Supporting information

-for-

Role of $(H_2O)_n$ (n =1-3) Cluster on the $HO_2 + HO \rightarrow {}^3O_2 + H_2O$ Reaction: Mechanistic and Kinetic Study

Tianlei Zhang[a,], Xinguang Lan[a,§], Zhangyu Qiao[a,], Rui Wang[a], Xiaohu Yu[a], Qiong Xu[a], Zhiyin Wang[a], Zhuqing Wang [b,*]

[a] *Shaanxi Key Laboratory of Catalysis, School of Chemical & Environment Science, Shaanxi University of Technology, Hanzhong, Shaanxi 723001, China*;

[b]*Analytical and Testing Center, Sichuan University of Science &Engineering, Zigong 643000, Sichuan Province, P. R. China*

Table S1 Rate constants (cm^3·$molecules^{-1}$·s^{-1}) of HO_2 + HO → $^3O_2$ + H_2O reaction within the temperature range of 240.0~425.0 K[a]

T(K)	k(^{3}TS1)	k(^{3}TS2)	k_{R1}
240	8.49E-11	1.30E-12	8.62E-11
250	7.32E-11	1.30E-12	7.45E-11
278	7.23E-11	1.33E-12	7.36E-11
288	6.72E-11	1.34E-12	6.85E-11
298	6.50E-11	1.35E-12	6.64E-11
308	5.18E-11	1.37E-12	5.32E-11
325	4.09E-11	1.40E-12	4.23E-11
375	3.74E-11	1.51E-12	3.89E-11
425	2.08E-11	1.65E-12	2.24E-11

[a] k(^{3}TS1) is the rate constant of the process of HO_2 + HO → ^{3}IM1 → ^{3}TS1 → H_2O + $^3O_2$; and k(^{3}TS2) is the rate constant of the process of HO_2 + HO → ^{3}IM1 → ^{3}TS2 → H_2O + $^3O_2$;. k_{R1}= k(^{3}TS1) + k(^{3}TS2)

At 298 K, the calculated value of k_{R1} was 6.64 × 10^{-11} cm^3•$molecule^{-1}$•s^{-1}, which was in good agreement with experimental reports reported by Schwab [1] (8.0 × 10^{-11} ± 2.99 × 10^{-11} cm^3•$molecule^{-1}$•s^{-1} at 298 K), Dransfeld [2] (5.98 × 10^{-11} ± 1.49 × 10^{-11} cm^3•$molecule^{-1}$•s^{-1} at 298 K), Rozenshtein [3] (5.2 × 10^{-11} ± 1.2 × 10^{-11} cm^3•$molecule^{-1}$•s^{-1} at 300 K), Temps [4] (6.64 × 10^{-11} ± 2.32 × 10^{-11} cm^3•$molecule^{-1}$•s^{-1} at 296 K), and theoretical values reported by Gonzalez [5] (8.55 × 10^{-11} cm^3•$molecule^{-1}$•s^{-1} at 300 K).

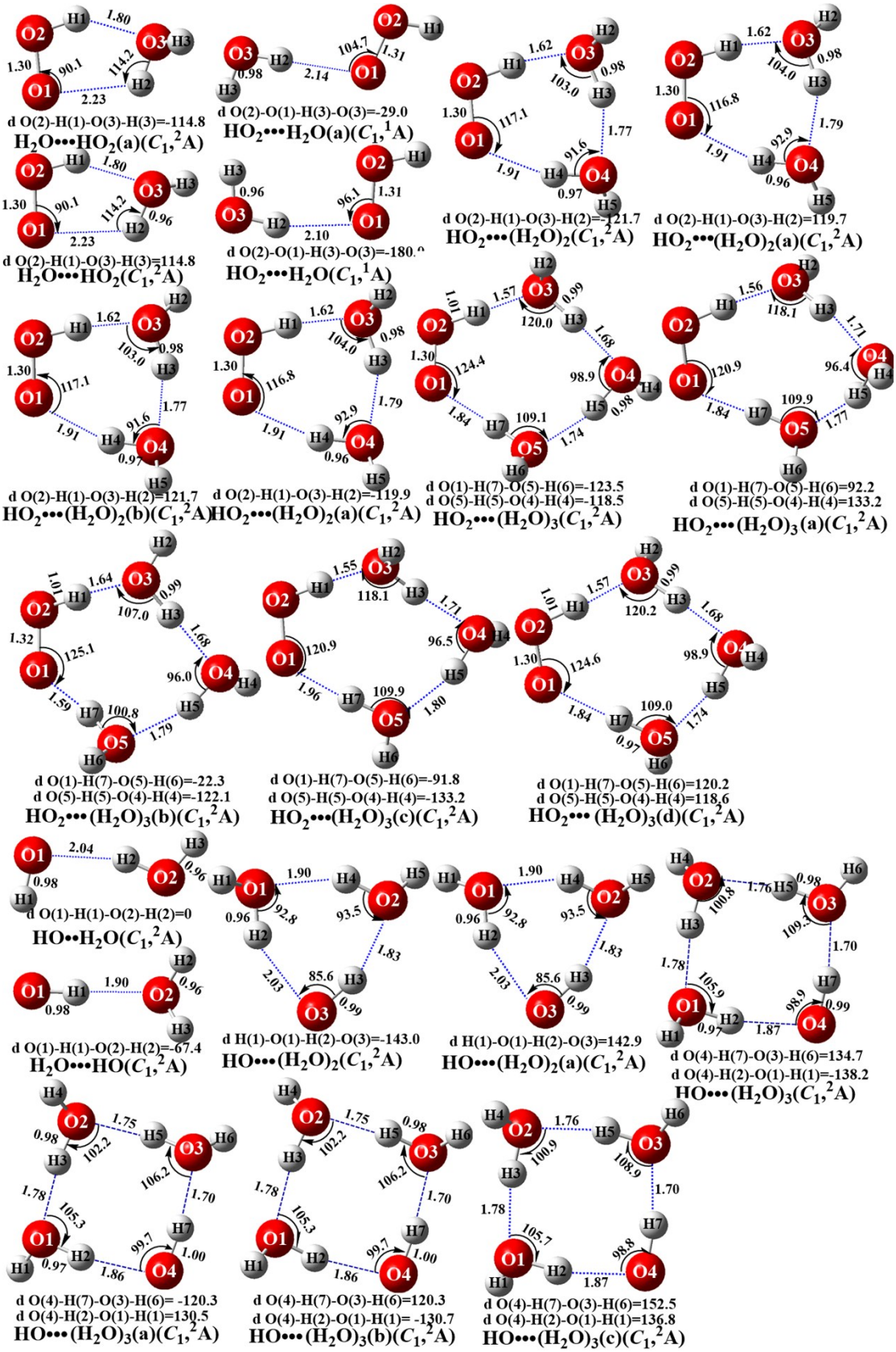

Fig. S1 The optimized geometrical complexes between HO_2 radical and $(H_2O)_n$ (n= 1-3), as well as the complexes between HO radical and $(H_2O)_n$ (n= 1-3) at the M06-2X/aug-cc-pVTZ level of theory (bond length Å, bond angle °)

Table S2 Equilibrium constants of complexes between HO_2 radical and $(H_2O)_n$ (n= 1-3); as well as complexes between HO radical and $(H_2O)_n$ (n= 1-3) [a,b,c]

T/K	H_2O•••HO_2	H_2O•••HO_2(a)	HO_2•••H_2O	HO_2•••H_2O(a)	H_2O•••HO	[H_2O]	[$(H_2O)_2$]	[$(H_2O)_3$]
240	3.63E-18	1.57E-18	5.23E-22	8.21E-24	3.12E-21	8.29E+15	1.87E+12	1.72E+09
250	2.86E-18	1.05E-18	4.32E-22	7.63E-24	2.31E-21	2.21E+16	1.02E+13	1.22E+10
278	7.06E-19	8.56E-19	1.21E-22	6.88E-24	1.12E-21	2.25E+17	5.71E+14	1.23E+12
288	5.32E-19	6.27E-19	1.11E-22	5.99E-24	9.01E-22	4.25E+17	1.69E+15	4.01E+12
298	3.68E-19	3.56E-19	1.01E-22	5.16E-24	7.38E-22	7.64E+17	4.59E+15	1.19E+13
298	(8.43E+07)[c]	(8.43E+07)[c]	(2.31E+04)[c]	(118.27)[c]	(1.69E+04)[c]			
308	3.89E-19	2.36E-19	9.99E-23	4.75E-24	6.13E-22	1.31E+18	8.57E+15	2.07E+13
325	1.89E-19	3.12E-19	8.80E-23	3.89E-24	4.63E-22	3.04E+18	4.86E+16	1.53E+14
375	6.78E-20	7.50E-20	8.01E-23	3.76E-24	2.45E-22	2.12E+19	1.35E+18	5.29E+15
425	2.70E-20	2.61E-20	7.05E-23	2.43E-24	1.57E-22	8.56E+19	1.49E+19	6.45E+16

T/K	HO_2•••$(H_2O)_2$	HO_2•••$(H_2O)_2$(a)	HO_2•••$(H_2O)_2$(b)	HO_2•••$(H_2O)_2$(c)	HO•••$(H_2O)_2$	HO•••$(H_2O)_2$(a)	HO_2•••$(H_2O)_3$	HO_2•••$(H_2O)_3$(a)
240	3.74E-16	2.37E-16	2.16E-16	3.73E-16	1.68E-18	5.32E-19	9.70E-16	4.94E-16
250	1.20E-16	7.88E-17	7.19E-17	1.20E-16	7.90E-19	2.66E-19	3.39E-16	1.71E-16
278	7.75E-18	5.53E-18	5.06E-18	7.73E-18	1.27E-19	5.00E-20	2.70E-17	1.32E-17
288	3.32E-18	2.43E-18	2.22E-18	3.31E-18	7.23E-20	2.98E-20	1.24E-17	6.01E-18
298	1.50E-18	1.13E-18	1.04E-18	1.50E-18	4.26E-20	1.84E-20	5.98E-18	2.88E-18
298	(2.07E+06)[c]	(1.56E+06)[c]	(1.43E+06)[c]	(2.07E+06)[c]	(1.96E+03)[c]	(8.47E+02)[c]	(2.14E+04)[c]	(1.03E+04)[c]
308	7.19E-19	5.53E-19	5.07E-19	7.17E-19	2.60E-20	1.18E-20	3.03E-18	1.45E-18
325	2.28E-19	1.82E-19	1.67E-19	2.27E-19	1.21E-20	5.86E-21	1.06E-18	4.97E-19
375	1.43E-20	1.26E-20	1.15E-20	1.43E-20	1.88E-21	1.10E-21	8.45E-20	3.83E-20
425	1.77E-21	1.66E-21	1.53E-21	1.76E-21	4.58E-22	3.14E-22	1.26E-20	5.53E-21

T/K	HO_2•••$(H_2O)_3$(b)	HO_2•••$(H_2O)_3$(c)	HO_2•••$(H_2O)_3$(d)	HO•••$(H_2O)_3$	HO•••$(H_2O)_3$(a)	HO•••$(H_2O)_3$(b)	HO•••$(H_2O)_3$(c)
240	1.21E-19	9.54E-16	4.71E-16	1.25E-17	7.24E-18	1.19E-17	7.34E-18
250	5.18E-20	3.34E-16	1.63E-16	5.77E-18	3.48E-18	5.48E-18	3.52E-18
278	6.65E-21	2.66E-17	1.26E-17	8.88E-19	5.95E-19	8.47E-19	6.02E-19
288	3.52E-21	1.22E-17	5.72E-18	4.98E-19	3.45E-19	4.76E-19	3.48E-19
298	1.94E-21	5.89E-18	2.74E-18	2.90E-19	2.07E-19	2.78E-19	2.09E-19
298	(6.94)[c]	(2.11E+04)[c]	(9.79E+03)[c]	(34.6)[c]	(24.7)[c]	(33.1)[c]	(25.0)[c]
308	1.11E-21	2.99E-18	1.38E-18	1.75E-19	1.29E-19	1.68E-19	1.30E-19
325	4.68E-22	1.04E-18	4.73E-19	8.02E-20	6.17E-20	7.71E-20	6.23E-20
375	5.79E-23	8.32E-20	3.64E-20	1.23E-20	1.05E-20	1.19E-20	1.06E-20
425	1.18E-23	1.24E-20	5.25E-21	2.98E-21	2.79E-21	2.89E-21	2.81E-21

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

[b] All equilibrium constants were calculated by using energies computed at CCSD(T)/aug-cc-PVTZ level and partition functions obtained at M06-2X/aug-cc-PVTZ level.

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

The equilibrium constant of H_2O•••HO_2 and HO_2•••H_2O at 298 K is respectively 3.68×10^{-19}, 1.01×10^{-22}, cm^3•$molecule^{-1}$. The equilibrium constant of H_2O•••HO at 298 K is 7.38×10^{-22} cm^3•$molecule^{-1}$, which is lower by 6.7 times than that reported by Anglada et al. (*Phys. Chem. Chem. Phys.*, 2017, 19, 12331.). Due to the fact that the free energy of the H_2O•••HO (Table S3) is very close to the value reported that reported by Anglada et al. (*Phys. Chem. Chem. Phys.*, 2017, 19, 12331.), this difference is possible due to the fact that different levels of theory used for the partition functions calculation. The H_2O•••HO complex is in equilibrium with HO···H_2O) according to the results reported by Gao and co-workers [6] Taking into account typical tropospheric concentrations of 1.0×10^7 cm^3•$molecule^{-1}$ of HO and 3.0×10^8 cm^3•$molecule^{-1}$ of HO_2, it is estimated that the atmospheric concentration of the H_2O•••HO_2, HO_2•••H_2O and H_2O•••HO complex is respectively 8.43×10^7 cm^3•$molecule^{-1}$, 2.31×10^4 cm^3•$molecule^{-1}$, and 1.69×10^4 cm^3•$molecule^{-1}$, respectively. These results are good agreement with the report of *Alongi et al* [7] that the concentration of H_2O•••HO_2 and HO_2•••H_2O was respectively 6.6×10^7 cm^3•$molecule^{-1}$ and 6.9×10^4 cm^3•$molecule^{-1}$, meanwhile our results are also consistent with previous values of Gonzalez and coworkers[8] where the concentration of H_2O•••HO was predicted to be 6.31×10^4 cm^3•$molecule^{-1}$.

For HO_2•••$(H_2O)_2$ complex, at 298 K, our predicted value is 2.07×10^6 cm^3•$molecule^{-1}$, which is close to the value reported by *Alongi et al* [7] (1.9×10^6 cm^3•$molecule^{-1}$), meanwhile, for HO•••$(H_2O)_2$ and HO•••$(H_2O)_3$ complexes, at 298 K, our predicted value are 1.96×10^3 cm^3•$molecule^{-1}$, and 34.6 cm^3•$molecule^{-1}$, which is also chose to reported values of Gonzalez and coworkers [8] where HO•••$(H_2O)_2$ and HO•••$(H_2O)_3$ complexes at 75 % relative humidities and 298 K were respectively 2.24×10^2 and 6.58×10^2 cm^3•$molecule^{-1}$.

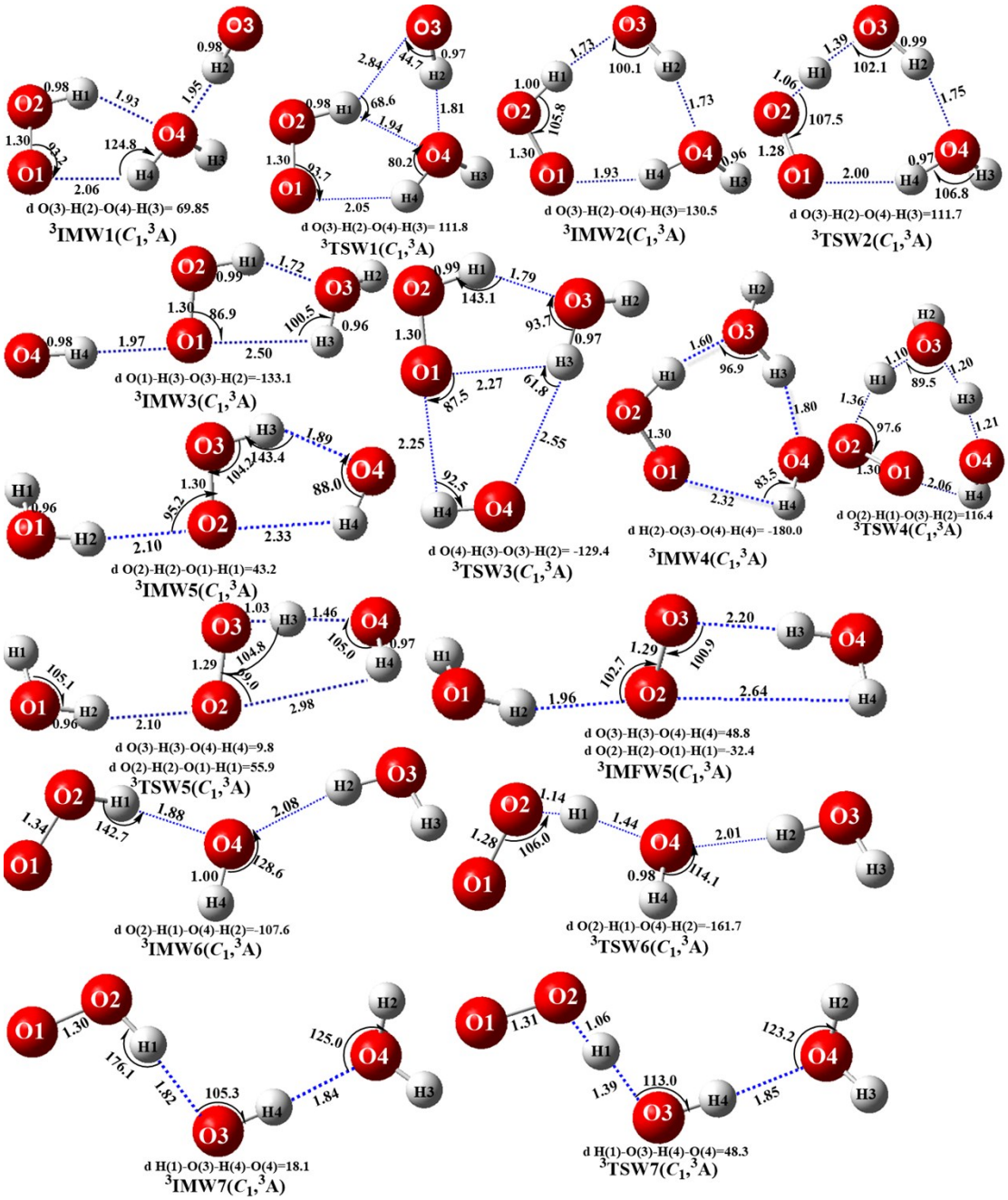

Fig. S2 The geometrical structures of the optimized intermediates and transitions states in H_2O•••HO_2 + HO, HO_2•••H_2O + HO, and H_2O•••HO + HO_2 reactions (bond length Å, bond angle °)

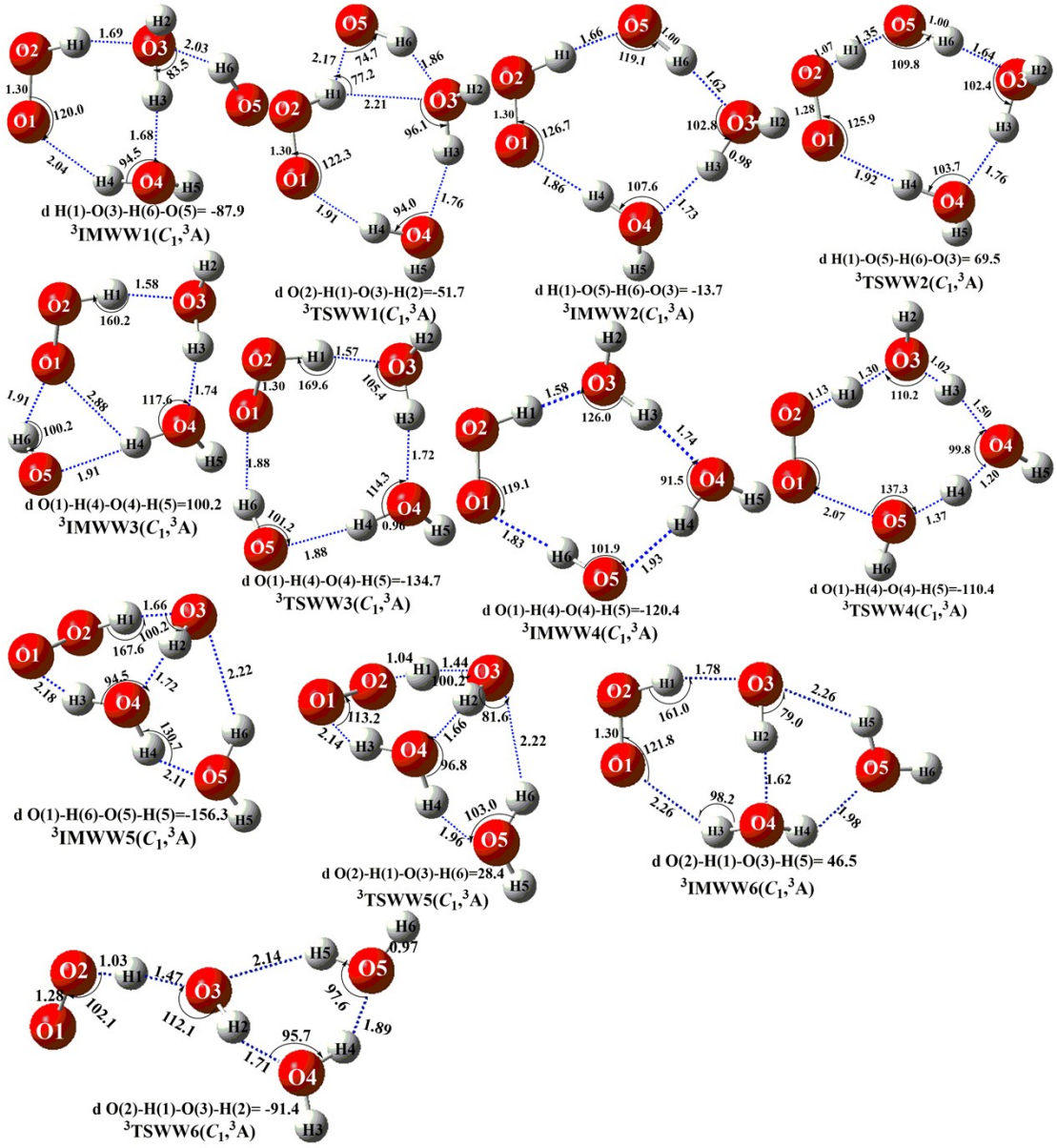

Fig. S3 The geometrical structures of the optimized transitions states and intermediates in $HO_2\cdots(H_2O)_2$ + HO and $HO\cdots(H_2O)_2$ + HO_2 reactions

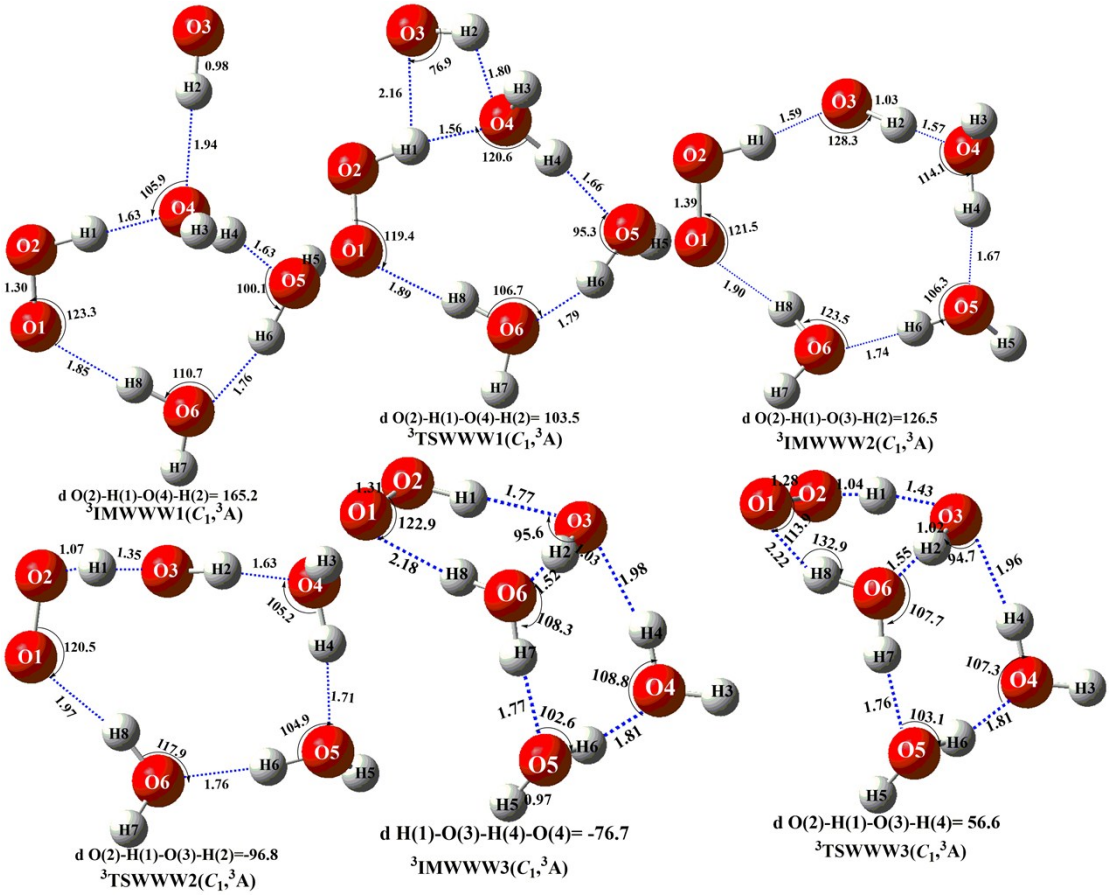

Fig. S4 The geometrical structures of the optimized transitions state and intermediates in $HO_2\cdots(H_2O)_3$ + HO and $HO\cdots(H_2O)_3$ + HO_2 reactions

Table S3 Zero point energy (ZPE/(kcal•mol^{-1})), entropies (S/(cal·mol^{-1}•K^{-1})), relative energies (ΔE and $\Delta(E + \text{ZPE})$/(kcal•mol^{-1})), enthalpies (ΔH(298 K)/(kcal•mol^{-1})), free energies (ΔG(298 K)/(kcal•mol^{-1})), and T_1 diagnostic values for complexes between HO_2 radical and $(H_2O)_n$ (n= 1-3) as well as complexes between HO radical and $(H_2O)_n$ (n= 1-3) [a]

Species	ZPE	S	ΔE	ΔH	ΔG	$\Delta(E + \text{ZPE})$	T_1
				water-assisted			
$H_2O + HO_2$	22.7	99.7	0.0	0.0	0.0	0.0	
$H_2O•••HO_2$	25.4	70.7(-85±14)[c]	-9.4	-7.6(-7.4±0.9)[b](-4.76)[d]	1.0	-6.7(-6.73)[e](-6.37)[f](-6.10)[g]	0.0249
$H_2O•••HO_2$(a)	25.4	70.7(-85±14)[c]	-9.4	-7.6(-7.4±0.9)[b](-4.76)[d]	1.0	-6.7(-6.73)[e](-6.37)[f](-6.10)[g]	0.0249
$HO_2•••H_2O$	24.4	78.5	-3.4	-1.9	4.4	-1.7(-1.86)[e](-2.38)[h]	0.0242
$HO_2•••H_2O$(a)	24.9	73.1	-3.1	-1.6	6.3	-0.9	0.0245
$H_2O + HO$	18.9	87.6	0.00	0.00	0.00	0.0	
$H_2O•••HO$	20.9	66.8(67.3)[j]	-5.9(-5.90)[j]	-4.5(-6.9)[i]	1.7(1.54)[j]	-3.9(-3.85)[j]	0.0101
$HO•••H_2O$	20.4	68.9	-3.7	-2.6(-8.8)[i]	3.0	-2.1	0.0105
				water dimer-assisted			
$H_2O + H_2O$	27.0	90.2	0.0	0.0	0.0	0.0	
$(H_2O)_2$	29.3	69.7	-5.2	-3.5	2.9	-3.0	0.0102
$HO_2 + (H_2O)_2$	38.5	123.3	0.0	0.0	0.0	0.0	
$HO_2\cdots(H_2O)_2$	41.5	83.2	-15.8	-14.1	-2.1	-12.8	0.0225
$HO_2\cdots(H_2O)_2$(a)	41.4	84.0	-15.3	-13.6	-1.9	-12.4	0.0225
$HO_2\cdots(H_2O)_2$(b)	41.4	84.1	-15.3	-13.7	-2.0	-12.5	0.0225
$HO_2\cdots(H_2O)_2$(c)	41.5	83.2	-15.8	-14.1	-2.1	-12.8	0.0225
$HO + (H_2O)_2$	34.7	111.2	0.0	0.0	0.0	0.0	
$HO\cdots(H_2O)_2$	37.3	80.2	-10.3	-8.8	0.5	-7.7	0.0106
$HO\cdots(H_2O)_2$(a)	37.3	80.2	-10.3	-8.8	0.5	-7.7	0.0106
				water trimer-assisted			

$(H_2O)_2 + H_2O$	42.9	113.74	0.0	0.0	0.0	0.0	
$(H_2O)_3$	46.1	79.72	-11.1	-9.1	1.1	-7.9	0.0104
$HO_2 + (H_2O)_3$	55.2	134.3	0.0	0.0	0.0	0.0	
$HO_2\cdots(H_2O)_3$	57.2	98.6	-14.5	-13.2	-2.5	-12.5	0.0206
$HO_2\cdots(H_2O)_3$(a)	57.2	98.7	-14.5	-13.2	-2.5	-12.5	0.0205
$HO_2\cdots(H_2O)_3$(b)	56.9	92.3	-11.1	-10.7	1.8	-9.3	0.0206
$HO_2\cdots(H_2O)_3$(c)	56.9	100.6	-14.2	-13.0	-3.0	-12.5	0.0206
$HO_2\cdots(H_2O)_3$(d)	56.9	100.7	-14.2	-13.0	-3.0	-12.5	0.0206
$HO + (H_2O)_3$	51.4	122.3	0.0	0.0	0.0	0.0	
$HO\cdots(H_2O)_3$	53.3	93.4	-10.9	-9.8	-1.2	-8.9	0.0107
$HO\cdots(H_2O)_3$(a)	53.4	93.9	-10.4	-9.2	-0.8	-8.4	0.0107
$HO\cdots(H_2O)_3$(b)	53.3	93.4	-10.8	-9.8	-1.1	-8.9	0.0111
$HO\cdots(H_2O)_3$(c)	53.3	94.5	-10.4	-9.3	-1.0	-8.5	0.0111

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

Experimentally:

[b] Value was from Ref. [9] and was calculated using near-infrared two-tone frequency modulation spectroscopy at 250–350 K and 50 Torr with N_2 diluent.

[c] Value was from Ref. [10]and was obtained using Fourier transform infrared absorption spectroscopy.

[i] Value was from Ref. [11] and was obtained using Laser induced fluorescence.

Theoretically

[d] Value was from Ref. [12]and was calculated at the CCSD(T)/6-311++G(2*df*,2*p*)

[e] Value was from Ref. [13] and was calculated at the UCCSD(T)/aug-cc-pV*TZ*//UMP2/6-311+g(2*df*, 2*p*) level of theory.

[f] Value was from Ref. [14] and was calculated at the CCSD(T)/6-311++G(3*d*, 2*p*)//B3LYP/6-311G(2*d*, 2*p*) level of theory.

[g] Value was from Ref.[15] and was calculated at the G2M/B3LYP-6-311G(*d*, *p*) level of theory.

[h] Value was from Ref. [16]and was calculated at the G3//HF/6-31G* level of theory.

[j] Value was from Ref. [8] and was calculated at the CCSD(T)/aug-cc-pV*TZ*//BH&HLYP/6-311+G(2*df*, 2*p*) level of theory.

Table S4 Zero point energy (ZPE/(kcal•mol^{-1})), relative energies (ΔE and $\Delta(E + \mathrm{ZPE})$/(kcal•mol^{-1})), enthalpies (ΔH(298 K)/(kcal•mol^{-1})), and free energies (ΔG(298 K)/(kcal•mol^{-1})) for the $HO_2 + HO \rightarrow {}^3O_2 + H_2O$ reaction [a]

System	ZPE	ΔE	ΔH(298 K)	ΔG(298 K)	$\Delta(E + \mathrm{ZPE})$
$HO_2 + HO$	14.5	0.0	0.0	0.0	0.0
^{3}IM1	16.8	-7.3	-5.9	2.3	-5.0
^{3}TS1	13.6	-2.1	-4.0	4.2	-3.0
^{3}TS2	15.1	-2.2	-3.1	6.2	-1.7
$^3O_2 + H_2O$	16.0	-69.6	-68.1(-69.63)[b]	-67.1	-68.1

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

[b] Value was from [17]

The value of HO_2 was from Ref. [18, 19] and was obtained by direct measurement or well-founded calculation and observed by difference frequency laser anddiode laser spectroscopy with Zeeman modulation

The value of HO_2 and HO_2 was from Ref. [20]

The value of HO and $^3O_2$ was from Ref. [21]

Table S5 Zero point energy (ZPE/(kcal•mol^{-1})), relative energies (ΔE and $\Delta(E + ZPE)$/(kcal•mol^{-1})), enthalpies (ΔH(298 K)/(kcal•mol^{-1})), and free energies (ΔG(298 K)/(kcal•mol^{-1})) for water-assisted the $HO_2 + HO \rightarrow {}^3O_2 + H_2O$ reaction [a]

System	ZPE	ΔE	ΔH	ΔG	$\Delta(E + ZPE)$
$HO + H_2O\bullet\bullet\bullet HO_2$	30.7	0.0	0.0	0.0	0.0
^{3}IMW1	32.7	-4.2	-2.8	4.4	-2.2
^{3}TSW1	32.4	-3.5	-2.8	6.0	-1.9
^{3}IMW2	32.6	-9.2	-8.0	0.4	-7.3
^{3}TSW2	29.5	-3.4	-5.8	3.8	-4.6
^{3}TSW2'	29.0	21.0	17.1	28.9	19.3
^{3}IMW2'	32.8	-7.1	-5.8	3.3	-5.0
^{3}IMW3	32.0	-5.0	-3.9	2.4	-3.7
^{3}TSW3	32.2	-3.0	-2.4	6.5	-1.6
^{3}IMW4	32.8	-7.5	-6.3	2.8	-5.0
^{3}TSW4	32.0	-4.8	-5.9	7.3	-1.7
$^3O_2 + H_2O\bullet\bullet\bullet H_2O$	31.8	-65.4	-64.0	-65.3	-68.8
$HO + HO_2\bullet\bullet\bullet H_2O$	29.7	0.0	0.0	0.0	0.0
^{3}IMW5	31.7	-7.1	-6.4	4.2	-5.1
^{3}TSW5	28.6	-2.0	-3.9	4.4	-3.1
^{3}IMFW5	32.9	-73.5	-72.0	-60.6	-70.3
$^3O_2 + H_2O + H_2O$	29.6	-66.2	-66.2	-71.6	-69.3
$HO_2 + H_2O\bullet\bullet\bullet HO$	30.1	0.0	0.0	0.0	0.0
^{3}IMW6	31.6	-2.8	-2.5	10.2	-0.7
^{3}TSW6	29.2	6.0	3.9	16.5	5.7
^{3}IMW7	31.8	-6.6	-5.5	4.0	-4.8
^{3}TSW7	28.4	3.8	1.3	11.8	2.1
$^3O_2 + H_2O\bullet\bullet\bullet H_2O$	31.8	-68.9	-67.1	-66.0	-67.2

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

Table S6 Zero point energy (ZPE/(kcal•mol^{-1})), relative energies (ΔE and $\Delta(E + ZPE)$/(kcal•mol^{-1})), enthalpies (ΔH(298 K)/(kcal•mol^{-1})), and free energies (ΔG(298 K)/(kcal•mol^{-1})) for water dimer-assisted the $HO_2 + HO \rightarrow {}^3O_2 + H_2O$ reaction [a]

System	ZPE	ΔE	ΔH	ΔG	$\Delta(E + ZPE)$
$HO + HO_2 \bullet\bullet\bullet (H_2O)_2$	46.9	0.0	0.0	0.0	0.0
^{3}IMWW1	48.8	-5.2	-3.8	4.2	-3.3
^{3}TSWW1	47.9	-2.6	-2.0	6.0	-1.6
^{3}IMWW2	48.4	-7.5	-6.4	0.5	-6.0
^{3}TSWW2	45.3	-1.4	-3.8	4.9	-3.0
^{3}IMWW3	48.0	-5.9	-4.9	2.1	-4.8
^{3}TSWW3	48.0	-4.1	-3.8	5.2	-3.0
^{3}IMWW4	48.3	-3.7	-3.7	5.8	-3.3
^{3}TSWW4	45.3	0.1	-3.4	8.3	-1.5
$^3O_2 + (H_2O)_3$	48.6	-64.8	-63.1	-63.9	-63.1
$HO_2 + HO \bullet\bullet\bullet (H_2O)_2$	46.4	0.0	0.0	0.0	0.0
^{3}IMWW5	48.2	-8.4	-6.9	3.3	-6.6
^{3}TSWW5	45.5	-4.3	-6.0	5.1	-5.2
^{3}IMWW6	47.9	-8.4	-7.0	2.1	-6.9
^{3}TSWW6	45.4	-3.0	-4.6	5.1	-4.1
$^3O_2 + (H_2O)_3$	48.6	-70.4	-68.4	-66.5	-68.2

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

Table S7 Zero point energy (ZPE/(kcal•mol^{-1})), relative energies (ΔE and $\Delta(E + ZPE)$/(kcal•mol^{-1})), enthalpies (ΔH(298 K)/(kcal•mol^{-1})), and free energies (ΔG(298 K)/(kcal•mol^{-1})) for water trimer-assisted the $HO_2 + HO \rightarrow {}^3O_2 + H_2O$ reaction [a]

System	ZPE	ΔE	ΔH	ΔG	$\Delta(E + ZPE)$
$HO + HO_2\bullet\bullet\bullet(H_2O)_3$	62.6	0.0	0.0	0.0	0.0
^{3}IMWWW1	64.1	-4.7	-3.4	3.2	-3.1
^{3}TSWWW1	64.6	-2.1	-2.4	10.6	-0.1
^{3}IMWWW2	63.8	-5.7	-5.4	3.6	-4.5
^{3}TSWWW2	60.9	-1.5	-3.9	4.2	-3.2
$^3O_2 + (H_2O)_4$	64.2	-67.3	-65.7	-66.7	-65.7
$HO_2 + HO\bullet\bullet\bullet(H_2O)_3$	62.5	0.0	0.0	0.0	0.0
^{3}IMWWW3	64.2	-8.7	-7.4	2.9	-7.0
^{3}TSWWW3	61.3	-4.6	-6.6	4.6	-5.9
$^3O_2 + (H_2O)_4$	64.2	-71.4	-69.6	-68.4	-69.2

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

Table S8 Calculated total electronic energies (*E*) for the reactants, intermediates, transition states and products for the reaction of $HO_2 + HO_2 \rightarrow H_2O_2 + {}^3O_2$ without water, complexes between HO_2 radical and H_2O, and complexes between HO radical and H_2O at the CCSD(T) level in conjunction with the aug-cc-pVTZ, aug-cc-pVQZ and aug-cc-pV5Z basis sets as well as at the M06-2X/aug-cc-pVTZ level of theory.

System	*E*/ CCSD(T)/ aug-cc-pVTZ	*E*/ CCSD(T)/ aug-cc-pVQZ	*E*/ CCSD(T)/ aug-cc-pV5Z	*E*/ CCSD(T)/CBS	ΔE [a]
			without water		
HO_2	-150.7260394	-150.7650376	-150.7777261	-150.7241007	0.001939
HO	-75.6455847	-75.6644932	-75.6706180	-75.6446447	0.000940
^{3}IM1	-226.3832260	-226.4398459	-226.4337016	-226.3804112	0.002815
^{3}TS1	-226.3750346	-226.4330346	-226.4520346	-226.3721512	0.002883
^{3}TS2	-226.3751904	-226.4331106	-226.4517463	-226.3723110	0.002879
H_2O	-76.3422890	-76.3635635	-76.3702749	-76.3412314	0.001058
$^3O_2$	-150.1402464	-150.1781986	-150.1905918	-150.1383597	0.001887
			water molecule		
H_2O•••HO_2	-227.0833721	-227.1434851	-227.1627415	-227.0803837	0.002988
HO_2•••H_2O	-227.0737271	-227.1337567	-227.1530155	-227.0707428	0.002984
H_2O•••HO	-151.9972478	-152.0373099	-152.0464576	-151.9952562	0.001992
HO•••H_2O	-151.99373	-152.0337274	-152.0500286	-151.9917416	0.001988

[a] ΔE = E(CBS) - E(aug-cc-pVTZ)

$E_{SCF(n)} = E_{SCF(\infty)} + A\exp(-\alpha n)$

the various A and α values denote the constant, $E_{SCF(\infty)}$ and *n* stand for the total electronic energies at CCSD(T)/CBS and the maximum angular quantum number of the base function contained in the base group, respectively.

Table S9 Rate constants and effective rate constants ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$) of $HO_2 + HO \rightarrow H_2O + {}^3O_2$ reaction with $(H_2O)_n$ (n = 1-3) within the temperature range of 240-425 K in the Earth's atmosphere.

T/K	k(RW1a)	k(RW2)	k(RW4)	k(RWW2)	k(RWW4)
240	4.10E-32	7.22E-13	3.51E-14	2.96E-13	2.83E-09
250	1.18E-31	6.44E-13	2.62E-14	2.48E-13	1.89E-09
278	2.25E-30	4.94E-13	1.35E-14	1.64E-13	7.32E-10
288	6.22E-30	4.57E-13	1.11E-14	1.45E-13	5.52E-10
298	1.67E-29	4.26E-13	9.39E-15	1.29E-13	4.26E-10
308	4.33E-29	3.99E-13	8.08E-15	1.16E-13	3.36E-10
325	2.02E-28	3.63E-13	6.49E-15	9.92E-14	2.35E-10
375	1.02E-26	2.96E-13	4.22E-15	6.93E-14	1.05E-10
425	2.36E-25	2.62E-13	3.41E-15	1.61E-14	6.03E-11
T/K	k'(RW1a)	k'(RW2)	k'(RW4)	k'(RWW2)	k'(RWW4)
240	5.54E-35	9.40E-16	9.08E-19	2.07E-16	8.91E-19
250	2.32E-34	1.21E-15	1.34E-18	3.04E-16	1.53E-18
278	1.04E-32	2.21E-15	3.40E-18	7.26E-16	5.33E-18
288	3.49E-32	2.47E-15	4.25E-18	8.14E-16	6.74E-18
298	1.11E-31	2.72E-15	5.29E-18	8.88E-16	8.34E-18
308	2.88E-31	2.56E-15	6.49E-18	9.15E-16	7.49E-18
325	1.98E-30	3.44E-15	9.13E-18	1.10E-15	1.37E-17
375	1.69E-28	4.71E-15	2.19E-17	1.34E-15	2.66E-17
425	5.46E-27	5.85E-15	4.58E-17	4.25E-15	4.12E-17

k(RW1a), k(RW2), k(RW4) and k(RW5) is the rate constants of water-assisted $HO_2 + HO \rightarrow H_2O + {}^3O_2$ reaction occurring through Channels RW1a, RW2, RW4 and RW5, respectively; k(RWW2) and k(RWW4) is respectively the rate constants of water dimer-assisted $HO_2 + HO \rightarrow H_2O + {}^3O_2$ reaction occurring through Channels RWW2 and RWW4; k'(RW1a), k'(RW2), k'(RW4) and k'(RW5) is the effective rate constants of Channels RW1a, RW2, RW4 and RW5, respectively; k'(RWW2) and k'(RWW4) is the effective rate constants occurring through the Channels RWW2 and RWW4, respectively.

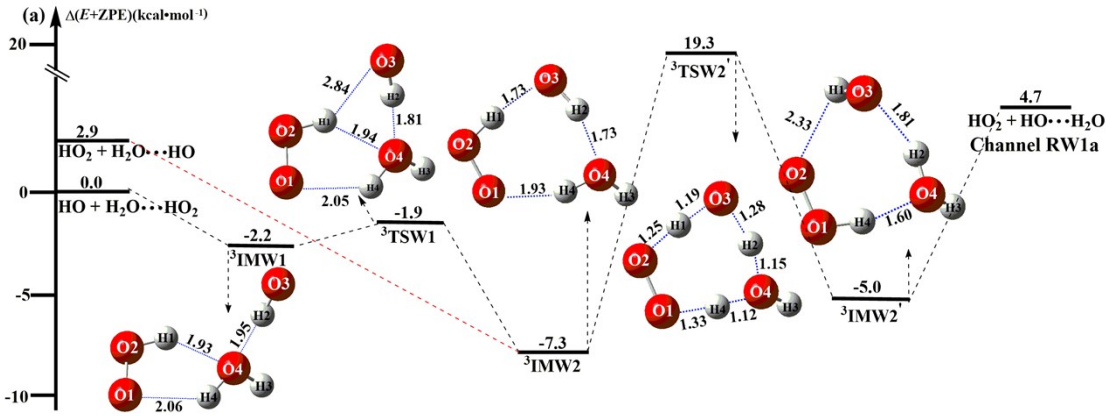

Fig. S5 Schematic energy diagrams of water-assisted $HO_2 + HO \rightarrow {}^3O_2 + H_2O$ reaction

Reference

[1] J. J. Schwab, W. H. Brune and J. G. Anderson, *J. Phys. Chem.*, 1989, **93**, 1030-1035.

[2] H. G. W. P. Dransfeld, *Z. Naturforsch. A.*, 1987, **42**, 471-476.

[3] V. B. Rozenshtein, Y. M. Gershenzon, S. D. Il'In and O. P. Kishkovitch, *Chem. Phys. Lett.*, 1984, **112**, 473-478.

[4] F. Temps and H. Gg. Wagner, *Ber. Bunsenges. Phys. Chem.*, 1982, **86**, 119-125.

[5] J. T. Carlos Gonzalez, Ling Zhu, H. Bernhard Schlegel, William L. Hase, E. W. Kaiser, *J. Phys. Chem.*, 1991, **95**, 6784–6792.

[6] A. F. Gao, G. L. Li, B. Peng, Y. M. Xie and H. F. Schaefer, *J. Phys. Chem. A*, 2016, **120**, 10223–10230.

[7] K. S. Alongi, T. S. Dibble, G. C. Shields and K. N. Kirschner, *J. Phys. Chem. A*, 2006, **110**, 3686–3691.

[8] J. Gonzalez, M. Caballero, A. A. Mogas, M. T. Sucarray, R. Crehuet, A. Solé, X. Giménez, S. Olivella, J. M. Bofill and J. M. Anglada, *Theor. Chem. Acc*., 2011, **128**, 579–592.

[9] N. Kanno, K. Tonokura and M. Koshi, *J. Geophys. Res. Atmos.*, 2006, **111**, 393-411.

[10] S. Aloisio, J. S. Francisco and R. R. Friedl, *J. Phys. Chem. A*, 2000, **104**, 6597-6601.

[11] D. C. McCabe, B. Rajakumar, P. Marshall, I. W. M. Smith and A. R. Ravishankara, *Phys. Chem. Chem. Phys.*, 2006, **8**, 4563-4574.

[12] S. A. And and J. S. Francisco, *J. Phys. Chem. A*,1998, **102**, 1899-1902.

[13] T. Zhang, R. Wang, W. Wang, S. Min, Q. Xu, Z. Wang, C. Zhao and Z. Wang, *Comput. Theor. Chem.*, 2014, **1045**, 135-144.

[14] T. Zhang, W. Wang, P. Zhang, J. Lu and Y. Zhang, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20794-20805.

[15] R. Zhu and M. C. Lin, *Chem. Phys. Lett.*, 2002, **354**, 217-226.

[16] K. S. Alongi, T. S. Dibble, G. C. Shields and K. N. Kirschner, *J. Phys. Chem. A*, 2006, **110**, 3686-3691.

[17] From ChemistryWebbook, http:// webbook.nist.gov/chemistry.

[18] A. Charo and F. C. D. Lucia, *J. Mol. Spectrosc.*, 1982, **94**, 426-436.

[19] K. G. Lubic, T. Amano, H. Uehara, K. Kawaguchi and E. Hirota, *J. Chem. Phys.*, 1984, **81**, 4826-4831.

[20] B. Ruscic, R. E. Pinzon, M. L. Morton, N. K. Srinivasan, M.-C. Su, J. W. Sutherland and J. V. Michael, *J. Phys. Chem. A*, 2006, **110**, 6592-6601.

[21] K. K. Irikura, *J.Phys. Chem. Ref. Data*, 2007, **36**, 389-397.