23931200 -0.80428400 -1.05158800 O 1.37441300 1.27835500 0.23832500 O 3.39979900 0.17255000 -0.44778100 H 2.70291100 -1.44014800 1.36722900 H -0.18620200 -0.73007100 -1.18374100	O -2.48491800 -1.43855800 -0.01619600 H -1.51436400 -1.31289800 -0.18059200 O -2.98980400 -0.24352000 0.01048900 S 1.15682400 -0.18805500 0.09533300 O 2.32702200 -0.22800700 -0.95662900 O 1.00524700 1.31434900 0.37022500 O -0.04573500 -0.63535800 -0.57850900 O 1.62833100 -0.88728100 1.23023600 H 2.03415100 0.14344700 -1.79925300 H 0.02834100 1.62464000 0.19878800 O -1.35883700 1.96917300 -0.07801100 H -1.91445300 1.16090500 -0.11227400 H -1.79331300 2.58640700 0.51517400
c-IM_SW1	c-TS_SW1
S 2.09585100 -0.40893100 -0.38124200 O 0.71201500 -0.76900300 -0.53593700 O 3.05265400 -1.42644300 -0.15619500 O 2.49922500 0.81204500 -1.01260400 O 0.85866200 0.46263000 1.94015000	$ \begin{bmatrix} S & -2.08169800 & -0.33004800 & 0.40833400 \\ O & -0.70412500 & -0.68126800 & 0.64331500 \\ O & -3.05976500 & -1.35278300 & 0.39542400 \\ O & -2.45420400 & 0.99177600 & 0.82570600 \\ O & -0.84104000 & 0.13475300 & -1.97468400 \\ \end{bmatrix} $
H-0.010985000.212882001.34593600O2.004462000.261950001.41132500S-2.26260300-0.198606000.02443900	H 0.11639600 0.00693200 -1.34644600 O -1.99005700 -0.01145700 -1.43660600 S 2.23537300 -0.20442500 0.00954700
O -1.89386700 0.79325900 -1.09178500 O -1.88437500 -1.58997100 -0.56672700 O -1.39356300 0.06872400 1.16615100 O -3.65428600 -0.20833800 0.25014000	O 1.86634900 0.90024900 0.99993300 O 1.83559300 -1.52287400 0.72712300 O 1.38423500 -0.04795900 -1.17882000 O 3.62374600 -0.25331700 -0.22447700
H -1.05843600 1.33133200 -0.88180300 H -0.92003100 -1.64298600 -0.69844300 O 0.14917900 2.18363100 -0.49076400	H 1.04299300 1.45212500 0.72108700 H 0.87154600 -1.53673100 0.88610000 O -0.09879600 2.26298100 0.25241900
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t-IMF_SW1HO2: $\cdot\cdot\cdot(H_2SO_4)_2$ S2.18473000-0.32088600-0.29349800O0.031267002.616182000.54548600O1.03199000-0.34898700-1.15516200H0.742305002.040421000.91997500O3.32788100-1.09826900-0.57304200O-0.206306002.13819900-0.63613900O2.510846001.089017000.10746300S2.08790100-0.387379000.07232200O0.57445400-0.323512001.58668200O1.44562500-1.74738200-0.28014000H-0.50831100-0.87535600-0.90614800O1.977441000.44678800-1.24186400O1.62283000-0.969258001.17721700O1.232051000.283704001.04983400S-2.34696500-0.08537000-0.17600900O3.44688700-0.592393000.37758100O-1.702703001.19039700-0.29885000H0.50562400-1.60691300-0.56708200O-1.45012700-1.17403800-0.81305900S-2.01508300-0.53162200-0.02230600O-3.67173300-0.28036200-0.64028100O-2.711311000.79521700-0.46174700H-2.92652200-1.111331001.57295300O-3.03273900-1.493914000.13430900H-0.263255001.995217000.06823700O-0.90374900-0.77080800-0.92290100O05.53040002.523441								
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O -1.70270300 1.19039700 -0.29885000 H 1.12100100 0.92171000 -1.26081300 O -1.45012700 -1.17403800 -0.81305900 S -2.01508300 -0.53162200 -0.02230600 O -3.67173300 -0.28036200 -0.64028100 O -2.71131100 0.79521700 -0.46174700 H -2.92652200 -1.11133100 1.57295300 O -3.03273900 -1.49391400 0.13430900 H -0.26325500 1.99521700 0.06823700 O -0.90374900 -0.77080800 -0.92290100 O 0.56304000 2.52344100 0.14626700 O -1.40963700 -0.18371000 1.37059300 H 1.62543200 1.75193100 0.11662700 H -2.05920900 1.48162000 -0.68731200 H 0.537700000 3.18536300 0.55055600 H 0.43103800 0.06788500 1.31488400		-2.29015000	-0.41414500	1.36415500		0.50562400	-1.60691300	-0.56/08200
O -1.43012700 -1.17403800 -0.81303900 S -2.01508300 -0.33162200 -0.02230600 O -3.67173300 -0.28036200 -0.64028100 O -2.71131100 0.79521700 -0.46174700 H -2.92652200 -1.11133100 1.57295300 O -3.03273900 -1.49391400 0.13430900 H -0.26325500 1.99521700 0.06823700 O -0.90374900 -0.77080800 -0.92290100 O 0.56304000 2.52344100 0.14626700 O -1.40963700 -0.18371000 1.37059300 H 1.62543200 1.75193100 0.11662700 H -2.05920900 1.48162000 -0.68731200 H 0.537700000 3.18536300 0.55065600 H 0.43103800 0.06788500 1.31488400		-1./02/0300	1.19039/00	-0.29885000		1.12100100	0.921/1000	-1.20081300
G -5.67175500 -0.28056200 -0.04028100 G -2.71131100 0.79521700 -0.46174700 H -2.92652200 -1.11133100 1.57295300 O -3.03273900 -1.49391400 0.13430900 H -0.26325500 1.99521700 0.06823700 O -0.90374900 -0.77080800 -0.92290100 O 0.56304000 2.52344100 0.14626700 O -1.40963700 -0.18371000 1.37059300 H 1.62543200 1.75193100 0.11662700 H -2.05920900 1.48162000 -0.68731200 H 0.53770000 3.18536300 0.55065500 H 0.43103800 0.06788500 1.31488400		-1.45012/00	-1.1/403800	-0.81303900	S	-2.01508300	-0.33162200	-0.02230600
H -2.92632200 -1.11155100 1.37293300 O -3.03273900 -1.49391400 0.13430900 H -0.26325500 1.99521700 0.06823700 O -0.90374900 -0.77080800 -0.92290100 O 0.56304000 2.52344100 0.14626700 O -1.40963700 -0.18371000 1.37059300 H 1.62543200 1.75193100 0.11662700 H -2.05920900 1.48162000 -0.68731200 H 0.53770000 2.18536300 0.55055600 H 0.43103800 0.06788500 1.31488400		-3.0/1/3300	-0.28036200	-0.04028100		-2./1131100	0./9521/00	-0.401/4/00
H -0.20525500 1.99521700 0.00825700 O -0.90574900 -0.77080800 -0.92290100 O 0.56304000 2.52344100 0.14626700 O -1.40963700 -0.18371000 1.37059300 H 1.62543200 1.75193100 0.11662700 H -2.05920900 1.48162000 -0.68731200 H 0.53770000 3.18536300 0.55065600 H 0.43103800 0.06788500 1.31488400		-2.92032200	-1.11133100	1.3/293300		-3.032/3900	-1.49391400	0.13430900
G 0.30304000 2.32344100 0.14020700 G -1.40905700 -0.18371000 1.37059300 H 1.62543200 1.75193100 0.11662700 H -2.05920900 1.48162000 -0.68731200 H 0.53770000 2.18536300 0.55065600 H 0.42103800 0.06788500 1.31488400		-0.20525500	1.99321700	0.00823/00		-0.903/4900	-0.//080800	1 27050200
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	ч	1 62542200	2.32344100	0.14020700		-1.40903/00	-0.165/1000	-0.68731200
$ \square = 0.33/(9000) = 3.16330300 = 0.33003000 = \square = 0.43103600 = 0.00766300 = 1.14666400$	Г	0.53779000	3,18536300	-0.55065600		-0.43103800	-0.06788500	1.31488400

		IM_SD1				TS_SD1	
S	-2.27613700	-1.07355100	-0.48583600	S	-1.73923000	-1.56256100	-0.45273800
0	-2.74031700	0.28519300	-0.44802300	0	-2.55426300	-0.44528500	-0.85977800
0	-3.19573000	-2.10544800	-0.76836300	0	-2.19311500	-2.86970100	-0.73218300
0	-0.88342500	-1.25049400	-0.77529500	0	-0.32683200	-1.29245300	-0.39438500
0	-1.38261400	-0.59438500	2.06476500	0	-1.70358600	-0.49489700	1.99934500
Н	-0.84024700	0.07754600	1.43922900	Н	-1.06715900	0.27844900	1.39231600
0	-2.19003000	-1.35794600	1.42691600	0	-2.11942000	-1.52975600	1.37164400
S	-0.01274300	2.13703500	-0.01204000	S	-0.63630000	2.15865600	-0.07727000
0	0.17119700	1.55301500	-1.41642400	0	-0.04028600	1.58964400	-1.35725100
0	-1.48140100	2.59206300	-0.04465000	0	-2.14263300	2.05861000	-0.33340000
0	0.11278200	1.00544200	0.93679700	0	-0.30081300	1.18786200	1.01583200
0	0.81676400	3.24204000	0.26872700	0	-0.27224700	3.48826300	0.20470000
Н	0.89610700	0.84320900	-1.40890000	Η	0.84806700	1.09744700	-1.20603500
Н	-2.06900700	1.83251300	-0.27664900	Η	-2.38851800	1.13126000	-0.62269600
S	2.59225900	-0.94690300	-0.13247300	S	2.78415800	-0.45562400	-0.02703900
0	1.49742300	-1.96360100	0.32205900	0	2.31742500	-1.89988300	-0.35249900
0	3.82055900	-1.61302500	-0.30816300	0	4.18723300	-0.47884000	0.08437900
0	2.03354700	-0.17715800	-1.22445100	0	2.16050900	0.46251100	-0.96050900
0	2.74355000	-0.02658600	1.11775500	0	2.15911400	-0.17541200	1.37895900
H	0.65823100	-1.80750200	-0.15666400	H	1.34595900	-1.93099300	-0.46797700
H	1.92241000	0.47606000	1.27536200	H	1.35491500	0.37101500	1.29829400
		IMF_SD1					
S	-2.29571100	-1.13970700	-0.37430100				
0	-2.96228700	0.17936800	-0.69434800				
0	-3.03687100	-2.23598300	-0.84998600				
0	-0.87278900	-1.03817300	-0.51593900				
0	-1.73153800	-0.44747600	1.97377900				
Н	-0.25226000	0.47763800	1.24093700				
0	-2.53607400	-1.21948500	1.32636200				
S	-0.11543800	2.15880400	-0.07092700				
0	0.26691200	1.52035700	-1.40896800				
0	-1.56344500	2.11241200	0.01307500				
0	0.44037800	1.12933200	1.00092200				
0	0.53566900	3.38891800	0.15534200				
Н	1.04452600	0.87425100	-1.34401100				
Н	-2.37082500	1.00458300	-0.45348700				
S	2.72061900	-0.94344200	-0.11236800				
0	1.55595600	-1.78489600	0.50412600				
0	3.83993900	-1.76143700	-0.35921200				
0	2.16075100	-0.15897200	-1.19198000				
0	3.09661700	0.00148800	1.07069700				
Н	0.72080800	-1.65420100	0.01280900				
Н	2.36046900	0.60363200	1.27432400				

Reference

- J. Gonzalez, M. Torrent-Sucarrat and J. M. Anglada, *Phys. Chem. Chem. Phys.*, 2010, 12, 2116-2125.
- [2] J. M. Anglada, G. J. Hoffman, L. V. Slipchenko, M. M. Costa, M. F. Ruiz-Lopez and J. S. Francisco, *J. Phys. Chem. A*, 2013, **117**, 10381-10396.
- [3] J. Liu, S. Fang, Z. Wang, W. Yi, F. M. Tao and J. Y. Liu, *Environ. Sci. Technol.*, 2015, 49, 13112-13120.
- [4] L. Liu, J. Zhong, H. Vehkamäki, T. Kurtén, L. Du, X. H. Zhang, J. S. Francisco and X. C. Zeng Proc. Natl. Acad. Sci. U. S. A., 2019, 116, 24966-24971.
- [5] X. T. Le, T. V. T. Mai, K. C. Lin and L. K. Huynh, J. Phys. Chem. A, 2018, 122, 8259-8273.
- [6] X. T. Le, T. V. T. Mai, M. V. Duong and L. K. Huynh, Chem. Phys. Lett., 2019, 728, 142-147.
- [7] T. V. T. Mai, M. V. Duong, H. T. Nguyen and L. K. Huynh, Phys. Chem. Chem. Phys., 2018, 20, 6677-6687.
- [8] T. V. T. Mai, P. Raghunath, X. T. Le, L. K. Huynh, P. C. Nam and M. C. Lin, Chem. Phys. Lett., 2014, 592, 175-181.
- [9] T. V. T. Mai, A. Ratkiewicz, M. V. Duong and L. K. Huynh, Chem. Phys. Lett., 2016, 646, 102-109.
- [10] T. V. T. Mai, M. V. Duong, H. T. Nguyen, K. C. Lin and L. K. Huynh, J. Phys. Chem. A, 2017, 121, 3028-3036.
- [11] T. V. T. Mai, M. V. Duong, H. T. Nguyen, K. C. Lin and L. K. Huynh, *Chem. Phys. Lett.*, 2018, 706, 280-284.
- [12] T. V. T. Mai and L. K. Huynh, Phys. Chem. Chem. Phys., 2019, 21, 17232-17239.
- [13] T. V. T. Mai, H. T. Nguyen and L. K. Huynh, Phys. Chem. Chem. Phys., 2019, 21, 23733-23741.
- [14] T. V. T. Mai, H. T. Nguyen and L. K. Huynh, Atmos. Environ., 2020, 242, 117833.
- [15] T. Zhang, K. Zhai, Y. Zhang, L. Geng, Z. Geng, M. Zhou, Y. S. Lu, X. Z. Shao and M. Lily, *Comput. Theor. Chem.*, 2020, **1176**, 112747.
- [16] M. A. Ali, M. Balaganesh and S. Jang, Atmos. Environ., 2019, 207, 82-92.
- [17] S. Ghoshal and M. K. Hazra, RSC Adv., 2015, 5, 17623-17635.