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

Supporting information

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Catalytic effect of water, water dimer and water trimer on the H_2S +$^3O_2$ formations from the HO_2+ HS reaction in tropospheric conditions†

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Part A The H_2S +$^3O_2$ formations from the HO_2+ HS without catalyst(pS2-pS7)

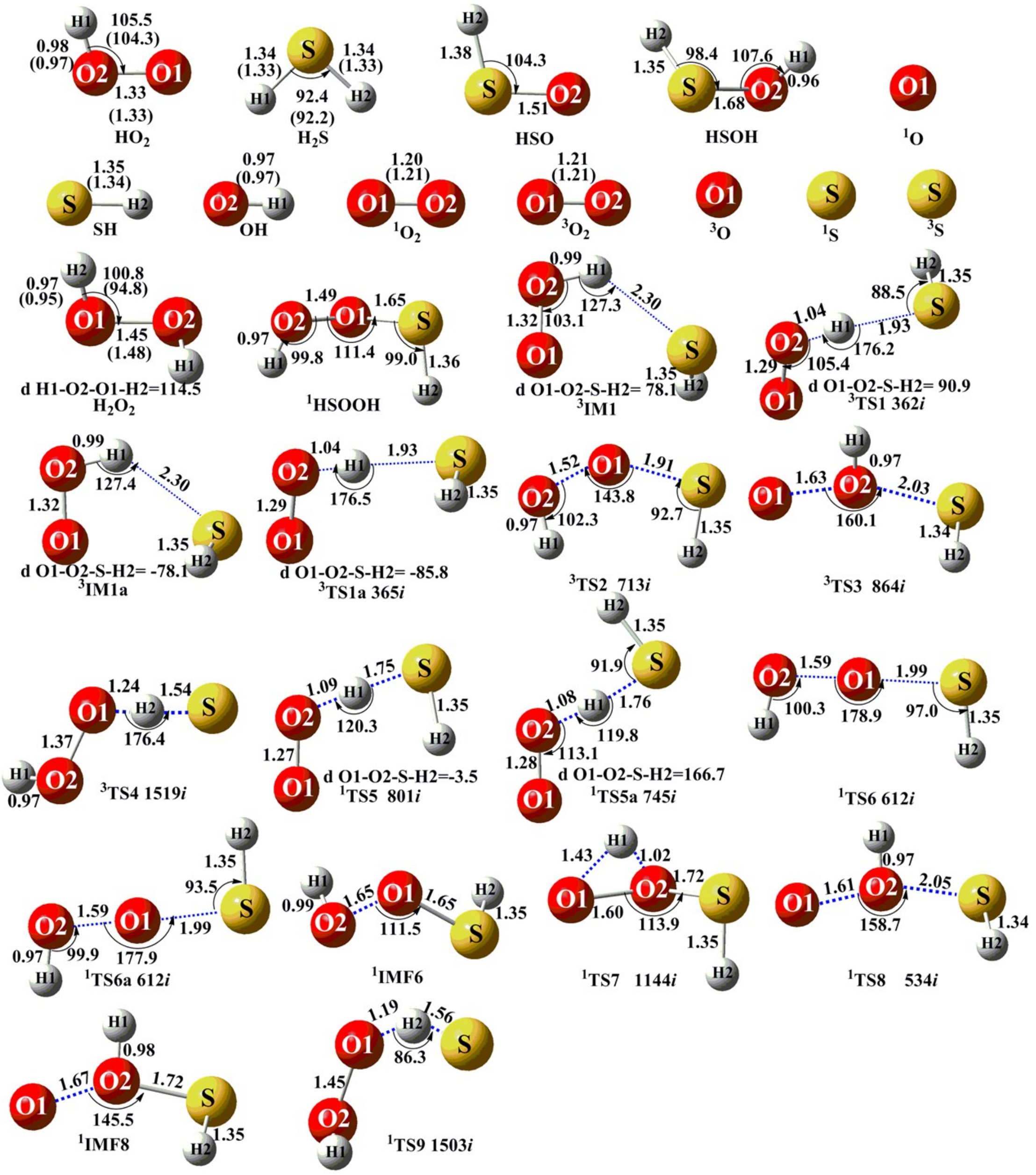

Figure S1 Geometrical parameters for the naked reaction of HO_2 + HS optimized at the CCSD(T)/6-311++G(3df,2pd)//B3LYP/6-311+G(2df,2p) level of theory

Table S1 Zero point energy (ZPE/(kcal·mol^{-1})), relative energies (ΔE and $\Delta(E$+ZPE)/(kcal·mol^{-1})), enthalpies (ΔH(298)/(kcal·mol^{-1})), and free energies (ΔG(298)/(kcal·mol^{-1})) for the HO_2 + HS reaction[a]

Species	ZPE	S	ΔE	ΔH(298)	ΔG(298)	Δ(E+ZPE)
HO_2 + HS	12.7	100.6	0.0	0.0	0.0	0.0
^{3}IM1	14.4	73.8	-4.7	-3.6	4.4	-3.0
^{3}IM1a	14.4	73.8	-4.7	-3.6	4.4	-3.0
^{3}TS1	12.0	74.1	-0.5	-2.0	5.9	-1.2
^{3}TS1a	12.0	74.2	-0.5	-2.0	5.9	-1.2
H_2S + $^3O_2$	11.8	99.5	-40.9	-41.8	-41.5	-41.8
^{3}TS2	13.9	69.4	13.5	13.6	22.9	14.6
HSO + OH	11.8	100.3	-30.6	-31.5	-31.4	-31.5
^{3}TS3	13.4	70.8	26.4	26.2	35.1	27.1
HSOH + ^{3}O	14.1	94.7	-5.8	-4.8	-3.1	-4.4
^{3}TS4	12.4	69.9	25.2	23.7	32.8	24.9
H_2O_2 + ^{3}S	16.7	92.0	-16.2	-12.5	-10.6	-12.2
^{1}TS5	12.3	68.0	12.1	10.7	20.4	11.7
^{1}TS5a	12.3	68.0	12.2	10.8	20.5	11.8
H_2S + $^1O_2$	11.7	97.3	-10.6	-11.6	-10.6	-11.6
^{1}TS6	13.3	69.1	35.8	0.1	35.3	44.7
^{1}TS6a	15.4	64.9	35.5	4.1	36.9	47.5
^{1}IMF6	17.5	76.0	-46.7	-43.7	-33.3	-45.1
HSO + OH	11.7	100.3	-30.6	-1.9	-31.5	-31.5
^{1}TS7	13.4	66.8	13.7	13.3	23.3	14.4
^{1}HSOOH	15.9	66.4	-44.4	-42.4	-32.2	-41.3
^{1}TS8	13.4	70.8	34.6	34.8	44.7	35.9
HSOH + ^{1}O	14.1	92.5	45.4	46.4	48.8	46.8
^{1}TS9	14.1	66.0	-21.5	-22.6	-13.2	33.6
H_2O_2 + ^{1}S	16.7	92.0	15.0	18.6	21.1	18.9

[a] ZPE and S values obtained at B3LYP/6-311+G(2df,2p) level of theory; The energy values are obtained at CCSD(T)/ 6-311++G(3df,2pd) level whereas the *H* and *G* corrections are taken from the B3LYP/6-311+G(2df,2p) level.

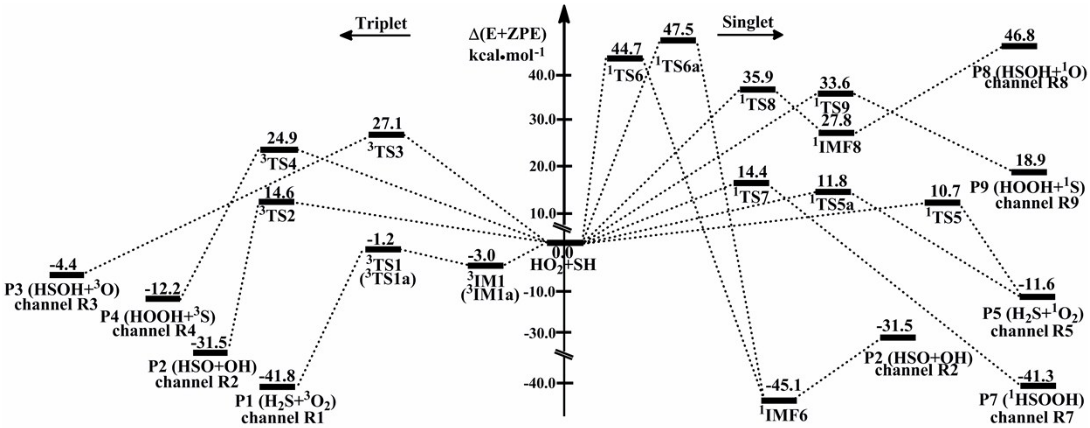

Figure S2 Schematic energy diagram of the naked HO_2 + HS reaction energies (kcal·mol^{-1}) computed at the CCSD(T)/6-311++G(3df,2pd)//B3LYP/6-311+G(2df,2p) level include zero-point energy correction.

Table S2 Rate constants ($cm^3 \cdot molecules^{-1} \cdot s^{-1}$) for main reaction of the HO_2 + HS reaction within the temperature range of 240.0-425.0 K

T/K	k_{R1a}	k_{R1b}	k_{R1}
240	2.60E-11	2.90E-11	5.49E-11
250	2.35E-11	2.62E-11	4.98E-11
278	1.88E-11	2.09E-11	3.97E-11
288	1.76E-11	1.95E-11	3.72E-11
298	1.66E-11	1.84E-11	3.50E-11
308	1.58E-11	1.74E-11	3.32E-11
325	1.46E-11	1.61E-11	3.07E-11
375	1.24E-11	1.36E-11	2.60E-11
425	1.13E-11	1.24E-11	2.37E-11

k_{R1} is the rate constant of Channel R1; k_{R1a} is the rate constant of the process of HO_2 + HS $\rightarrow$ ^{3}IM1 $\rightarrow$ ^{3}TS1 $\rightarrow$ H_2S + $^3O_2$; and k_{R1b} is the rate constant of the process of HO_2 + HS $\rightarrow$ ^{3}IM1a $\rightarrow$ ^{3}TS1 $\rightarrow$ H_2S + $^3O_2$;. k_{R1}= k_{R1a}+ k_{R1b} .

The predicated concentration of HS based on previous experimental and theoretical reports at 298 K

The main source of HS radical is the reaction of H_2S with OH radical[1]:

$$H_2S + OH \rightarrow H_2O + HS \quad 5.48E\text{-}12 \ (298\ K) \quad k_1 \quad (1)$$

The formed HS radical is mainly dispelled by the reacts with atoms or molecules, such as HO_2[2], O_3[3], O_2[4], NO[5], NO_2[6] :

$$HO_2 + HS \rightarrow {}^3O_2 + H_2S \quad 3.50E\text{-}11\ (298\ K) \quad k_2 \quad (2)$$

$$O_3 + HS \rightarrow {}^3O_2 + HSO \quad 3.71E\text{-}12 (298\ K) \quad k_3 \quad (3)$$

$$O_2 + HS \rightarrow OH + SO \quad 4.00E\text{-}19 (298\ K) \quad k_4 \quad (4)$$

$$NO + HS \rightarrow HSN{=}O \quad 5.60E\text{-}13 (298\ K) \quad k_5 \quad (5)$$

$$NO_2 + HS \rightarrow HSO + NO \quad 7.00E\text{-}11 (298\ K) \quad k_6 \quad (6)$$

Assumed that the production rate and the depletion rate is comparable, the concentration of HS radical can be approximately equal to:

$[HS]=(k_1[H_2S][OH])/(k_2[HO_2]+k_3[O_3] +k_4[O_2] +k_5[NO] +k_6[NO_2])$

where k_1, k_2, k_3, k_4, k_5 and k_6 are rate constants for the reactions of R1, R2, R3, R4, R5 and R6, respectively. Therefore, the concentration of HS radical is calculated as a value of **10^6 molecules cm^{-3}** in the tropospheric conditon with 20% O_2, 10 ppbv O_3, 10ppbv NO, 10ppbv NO_2,10pptv HO_2, 1pptv OH and 10ppbv H_2S.

References

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Part B The H_2S + $^3O_2$ formations from the HO_2 + HS with catalyst *X* (*X* = H_2O) (pS8-pS13)

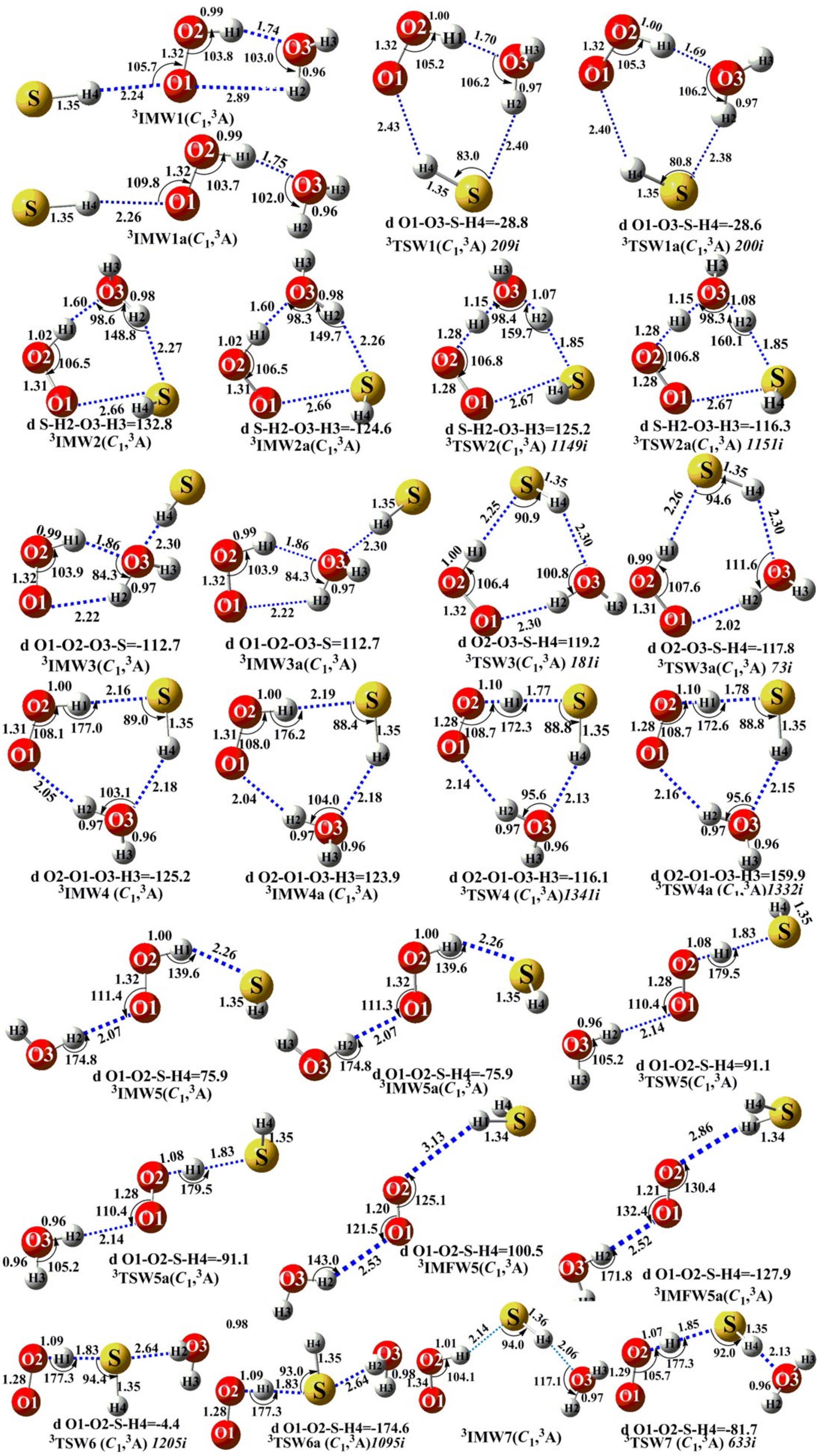

Figure S3 The geometrical structures of the optimized transitions state, intermediates, and complexes involved in water-assisted channels occurring through $H_2O\cdots HO_2$ + HS, $HO_2\cdots H_2O$ + HS, $HS\cdots H_2O$ + HO_2 and $H_2O\cdots HS$ + HO_2 reactants

Table S3 Zero point energy (ZPE/(kcal·mol^{-1})), entropies (S/ (cal·mol^{-1}·K^{-1})), relative energies (ΔE and Δ(E+ZPE)/(kcal·mol^{-1})), enthalpies (ΔH(298)/(kcal·mol^{-1})), and free energies (ΔG(298)/(kcal·mol^{-1})) for the binary complexes ($H_2O\cdots HO_2$, $HO_2\cdots H_2O$, $HS\cdots H_2O$, $HS\cdots H_2O$, and $H_2O\cdots H_2O$)

Species	ZPE	S	ΔE	ΔH	ΔG	Δ(E+ZPE)
$H_2O + HO_2$	22.3	99.7	0.0	0.0	0.0	0.0
$H_2O\cdots HO_2$	24.8	72.6	-9.4	-7.6	0.5	-6.9
$HO_2\cdots H_2O$	23.9	80.0	-3.5	-2.0	3.9	-1.9
H_2O + HS	17.2	91.0	0.0	0.0	0.0	0.0
$H_2O\cdots HS$	18.6	72.7	-3.0	-1.9	3.6	-1.6
$HS\cdots H_2O$	18.2	75.9	-2.7	-1.8	2.7	-1.7

[a] ZPE and S values obtained at B3LYP/6-311+G(2df,2p) level of theory; The energy values are obtained at CCSD(T)/6-311++G(3df,2pd) level whereas the *H* and *G* corrections are taken from the B3LYP/6-311+G(2df,2p) level.

Table S4 Zero point energy (ZPE/(kcal·mol^{-1})), relative energies (ΔE and Δ(E+ZPE)/(kcal·mol^{-1})), enthalpies (Δ*H*(298)/(kcal·mol^{-1})), and free energies (ΔG(298)/(kcal·mol^{-1})) for water-assisted the formation of H_2S + $^3O_2$ from the HO_2 + HS reaction[a]

Species	ZPE	ΔE	ΔH(298)	ΔG(298)	Δ(E+ZPE)
H_2O•••HO_2 + HS	28.6	0.0	0.0	0.0	0.0
^{3}IMW1	29.5	-3.4	-4.4	1.1	-2.6
^{3}IMW1a	29.5	-3.4	-4.5	1.3	-2.6
^{3}TSW1	29.6	-3.3	-5.0	3.8	-2.3
^{3}TSW1a	29.6	-3.2	-4.9	3.9	-2.2
^{3}IMW2	30.4	4.4	-4.1	5.7	-3.3
^{3}IMW2a	30.4	4.3	-4.2	5.6	-3.4
^{3}TSW2	27.3	17.1	4.7	16.3	6.3
^{3}TSW2a	27.3	17.0	4.6	16.1	6.2
^{3}IMW3	29.7	-3.8	-2.7	3.3	-2.7
^{3}IMW3a	29.7	-3.8	36.9	3.3	-2.7
^{3}TSW3	29.3	-3.2	-37.9	5.5	-2.5
^{3}TSW3a	28.6	-2.4	-2.7	5.1	-2.4
^{3}IMW4	28.6	-2.9	-2.9	4.0	-3.0
^{3}IMW4a	28.6	-3.0	-2.9	3.9	-3.0
^{3}TSW4	26.1	5.7	2.5	11.2	3.1
^{3}TSW4a	25.9	5.7	2.5	10.7	2.9
H_2O•••H_2S + $^3O_2$	26.5	-34.2	-35.6	-37.8	-36.3
HO_2•••H_2O + HS	28.4	0.0	0.0	0.0	0.0
^{3}IMW5	28.8	-6.9	-5.9	-1.3	-4.1
^{3}IMW5a	28.8	-6.9	-5.9	-1.2	-4.2
^{3}TSW5	25.6	0.5	-2.0	3.3	0.0
^{3}TSW5a	25.6	0.5	-2.0	3.3	-0.1
^{3}IMFW5	26.0	-40.1	-40.3	-43.6	-40.3
^{3}IMFW5a	27.1	-39.6	-39.7	-38.1	-40.6
H_2O+$^3O_2$ + H_2S	25.2	-38.8	-41.2	-49.1	-39.8
HO_2 + HS•••H_2O	27.1	0.0	0.0	0.0	0.0
^{3}TSW6	26.2	6.1	2.7	14.7	5.1
^{3}TSW6a	26.0	6.5	4.1	15.7	5.5
H_2S•••H_2O + $^3O_2$	27.3	-40.5	-41.0	-37.7	-40.3
H_2O•••HS + HO_2	27.5	0.0	0.0	0.0	0.0
^{3}IMW7	29.6	-10.3	-8.9	1.8	-8.2
^{3}TSW7	25.9	-0.2	-2.7	7.5	-1.8
H_2O•••H_2S + $^3O_2$	26.5	-40.7	-41.4	-40.9	-41.6

[a] ZPE values obtained at B3LYP/6-311+G(2df,2p) level of theory; The energy values are obtained at CCSD(T)/6-311++G(3df,2pd) level whereas the *H* and *G* corrections are taken from the B3LYP/6-311+G(2df,2p) level.

Table S5 Rate constants (cm^3·molecules^{-1}·s^{-1}) for the H_2S + $^3O_2$ formations from the HO_2 + HS reaction occurring through water-assisted Channels RW1a, RW1b, RW2 and RW3 within the temperature range of 240.0-425.0 K

T/K	Keq(IMW1)	Keq(IMW1a)	k_{TSW1}	k_{TSW1a}	k_{TSW2}	k_{TSW2a}	k_{RW1a}
240	4.51E-24	4.51E-24	2.88E-18	2.49E-18	2.53E+04	3.77E+04	5.37E-18
250	5.11E-24	5.11E-24	3.29E-18	3.09E-18	4.32E+04	6.38E+04	6.38E-18
278	7.14E-24	7.14E-24	4.68E-18	5.37E-18	1.73E+05	2.49E+05	1.01E-17
288	8.00E-24	8.00E-24	5.27E-18	6.44E-18	2.73E+05	3.88E+05	1.17E-17
298	8.93E-24	8.93E-24	5.91E-18	7.66E-18	4.21E+05	5.93E+05	1.36E-17
308	9.95E-24	9.95E-24	6.60E-18	9.05E-18	6.35E+05	8.88E+05	1.57E-17
325	1.19E-23	1.19E-23	7.93E-18	1.19E-17	1.22E+06	1.69E+06	1.98E-17
375	1.92E-23	1.92E-23	1.29E-17	2.41E-17	6.26E+06	8.37E+06	3.70E-17
425	2.96E-23	2.96E-23	2.00E-17	4.43E-17	2.27E+07	2.97E+07	6.43E-17
T/K	Keq(IMW3)	Keq(IMW3a)	k_{TSW3}	k_{TSW3a}	k_{TSW4}	k_{TSW4a}	k_{RW1b}
240	6.51E-12	2.27E-13	3.44E-08	2.00E-08	1.44E+12	1.74E+12	5.44E-08
250	1.87E-12	6.93E-14	2.01E-08	1.16E-08	1.45E+12	1.80E+12	3.17E-08
278	9.79E-14	4.18E-15	5.90E-09	3.32E-09	1.47E+12	1.97E+12	9.22E-09
288	4.02E-14	1.78E-15	4.13E-09	2.30E-09	1.48E+12	2.02E+12	6.43E-09
298	1.77E-14	8.19E-16	2.99E-09	1.66E-09	1.49E+12	2.07E+12	4.65E-09
308	8.28E-15	3.98E-16	2.23E-09	1.23E-09	1.50E+12	2.11E+12	3.46E-09
325	2.59E-15	1.31E-16	1.44E-09	7.85E-10	1.51E+12	2.18E+12	2.23E-09
375	1.70E-16	9.81E-18	5.47E-10	2.91E-10	1.54E+12	2.35E+12	8.38E-10
425	2.32E-17	1.48E-18	2.86E-10	1.50E-10	1.57E+12	2.47E+12	4.36E-10
T/K	k_{TSW5}	k_{TSW5a}	k_{RW2}	k_{TSW6}	k_{TSW6}	k_{RW3}	k_{RW4}
240	4.73E-09	4.77E-09	9.50E-09	5.44E-18	9.39E-19	6.38E-18	7.54E-14
250	3.97E-09	4.00E-09	7.97E-09	6.49E-18	1.19E-18	7.68E-18	7.26E-14
278	2.70E-09	2.72E-09	5.42E-09	1.03E-17	2.23E-18	1.25E-17	6.66E-14
288	2.42E-09	2.44E-09	4.86E-09	1.20E-17	2.76E-18	1.48E-17	6.51E-14
298	2.20E-09	2.22E-09	4.42E-09	1.40E-17	3.38E-18	1.73E-17	6.37E-14
308	2.03E-09	2.04E-09	4.07E-09	1.61E-17	4.12E-18	2.02E-17	6.26E-14
325	1.80E-09	1.81E-09	3.61E-09	2.04E-17	5.67E-18	2.60E-17	6.10E-14
375	1.41E-09	1.42E-09	2.83E-09	3.76E-17	1.31E-17	5.08E-17	5.84E-14
425	1.25E-09	1.26E-09	2.51E-09	6.37E-17	2.68E-17	9.05E-17	5.79E-14

Keq(IMW1) and Keq(IMW1a) is the equilibrium constant for the process of H_2O•••HO_2 + HS → ^{3}IMW1 and H_2O•••HO_2 + HS → ^{3}IMW1a, respectively; Keq(IMW3) and Keq(IMW3a) is the equilibrium constant for the process of H_2O•••HO_2 + HS → ^{3}IMW1 and H_2O•••HO_2 + HS → ^{3}IMW1a, respectively; k_{TSW1} and k_{TSW1a} is the rate constant for the process of H_2O•••HO_2 + HS → ^{3}IMW1 → ^{3}TSW1 → ^{3}IMW2 and H_2O•••HO_2 + HS → ^{3}IMW1a → ^{3}TSW1a → ^{3}IMW2a, respectively; k_{TSW2} and k_{TSW2a} is the rate constant for the process of ^{3}IMW2 → ^{3}TSW2 → H_2O•••H_2S + $^3O_2$ and ^{3}IMW2a → ^{3}TSW2a → H_2O•••H_2S + $^3O_2$, respectively; k_{TSW3} and k_{TSW3a} is the rate constant for the process of H_2O•••HO_2 + HS → ^{3}IMW3 → ^{3}TSW3 → ^{3}IMW4 and H_2O•••HO_2 + HS → ^{3}IMW3a → ^{3}TSW3a → ^{3}IMW4a, respectively; k_{TSW4} and k_{TSW4a} is the rate constant for the process of ^{3}IMW4 → ^{3}TSW4 → H_2O•••H_2S + $^3O_2$ and ^{3}IMW4a → ^{3}TSW4a → H_2O•••H_2S + $^3O_2$, respectively; k_{TSW5} and k_{TSW5a} is the rate constant for the process of HO_2•••H_2O + HS → ^{3}IMW5 → ^{3}TSW5 → ^{3}IMFW5 → H_2O + $^3O_2$ + H_2S and

HO_2•••H_2O + HS → ^{3}IMW5a → ^{3}TSW5a → ^{3}IMFW5a → H_2O + $^3O_2$ + H_2S, respectively; k_{TSW6} and k_{TSW6a} is the rate constant for the process of HS•••H_2O + HO_2 → ^{3}TSW6 → H_2S•••H_2O + $^3O_2$ and HS•••H_2O + HO_2 → ^{3}TSW6a → H_2S•••H_2O + $^3O_2$, respectively; k_{RW1a}, $k_{RW1b,}$ k_{RW2} , $k_{RW3,}$ and k_{RW4} is the rate constant of water dimer- assisted Channels RW1a, RWW1b, RWW2, RWW3 and RWW4. ($1/k_{RW1a} = 1/(k_{TSW1} + k_{TSW1a}) + 1/(k_{TSW2} + k_{TSW2a})$, $1/k_{RW1b} = 1/(k_{TSW3} + k_{TSW3a}) + 1/(k_{TSW4} + k_{TSW4a})$, $k_{RWW2} = k_{TSW5} + k_{TSW5a}$, $k_{RWW3} = k_{TSW6} + k_{TSW6a}$)

Part C The H_2S + $^3O_2$ formations from the HO_2 + HS with catalyst *X* (*X* = $(H_2O)_2$) (pS14-pS23)

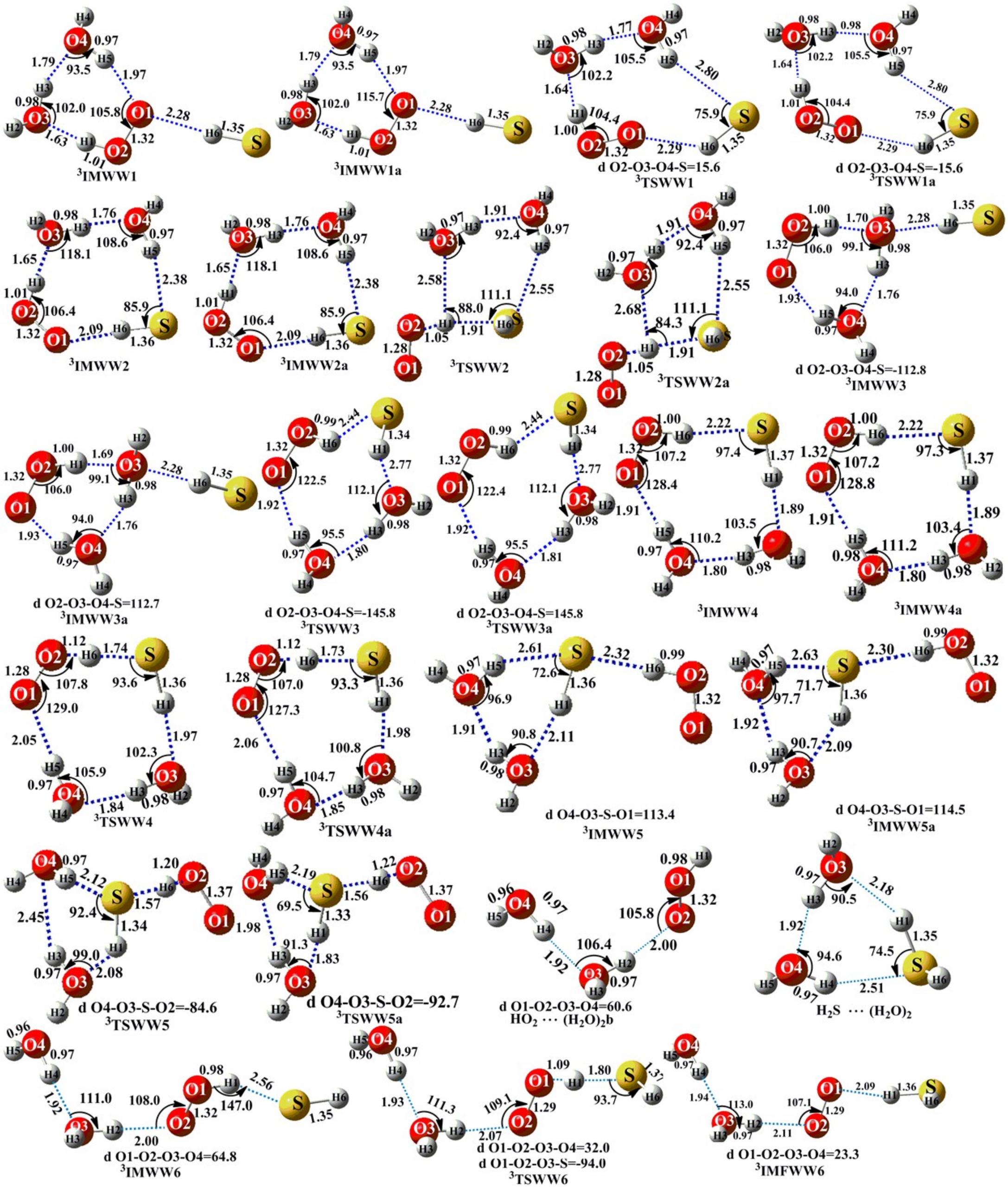

Figure S4 The geometrical structures of the optimized transitions state, intermediates, and complexes involving water dimer-assisted Channels occurring through $HO_2 \cdots (H_2O)_2$ ($HO_2 \cdots (H_2O)_2a$, $HO_2 \cdots (H_2O)_2b$) + HS and $HS \cdots (H_2O)_2$ ($HS \cdots (H_2O)_2a$) + HO_2

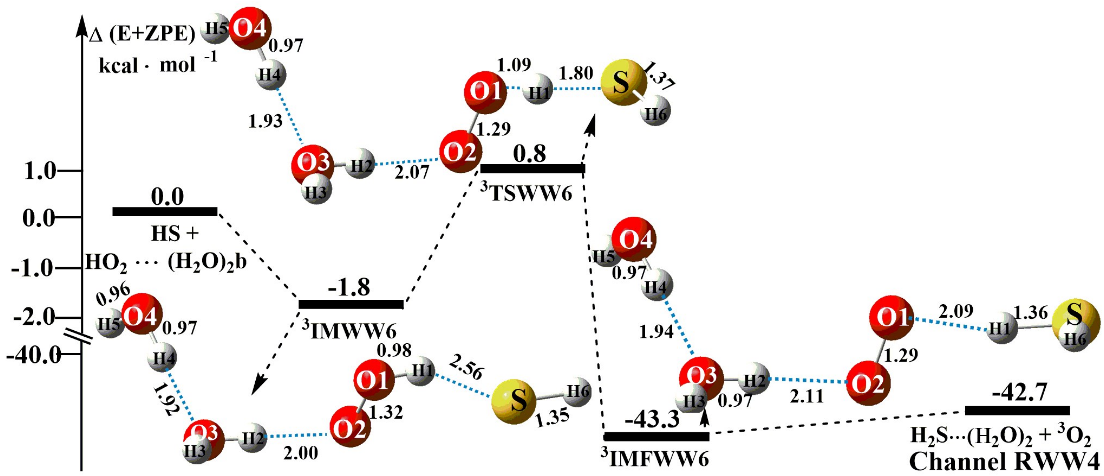

Figure S5 Schematic energy diagrams of water dimer-assisted the channel of H_2S + $^3O_2$ formations occurring through $HO_2\cdots(H_2O)_2b$ + HS

Table S6 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 (ΔH(298)/(kcal·mol^{-1})), and free energies (ΔG(298)/(kcal·mol^{-1})) for the trinary complexes ($HO_2\cdots(H_2O)_2$, $HO_2\cdots(H_2O)_2$a, $HO_2\cdots(H_2O)_2$b, $HS\cdots(H_2O)_2$, $HS\cdots(H_2O)_2$a and $(H_2O)_2$)

Species	ZPE	S	△E	△H	△G	△(E+ZPE)
$H_2O + H_2O$	26.8	90.2	0.0	0.0	0.0	0.0
$(H_2O)_2$	29.0	69.4	-5.3	-3.6	22.7	-3.1
$(H_2O)_2 + HO_2$	37.9	124.0	0.0	0.0	0.0	0.0
$HO_2\cdots (H_2O)_2$	41.2	83.6	-15.8	-13.9	-21.9	-12.6
$HO_2\cdots$ (H2O)$_2$a	41.2	83.6	-15.8	-13.9	-21.9	-12.6
$HO_2\cdots$ (H2O)$_2$b	39.5	101.0	-4.7	-3.2	-16.4	-3.2
$(H_2O)_2 + HS$	32.8	115.3	0.0	0.0	0.0	0.0
$HS\cdots (H_2O)_2$	34.7	85.9	-6.2	-5.0	-16.4	-4.3
$HS\cdots (H_2O)_2$a	34.7	85.8	-6.2	-5.0	-16.4	-4.3

[a] ZPE and S values obtained at B3LYP/6-311+G(2df,2p) level of theory; The energy values are obtained at CCSD(T)/6-311++G(3df,2pd) level whereas the *H* and *G* corrections are taken from the B3LYP/6-311+G(2df,2p) level.

Table S7 Zero point energy (ZPE/(kcal·mol^{-1})), relative energies (Δ*E* and Δ(*E*+ZPE)/(kcal·mol^{-1})), enthalpies (Δ*H*(298)/(kcal·mol^{-1})), and free energies (Δ*G*(298)/(kcal·mol^{-1})) for the HO_2 + HS with two water molecule reaction

Species	ZPE	ΔE	ΔH(298)	ΔG(298)	Δ(E+ZPE)
HO_2•••$(H_2O)_2$ + HS	45.0	0.0	0.0	0.0	0.0
HO_2•••$(H_2O)_2$a + HS	45.0	0.0	0.0	0.0	0.0
^{3}IMWW1	45.8	-3.7	-2.7	2.8	-2.8
^{3}IMWW1a	45.8	-3.7	-2.7	2.7	-2.8
^{3}TSWW1	45.2	-2.6	-2.5	4.5	-2.5
^{3}TSWW1a	45.2	-2.6	-2.5	4.5	-2.5
^{3}IMWW2	45.6	-3.2	-2.4	3.9	-2.7
^{3}IMWW2a	45.6	-3.2	-2.4	3.9	-2.7
^{3}TSWW2	42.5	10.9	9.4	15.3	8.9
^{3}TSWW2a	42.4	11.0	8.8	14.8	8.3
^{3}IMWW3	46.0	-2.5	-1.4	4.6	-1.5
^{3}IMWW3a	46.0	-2.5	-1.4	4.6	-1.5
^{3}TSWW3	44.6	1.9	1.8	8.3	1.6
^{3}TSWW3a	44.6	1.9	1.8	8.3	1.6
^{3}IMWW4	45.5	-3.8	0.3	6.9	-3.6
^{3}IMWW4a	45.5	-3.8	0.3	6.9	-3.6
^{3}TSWW4	41.8	9.4	6.1	13.3	6.0
^{3}TSWW4a	41.7	9.6	6.4	13.4	6.2
H_2S •••$(H_2O)_2$ + $^3O_2$	43.3	-29.1	-30.1	-32.1	-30.9
H_2S •••$(H_2O)_2$ a + $^3O_2$	43.3	-29.1	-30.2	-32.1	-31.0
HS•••$(H_2O)_2$ + HO_2	43.6	0.0	0.0	0.0	0.0
HS•••$(H_2O)_2$ a + HO_2	43.6	0.0	0.0	0.0	0.0
^{3}IMWW5	45.0	1.4	-4.7	-3.3	-3.3
^{3}IMWW5a	45.0	1.4	-4.9	-3.4	-3.4
^{3}TSWW5	40.5	-3.1	14.1	9.3	11.1
^{3}TSWW5a	41.5	-2.0	8.3	4.6	6.3
H_2S •••$(H_2O)_2$ + $^3O_2$	43.3	-0.3	-38.3	-38.9	-39.0
H_2S •••$(H_2O)_2$ a + $^3O_2$	43.3	-0.3	-38.8	-39.0	-39.1
HO_2•••$(H_2O)_2$b + HS	43.3	0.0	0.0	0.0	0.0
^{3}IMWW6	43.9	-2.5	-2.1	5.4	-1.8
^{3}TSWW6	41.2	2.8	-0.5	4.9	0.8
^{3}IMFWW6	43.2	-43.3	-43.3	-36.3	-43.3
H_2S •••$(H_2O)_2$ + $^3O_2$	42.9	-42.3	-43.3	-40.1	-42.7

^{a} ZPE and S values obtained at B3LYP/6-311+G(2df,2p) level of theory; The energy values are obtained at CCSD(T)/ 6-311++G(3df,2pd) level whereas the *H* and *G* corrections are taken from the B3LYP/6-311+G(2df,2p) level.

Table S8 Equilibrium Constants and concentration of water dimer within the temperature range of 240.0-425.0 K

T/K	$[H_2O]$	$Keq((H_2O)_2)$	$[(H_2O)_2]$
240	8.29E+15	4.36E-22	3.00E+10
250	2.21E+16	3.34E-22	1.63E+11
278	2.25E+17	1.78E-22	8.99E+12
288	4.25E+17	1.47E-22	2.65E+13
298	7.64E+17	1.23E-22	7.18E+13
308	1.31E+18	1.05E-22	1.79E+14
325	3.04E+18	8.15E-23	7.54E+14
375	2.12E+19	4.61E-23	2.07E+16
425	8.56E+19	3.09E-23	2.26E+17

$[(H_2O)_2] = Keq((H_2O)_2)\ [H_2O]^2$

Table S9 Rate constants ($cm^3\cdot molecules^{-1}\cdot s^{-1}$) for the H_2S + $^3O_2$ formations from the HO_2+ HS reaction occurring through water dimer-assisted Channels RWW1-RWW4 within the temperature range of 240.0-425.0 K

T/K	Keq(IMWW1)	Keq(IMWW1a)	k_{TSWW1}	k_{TSWW1a}	k_{TSWW2}	k_{TSWW2a}
240	4.20E-26	5.24E-26	2.63E-20	8.45E-20	6.75E+02	2.26E+02
250	4.63E-26	5.78E-26	5.14E-20	2.14E-19	1.77E+03	6.27E+02
278	5.52E-26	6.89E-26	3.32E-19	1.26E-18	1.85E+04	7.46E+03
288	6.01E-26	7.50E-26	9.76E-19	2.35E-18	3.84E+04	1.61E+04
298	6.37E-26	7.95E-25	1.92E-18	5.11E-18	7.58E+04	3.31E+04
308	6.80E-26	8.48E-25	4.22E-18	7.05E-18	1.44E+05	6.51E+04
325	7.30E-26	9.11E-25	8.27E-18	1.75E-17	3.90E+05	1.87E+05
375	9.37E-26	1.17E-24	9.32E-18	2.34E-17	4.41E+06	2.41E+06
425	1.04E-25	1.30E-24	5.21E-17	7.04E-17	2.86E+07	1.73E+07

k_{RWW1}	k_{RWW1a}	Keq(IMWW3)	Keq(IMWW3a)	k_{TSWW3}	k_{TSWW3a}	k_{TSWW4}
2.63E-20	8.45E-20	1.22E-23	1.23E-23	7.26E-17	7.17E-17	3.10E+08
5.14E-20	2.14E-19	1.30E-23	1.31E-23	9.01E-17	8.91E-17	3.95E+08
3.32E-19	1.26E-18	1.48E-23	1.48E-23	1.56E-16	1.54E-16	7.53E+08
9.76E-19	2.35E-18	1.58E-23	1.58E-23	1.86E-16	1.84E-16	9.38E+08
1.92E-18	5.11E-18	1.65E-23	1.66E-23	2.21E-16	2.18E-16	1.16E+09
4.22E-18	7.05E-18	1.73E-23	1.74E-23	2.60E-16	2.57E-16	1.43E+09
8.27E-18	1.75E-17	1.83E-23	1.84E-23	3.37E-16	3.33E-16	2.01E+09
9.32E-18	2.34E-17	2.24E-23	2.25E-23	6.59E-16	6.52E-16	4.93E+09
5.21E-17	7.04E-17	2.44E-23	2.45E-23	1.16E-15	1.14E-15	1.05E+10

k_{TSWW4a}	k_{RWW2}	k_{RWW2a}	k_{RWW3}	k_{RWW3a}	k_{RWW4}
3.31E+08	7.26E-17	7.17E-17	4.01E-22	3.83E-22	4.61E-15
4.24E+08	9.01E-17	8.91E-17	4.60E-22	4.15E-22	4.41E-15
8.25E+08	1.56E-16	1.54E-16	7.75E-22	6.03E-22	4.04E-15
1.03E+09	1.86E-16	1.84E-16	9.68E-22	7.19E-22	3.96E-15
1.29E+09	2.21E-16	2.18E-16	1.23E-21	8.71E-22	3.89E-15
1.59E+09	2.60E-16	2.57E-16	1.58E-21	1.07E-21	3.85E-15
2.24E+09	3.37E-16	3.33E-16	2.45E-21	1.55E-21	3.79E-15
5.51E+09	6.59E-16	6.52E-16	9.26E-21	4.86E-21	3.77E-15
1.18E+10	1.16E-15	1.14E-15	3.24E-20	1.45E-20	3.88E-15

Keq(IMWW1) and Keq(IMWW1a) is the equilibrium constant for the process of HO_2•••$(H_2O)_2$ + HS → ^{3}IMW1 and HO_2•••$(H_2O)_2$a + HS → ^{3}IMW1a respectively; Keq(IMWW3) and Keq(IMWW3a) is the equilibrium constant for the process of HO_2•••$(H_2O)_2$ + HS → ^{3}IMW3 and HO_2•••$(H_2O)_2$a + HS → ^{3}IMW3a respectively; k_{TSWW1} and k_{TSWW1a} is the rate constant for the process of HO_2•••$(H_2O)_2$ + HS → ^{3}IMWW1 → ^{3}TSWW1 → ^{3}IMWW2 and HO_2•••$(H_2O)_2$a + HS → ^{3}IMWW1a → ^{3}TSWW1a → ^{3}IMWW2a, respectively; k_{TSWW2} and k_{TSWW2a} is the rate constant for the process of ^{3}IMWW2 → ^{3}TSWW2 → H_2S•••$(H_2O)_2$ + $^3O_2$ and ^{3}IMWW2a → ^{3}TSWW2a → H_2S•••$(H_2O)_2$a + $^3O_2$, respectively; k_{RWW1} and k_{RWW1a} is the rate constant for the process of HO_2•••$(H_2O)_2$ + HS → ^{3}IMWW1 → ^{3}TSWW1 → ^{3}IMWW2 → ^{3}TSWW2 → H_2S•••$(H_2O)_2$ + $^3O_2$ and HO_2•••$(H_2O)_2$a + HS → ^{3}IMWW1a → ^{3}TSWW1a → ^{3}IMWW2a → ^{3}TSWW2a → H_2S•••$(H_2O)_2$a + $^3O_2$, respectively; k_{TSWW3} and k_{TSWW3a} is the rate constant for the process of HO_2•••$(H_2O)_2$ + HS → ^{3}IMWW3 → ^{3}TSWW3 → ^{3}IMWW4 and HO_2•••$(H_2O)_2$a + HS → ^{3}IMWW3a → ^{3}TSWW3a → ^{3}IMWW4a, respectively; k_{TSWW4} and k_{TSWW4a} is the rate constant for the process of ^{3}IMWW4 → ^{3}TSWW4 → H_2S•••$(H_2O)_2$ + $^3O_2$ and ^{3}IMWW4a → ^{3}TSWW4a → H_2S•••$(H_2O)_2$a + $^3O_2$, respectively; k_{RWW2} and k_{RWW2a} is the rate constant for the process of HO_2•••$(H_2O)_2$ + HS → ^{3}IMWW3 → ^{3}TSWW3 → ^{3}IMWW4 → ^{3}TSWW4 → H_2S•••$(H_2O)_2$ + $^3O_2$ and HO_2•••$(H_2O)_2$a + HS → ^{3}IMWW3a → ^{3}TSWW3a → ^{3}IMWW4a → ^{3}TSWW4a → H_2S•••$(H_2O)_2$a + $^3O_2$, respectively; k_{RWW3} and k_{RWW3a} is the rate constant for the process of HS•••$(H_2O)_2$ + HO_2 → ^{3}IMWW5 → ^{3}TSWW5 → H_2S•••$(H_2O)_2$ + $^3O_2$ and HS•••$(H_2O)_2$a + HO_2 → ^{3}IMWW5a → ^{3}TSWW5a → H_2S•••$(H_2O)_2$a + $^3O_2$, respectively; k_{RWW4} is the rate constant of water dimer-assisted Channels RWW4. ($1/k_{RWW1} = 1/k_{TSWW1} + 1/k_{TSWW2}$, $1/k_{RWW1a} = 1/k_{TSWW1a} + 1/k_{TSWW2a}$, $1/k_{RWW2} = 1/k_{TSWW3} + 1/k_{TSWW4}$, $1/k_{RWW2a} = 1/ k_{TSWW3a} + 1/k_{TSWW4a}$)

Table S10 Effective Rate constants ($cm^3 \cdot molecules^{-1} \cdot s^{-1}$) for the H_2S + $^3O_2$ formations from the HO_2+ HS reaction occurring through water dimer-assisted Channels RWW1, RWW2 RWW3 and RWW4 within the temperature range of 240.0-425.0 K

T/K	$[(H_2O)_2]$	$Keq(HO_2\cdots(H_2O)_2)$	$Keq(HO_2\cdots(H_2O)_2a)$	k_{RWW1}	k_{RWW1a}
240	3.00E+10	2.01E-16	2.04E-16	2.63E-20	8.45E-20
250	1.63E+11	6.57E-17	6.65E-17	5.14E-20	2.14E-19
278	8.99E+12	4.41E-18	4.46E-18	3.32E-19	1.26E-18
288	2.65E+13	1.91E-18	1.93E-18	9.76E-19	2.35E-18
298	7.18E+13	8.76E-19	8.86E-19	1.92E-18	5.11E-18
308	1.79E+14	4.23E-19	4.27E-19	4.22E-18	7.05E-18
325	7.54E+14	1.36E-19	1.38E-19	8.27E-18	1.75E-17
375	2.07E+16	8.92E-21	9.02E-21	9.32E-18	2.34E-17
425	2.26E+17	1.13E-21	1.14E-21	5.21E-17	7.04E-17

k'_{RWW1}	k'_{RWW1a}	k_{RWW2}	k_{RWW2a}	k'_{RWW2}	k'_{RWW2}
1.59E-25	5.16E-25	7.26E-17	7.17E-17	4.38E-22	4.38E-22
5.51E-25	2.32E-24	9.01E-17	8.91E-17	9.66E-22	9.65E-22
1.32E-23	5.05E-23	1.56E-16	1.54E-16	6.18E-21	6.18E-21
4.94E-23	1.20E-22	1.86E-16	1.84E-16	9.43E-21	9.43E-21
1.21E-22	3.25E-22	2.21E-16	2.18E-16	1.39E-20	1.39E-20
3.19E-22	5.39E-22	2.60E-16	2.57E-16	1.97E-20	1.96E-20
8.49E-22	1.82E-21	3.37E-16	3.33E-16	3.46E-20	3.46E-20
1.72E-21	4.37E-21	6.59E-16	6.52E-16	1.22E-19	1.22E-19
1.33E-20	1.82E-20	1.16E-15	1.14E-15	2.96E-19	2.96E-19

$Keq(HS\cdots(H_2O)_2)$	$Keq(HS\cdots(H_2O)_2a)$	k_{RWW3}	k_{RWW3a}	k'_{RWW3}	k'_{RWW3a}
3.20E-22	4.84E-22	4.01E-22	3.83E-22	3.85E-33	5.56E-33
2.09E-22	3.29E-22	4.60E-22	4.15E-22	1.57E-32	2.23E-32
7.44E-23	1.31E-22	7.75E-22	6.03E-22	5.18E-31	7.10E-31
5.41E-23	9.85E-23	9.68E-22	7.19E-22	1.39E-30	1.88E-30
4.02E-23	7.58E-23	1.23E-21	8.71E-22	3.55E-30	4.74E-30
3.04E-23	5.94E-23	1.58E-21	1.07E-21	8.60E-30	1.14E-29
1.98E-23	4.08E-23	2.45E-21	1.55E-21	3.66E-29	4.77E-29
7.04E-24	1.68E-23	9.26E-21	4.86E-21	1.35E-27	1.69E-27
3.24E-24	8.77E-24	3.24E-20	1.45E-20	2.37E-26	2.87E-26

$Keq(HO_2\cdots(H_2O)_2b)$	k_{RWW4}	k'_{RWW4}
1.16E-29	4.61E-15	1.60E-33
2.14E-29	4.41E-15	1.54E-32
9.60E-29	4.04E-15	3.49E-30
1.54E-28	3.96E-15	1.61E-29
2.40E-28	3.89E-15	6.70E-29
3.64E-28	3.85E-15	2.51E-28
7.03E-28	3.79E-15	2.01E-27
3.59E-27	3.77E-15	2.80E-25
1.32E-26	3.88E-15	1.16E-23

Keq($HO_2\cdots(H_2O)_2$) is the equilibrium constant of $HO_2\cdots(H_2O)_2$ complex; Keq($HO_2\cdots(H_2O)_2$a) is the equilibrium constant of $HO_2\cdots(H_2O)_2$a complex; Keq($HS\cdots(H_2O)_2$) is the equilibrium constant of $HS\cdots(H_2O)_2$ complex; Keq($HS\cdots(H_2O)_2$a) is the equilibrium constant of $HS\cdots(H_2O)_2$a complex; Keq($HO_2\cdots(H_2O)_2$b) is the equilibrium constant of $HO_2\cdots(H_2O)_2$b complex; k_{RWW1} and k_{RWW1a} is the rate constant for the process of $HO_2\bullet\bullet\bullet(H_2O)_2$ + HS → ^{3}IMWW1 → ^{3}TSWW1 → ^{3}IMWW2 → ^{3}TSWW2 → $H_2S\bullet\bullet\bullet(H_2O)_2$ + $^3O_2$ and $HO_2\bullet\bullet\bullet(H_2O)_2$a + HS → ^{3}IMWW1a → ^{3}TSWW1a → ^{3}IMWW2a → ^{3}TSWW2a → $H_2S\bullet\bullet\bullet(H_2O)_2$a + $^3O_2$, respectively; k_{RWW2} and k_{RWW2a} is the rate constant for the process of $HO_2\bullet\bullet\bullet(H_2O)_2$ + HS → ^{3}IMWW3 → ^{3}TSWW3 → ^{3}IMWW4 → ^{3}TSWW4 → $H_2S\bullet\bullet\bullet(H_2O)_2$ + $^3O_2$ and $HO_2\bullet\bullet\bullet(H_2O)_2$a + HS → ^{3}IMWW3a → ^{3}TSWW3a → ^{3}IMWW4a → ^{3}TSWW4a → $H_2S\bullet\bullet\bullet(H_2O)_2$a + $^3O_2$, respectively; k_{RWW3} and k_{RWW3a} is the rate constant for the process of $HS\bullet\bullet\bullet(H_2O)_2$ + HO_2 → ^{3}IMWW5 → ^{3}TSWW5 → $H_2S\bullet\bullet\bullet(H_2O)_2$ + $^3O_2$ and $HS\bullet\bullet\bullet(H_2O)_2$a + HO_2 → ^{3}IMWW5a → ^{3}TSWW5a → $H_2S\bullet\bullet\bullet(H_2O)_2$a + $^3O_2$, respectively; k_{RWW4} is the rate constant of water dimer-assisted Channels RWW4; [$(H_2O)_2$] is the concentration of the water dimer; k'_{RWW1} and k'_{RWW1a} is the effective rate constant for the process of $HO_2\bullet\bullet\bullet(H_2O)_2$ + HS → ^{3}IMWW1 → ^{3}TSWW1 → ^{3}IMWW2 → ^{3}TSWW2 → $H_2S\bullet\bullet\bullet(H_2O)_2$ + $^3O_2$ and $HO_2\bullet\bullet\bullet(H_2O)_2$a + HS → ^{3}IMWW1a → ^{3}TSWW1a → ^{3}IMWW2a → ^{3}TSWW2a → $H_2S\bullet\bullet\bullet(H_2O)_2$a + $^3O_2$, respectively; k'_{RWW2} and k'_{RWW2a} is the effective rate constant for the process of $HO_2\bullet\bullet\bullet(H_2O)_2$ + HS → ^{3}IMWW3 → ^{3}TSWW3 → ^{3}IMWW4 → ^{3}TSWW4 → $H_2S\bullet\bullet\bullet(H_2O)_2$ + $^3O_2$ and $HO_2\bullet\bullet\bullet(H_2O)_2$a + HS → ^{3}IMWW3a → ^{3}TSWW3a → ^{3}IMWW4a → ^{3}TSWW4a → $H_2S\bullet\bullet\bullet(H_2O)_2$a + $^3O_2$, respectively; k'_{RWW3} and k'_{RWW3a} is the effective rate constant for the process of $HS\bullet\bullet\bullet(H_2O)_2$ + HO_2 → ^{3}IMWW5 → ^{3}TSWW5 → $H_2S\bullet\bullet\bullet(H_2O)_2$ + $^3O_2$ and $HS\bullet\bullet\bullet(H_2O)_2$a + HO_2 → ^{3}IMWW5a → ^{3}TSWW5a → $H_2S\bullet\bullet\bullet(H_2O)_2$a + $^3O_2$, respectively; k'_{RWW4} the effective rate constant of water dimer-assisted Channels RWW4; ($k'_{RWW1} = k_{RWW1}$ · Keq($HO_2\cdots(H_2O)_2$) · [$(H_2O)_2$], $k'_{RWW1a} = k_{RWW1a}$ · Keq($HO_2\cdots(H_2O)_2$a) · [$(H_2O)_2$], $k'_{RWW2} = k_{RWW2}$ · Keq($HO_2\cdots(H_2O)_2$) · [$(H_2O)_2$], $k'_{RWW2a} = k_{RWW2a}$ · Keq($HO_2\cdots(H_2O)_2$a) · [$(H_2O)_2$], $k'_{RWW3} = k_{RWW3}$ · Keq($HS\bullet\bullet\bullet(H_2O)_2$) · [$(H_2O)_2$], $k'_{RWW3a} = k_{RWW3a}$ · Keq($HS\bullet\bullet\bullet(H_2O)_2$a) · [$(H_2O)_2$], $k'_{RWW4} = k_{RWW4}$ · Keq($HO_2\cdots(H_2O)_2$b) · [$(H_2O)_2$])

Part D The H_2S + $^3O_2$ formations from the HO_2 + HS with catalyst *X* (*X* = $(H_2O)_3$)(pS24-pS29)

Figure S6	The geometrical structures of the optimized transitions state, intermediates, and complexes involving in $HO_2\cdots(H_2O)_3$ ($HO_2\cdots(H_2O)_3$a) + HS reactions	**pS25**
Table S11	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 (ΔH(298)/(kcal·mol^{-1})), and free energies (ΔG(298)/(kcal·mol^{-1})) for the quadruple complexes ($HO_2\cdots(H_2O)_3$ and $HS\cdots(H_2O)_3$)	**pS26**
Table S12	Zero point energy (ZPE/(kcal·mol^{-1})), relative energies (ΔE and $\Delta(E$+ZPE)/(kcal·mol^{-1})), enthalpies (ΔH(298)/(kcal·mol^{-1})), and free energies (ΔG(298)/(kcal·mol^{-1})) for the HO_2 + HS with water trimer	**pS27**
Table S13	Equilibrium constants and concentration of water trimer-assisted the H_2S + $^3O_2$ formations from the HO_2 + HS reaction within the temperature range of 240.0-425.0 K	**pS28**
Table S14	Rate constants and effective rate constants (cm^3·molecules^{-1}·s^{-1}) for the H_2S + $^3O_2$ formations from the HO_2+HS reaction occurring through $HO_2\cdots(H_2O)_3$ ($HO_2\cdots(H_2O)_3$a) + HS reactions within the temperature range of 240.0-425.0 K	**pS29**

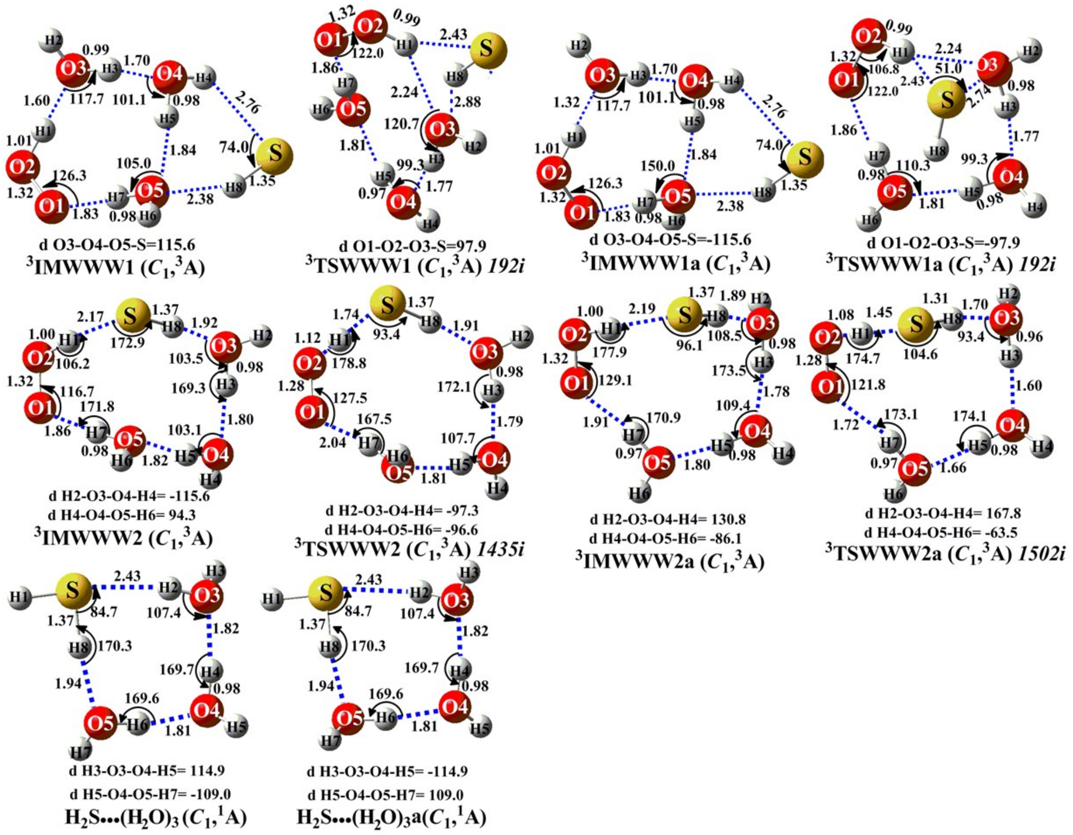

Figure S6 The geometrical structures of the optimized transitions state, intermediates, and complexes involving water trimer-assisted Channels occurring through $HO_2\cdots(H_2O)_3$ ($HO_2\cdots(H_2O)_3$a) + HS reactions

Table S11 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 (ΔH(298)/(kcal·mol^{-1})), and free energies (ΔG(298)/(kcal·mol^{-1})) for the quadruple complexes ($HO_2\cdots(H_2O)_3$ and $HS\cdots(H_2O)_3$)

Species	ZPE	S	△E	△H	△G	△(E+ZPE)
$(H_2O)_2 + H_2O$	42.4	114.5	0.0	0.0	0.0	0.0
$(H_2O)_3$	45.7	79.5	-11.0	-9.0	-18.7	-7.7
$(H_2O)_3 + HO_2$	54.6	134.2	0.0	0.0	0.0	0.0
$HO_2\cdots(H_2O)_3$	56.8	99.8	-14.6	-13.1	-2.8	-12.5
$HO_2\cdots(H_2O)_3$a	56.8	99.8	-14.6	-13.1	-2.8	-12.5
$(H_2O)_3 + HS$	49.5	125.4	0.0	0.0	0.0	0.0
$HS\cdots(H_2O)_3$	50.6	99.7	-4.9	-4.0	3.6	-3.8
$HS\cdots(H_2O)_3$a	50.6	99.7	-4.9	-4.0	3.6	-3.8

[a] ZPE and S values obtained at B3LYP/6-311+G(2df,2p) level of theory; The energy values are obtained at CCSD(T)/ 6-311++G(3df,2pd) level whereas the *H* and *G* corrections are taken from the B3LYP/6-311+G(2df,2p) level.

Table S12 Zero point energy (ZPE/(kcal·mol^{-1})), relative energies (ΔE and $\Delta(E$+ZPE)/(kcal·mol^{-1})), enthalpies (ΔH(298)/(kcal·mol^{-1})), and free energies (ΔG(298)/(kcal·mol^{-1})) for the HO_2 + HS with water trimer[a]

Species	ZPE	ΔE	ΔH	ΔG	Δ(E+ZPE)
$HO_2\cdots(H_2O)_3$+HS	60.6	0.0	0.0	0.0	0.0
$HO_2\cdots(H_2O)_3$+HSa	60.6	0.0	0.0	0.0	0.0
HS$\cdots(H_2O)_3+HO_2$	59.5	9.8	9.0	6.4	8.7
HS$\cdots(H_2O)_3+HO_2$a	59.5	9.8	9.0	6.4	8.7
^{3}IMWWW1	61.7	-4.1	-3.1	4.3	-3.0
^{3}IMWWW1a	61.7	-4.1	-3.1	4.3	-3.0
^{3}TSWWW1	60.8	1.6	1.8	10.0	1.9
^{3}TSWWW1a	60.8	1.6	1.8	10.0	1.9
^{3}IMWWW2	61.2	0.6	1.3	8.2	-0.8
^{3}IMWWW2a	61.0	1.5	2.1	8.4	-0.7
^{3}TSWWW2	57.5	10.3	7.2	14.6	7.3
^{3}TSWWW2a	57.4	10.7	7.5	14.3	7.5
$^3O_2+H_2S\cdots(H_2O)_3$	58.9	-31.0	-32.3	-33.6	-32.7
$^3O_2+H_2S\cdots(H_2O)_3$a	58.9	-31.0	-32.3	-33.6	-32.7

[a] ZPE values obtained at B3LYP/6-311+G(2df,2p) level of theory; The energy values are obtained at CCSD(T)/ 6-311++G(3df,2pd) level whereas the *H* and *G* corrections are taken from the B3LYP/6-311+G(2df,2p) level.

Table S13 Equilibrium constants and concentration of water trimer-assisted the H_2S + $^3O_2$ formation from the HO_2+ HS reaction within the temperature range of 240.0-425.0 K

T /K	Keq$(H_2O)_3$	$[(H_2O)_2]$	$[H_2O]$	$[(H_2O)_3]$
240	6.00E-20	3.00E+10	8.29E+15	1.49E+07
250	2.95E-20	1.63E+11	2.21E+16	1.06E+08
278	5.30E-21	8.99E+12	2.25E+17	1.07E+10
288	3.12E-21	2.65E+13	4.25E+17	3.51E+10
298	1.90E-21	7.18E+13	7.64E+17	1.04E+11
308	1.20E-21	1.79E+14	1.31E+18	2.82E+11
325	5.88E-22	7.54E+14	3.04E+18	1.35E+12
375	1.06E-22	2.07E+16	2.12E+19	4.66E+13
425	2.94E-23	2.26E+17	8.56E+19	5.69E+14

$[(H_2O)_3]$= Keq$(H_2O)_3$ · $[(H_2O)_2]$ · $[H_2O]$

Table S14 Rate constants and effective rate constants (cm^3·$molecules^{-1}$·s^{-1}) for the H_2S + $^3O_2$ formations from the HO_2+HS reaction occurring through $HO_2\cdots(H_2O)_3$ ($HO_2\cdots(H_2O)_3a$) + HS reactions within the temperature range of 240.0-425.0 K

T/K	Keq(TSWWW1)	Keq(TSWWW1a)	k_{TSWWW1}	$k_{TSWWW1a}$	k_{TSWWW2}	$k_{TSWWW2a}$
240	9.24E-26	1.89E-25	5.48E-18	7.31E-18	2.54E+08	1.05E+09
250	8.85E-26	1.85E-25	8.01E-18	2.10E-17	3.30E+08	1.32E+09
278	8.61E-26	1.86E-25	2.02E-17	3.57E-17	6.58E+08	2.40E+09
288	8.70E-26	1.91E-25	2.66E-17	4.78E-17	8.31E+08	2.94E+09
298	8.88E-26	1.97E-25	4.20E-17	7.05E-17	1.04E+09	3.57E+09
308	9.14E-26	2.05E-25	5.54E-17	9.78E-17	1.30E+09	4.33E+09
325	9.73E-26	2.21E-25	9.41E-17	1.90E-16	1.85E+09	5.90E+09
375	1.24E-25	2.88E-25	4.69E-16	7.11E-16	4.67E+09	1.33E+10
425	1.63E-25	3.86E-25	1.14E-15	2.43E-15	1.01E+10	2.65E+10

k_{RWWW1}	k_{RWWW1a}	Keq($HO_2\cdots(H_2O)_3$)	Keq($HO_2\cdots(H_2O)_3a$)	[$(H_2O)_3$]	k'_{RWWW1}	k'_{RWWW1a}
5.48E-18	7.31E-18	7.84E-16	7.84E-16	1.49E+07	6.40E-26	8.54E-26
8.01E-18	2.10E-17	2.73E-16	2.73E-16	1.06E+08	2.32E-25	6.08E-25
2.02E-17	3.57E-17	2.14E-17	2.14E-17	1.07E+10	4.63E-24	8.19E-24
2.66E-17	4.78E-17	9.76E-18	9.76E-18	3.51E+10	9.12E-24	1.64E-23
4.20E-17	7.05E-17	4.70E-18	4.70E-18	1.04E+11	2.05E-23	3.44E-23
5.54E-17	9.78E-17	2.37E-18	2.37E-18	2.82E+11	3.71E-23	6.54E-23
9.41E-17	1.90E-16	8.20E-19	8.20E-19	1.35E+12	1.04E-22	2.10E-22
4.69E-16	7.11E-16	6.43E-20	6.43E-20	4.66E+13	1.40E-21	2.13E-21
1.14E-15	2.43E-15	9.40E-21	9.40E-21	5.69E+14	6.10E-21	1.30E-20

Keq(IMWWW1) and Keq(IMWWW1a) is the equilibrium constant for the process of $HO_2\cdots(H_2O)_3$ + HS → ^{3}IMWWW1 and $HO_2\cdots(H_2O)_3a$ + HS → ^{3}IMWWW1a, respectively; k_{TSWWW1} and $k_{TSWWW1a}$ is the rate constant for the process of $HO_2\bullet\bullet\bullet(H_2O)_3$ + HS → ^{3}IMWWW1 → ^{3}TSWWW1 → ^{3}IMWWW2 and $HO_2\bullet\bullet\bullet(H_2O)_3a$ + HS → ^{3}IMWWW1a → ^{3}TSWWW1a → ^{3}IMWWW2a, respectively; k_{TSWWW2} and $k_{TSWWW2a}$ is the rate constant for the process of ^{3}IMWWW2 → ^{3}TSWWW2 → $H_2S\bullet\bullet\bullet(H_2O)_3$ + $^3O_2$ and ^{3}IMWWW2a → ^{3}TSWWW2a → $H_2S\bullet\bullet\bullet(H_2O)_3a$ + $^3O_2$, respectively; k_{RWWW1} and k_{RWWW1a} is the rate constant for the process of $HO_2\bullet\bullet\bullet(H_2O)_3$ + HS → ^{3}IMWWW1 → ^{3}TSWWW1 → ^{3}IMWWW2 → ^{3}TSWWW2 → $H_2S\bullet\bullet\bullet(H_2O)_3$ + $^3O_2$ and $HO_2\bullet\bullet\bullet(H_2O)_3a$ + HS → ^{3}IMWWW1a → ^{3}TSWWW1a → ^{3}IMWWW2a → ^{3}TSWWW2a → $H_2S\bullet\bullet\bullet(H_2O)_3a$ + $^3O_2$, respectively; Keq($HO_2\cdots(H_2O)_3$) is the equilibrium constant of $HO_2\cdots(H_2O)_3$ complex; Keq($HO_2\cdots(H_2O)_3a$) is the equilibrium constant of $HO_2\cdots(H_2O)_3a$ complex; [$(H_2O)_3$] is the concentration of the water trimer; k'_{RWWW1} and k'_{RWWW1a} is the effective rate constant for the process of $HO_2\bullet\bullet\bullet(H_2O)_3$ + HS → ^{3}IMWWW1 → ^{3}TSWWW1 → ^{3}IMWWW2 → ^{3}TSWWW2 → $H_2S\bullet\bullet\bullet(H_2O)_3$ + $^3O_2$ and $HO_2\bullet\bullet\bullet(H_2O)_3a$ + HS → ^{3}IMWWW1a → ^{3}TSWWW1a → ^{3}IMWWW2a → ^{3}TSWWW2a → $H_2S\bullet\bullet\bullet(H_2O)_3a$ + $^3O_2$, respectively; ($1/k_{RWWW1} = 1/k_{TSWWW1} + 1/k_{TSWWW2}$, $1/k_{RWWW1a} = 1/k_{TSWWW1a} + 1/k_{TSWWW2a}$, $k'_{RWWW1} = k_{RWWW1} \cdot$ Keq($HO_2\cdots(H_2O)_3$) $\cdot$ [$(H_2O)_3$]), $k'_{RWWW1a} = k_{RWWW1a} \cdot$ Keq($HO_2\cdots(H_2O)_3a$) $\cdot$ [$(H_2O)_3$])