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Supporting information

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Catalytic effect of a single water molecule on atmospheric reaction of HO_2 + OH: Fact or fiction? A mechanistic and kinetic study

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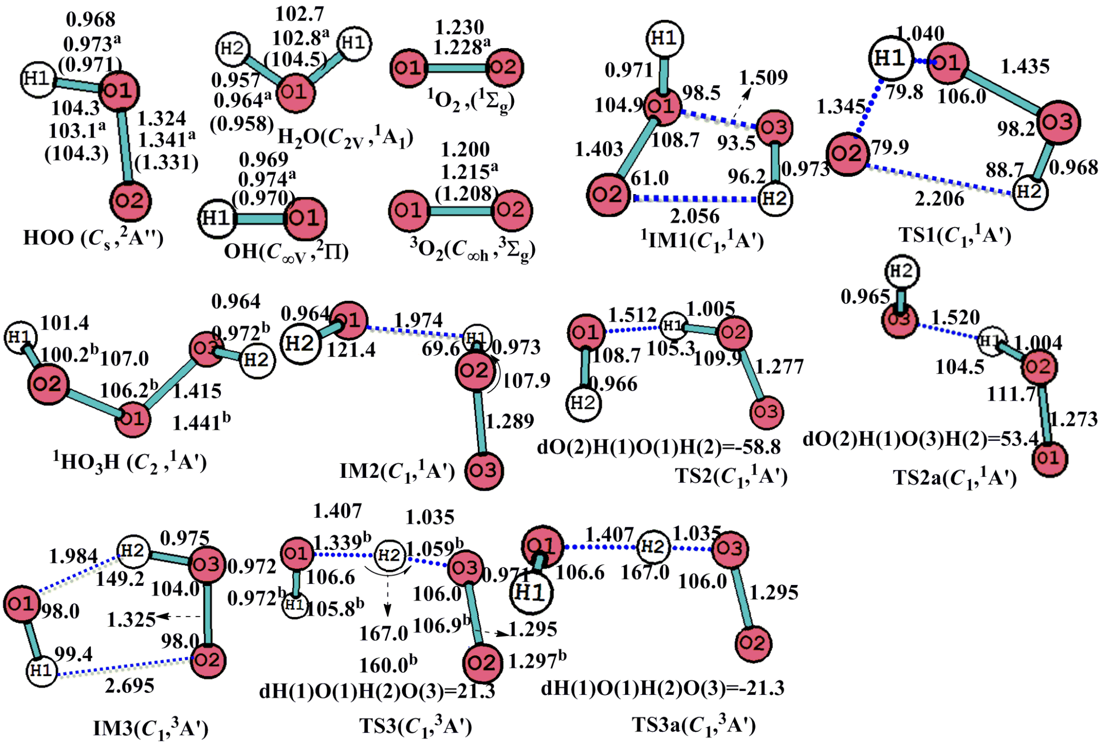
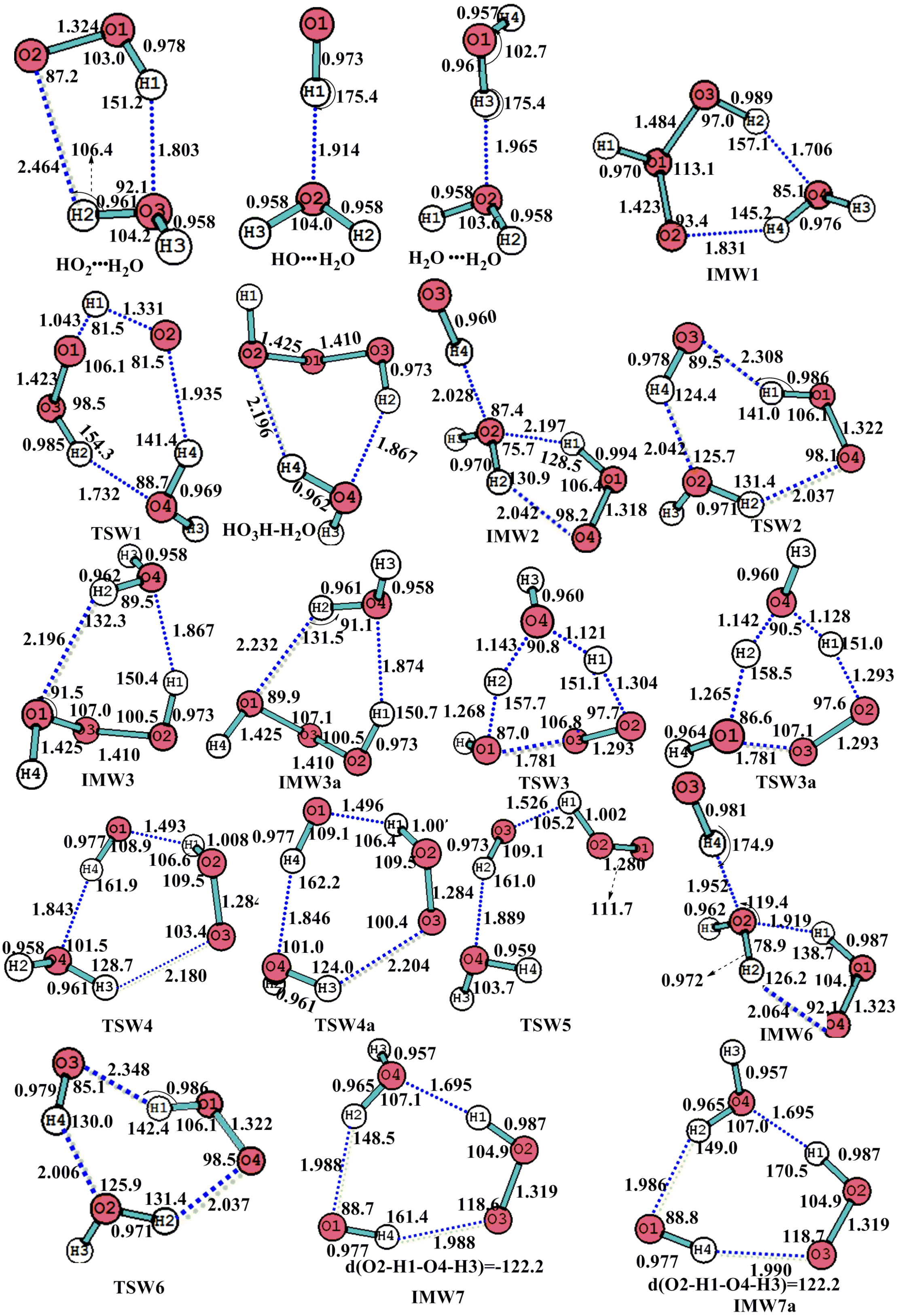


Fig. S1 Optimized geometries of all the species that involved in the HO_2 + OH reaction at the CCSD/6-311G(d,p) level. Bond lengths are in angstroms and angles are in degrees. The values with parentheses were the experimental data from the NIST chemistry webbook; [a] The values calculated at CASSCF/6-311G(d,p) level, [b] The values calculated at MP2/6-31G(d,p) level and obtained from reference 1 and 2.


HO2•••H2O
HO•••H2O
H2O •••H2O
IMW1
TSW1
HO3H-H2O
IMW2
TSW2
IMW3
IMW3a
TSW3
TSW3a
TSW4
TSW4a
TSW5
IMW6
TSW6
d(O2-H1-O4-H3)=-122.2
IMW7
d(O2-H1-O4-H3)=122.2
IMW7a

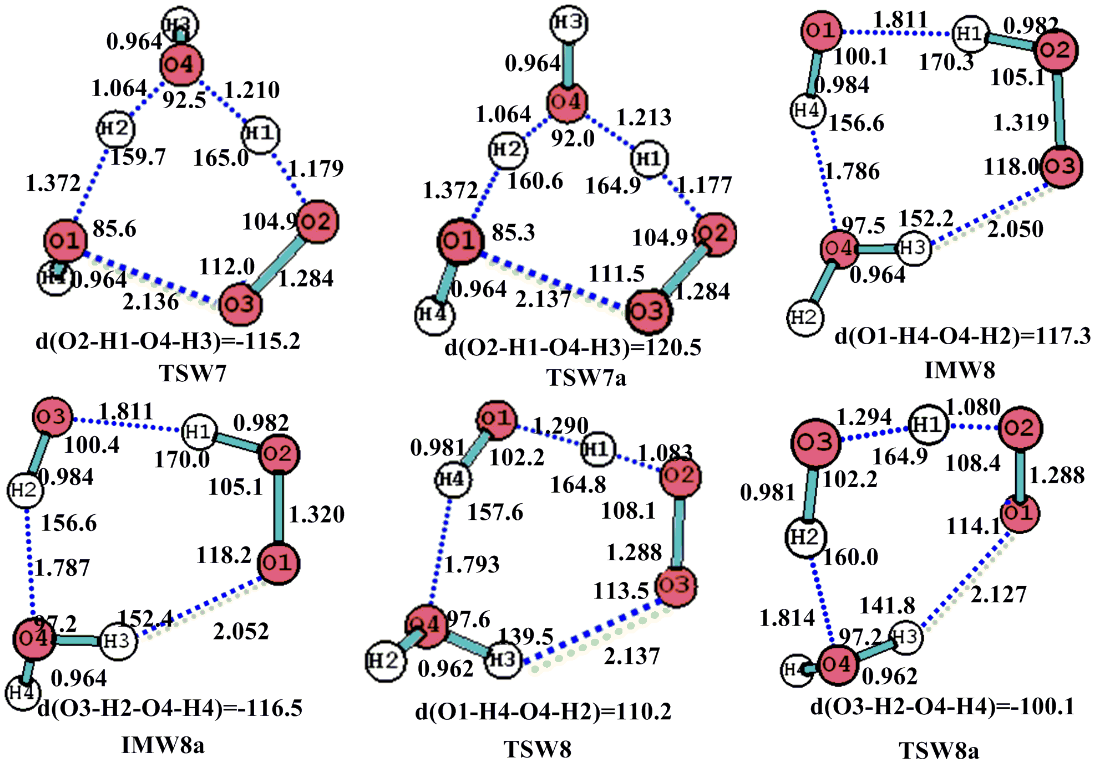


Fig. S2 Optimized geometries of all the species that involved in the reaction of HO_2 + OH with a water molecule at the CCSD/6-311G(d,p) level. Bond lengths are in angstroms and angles are in degrees.

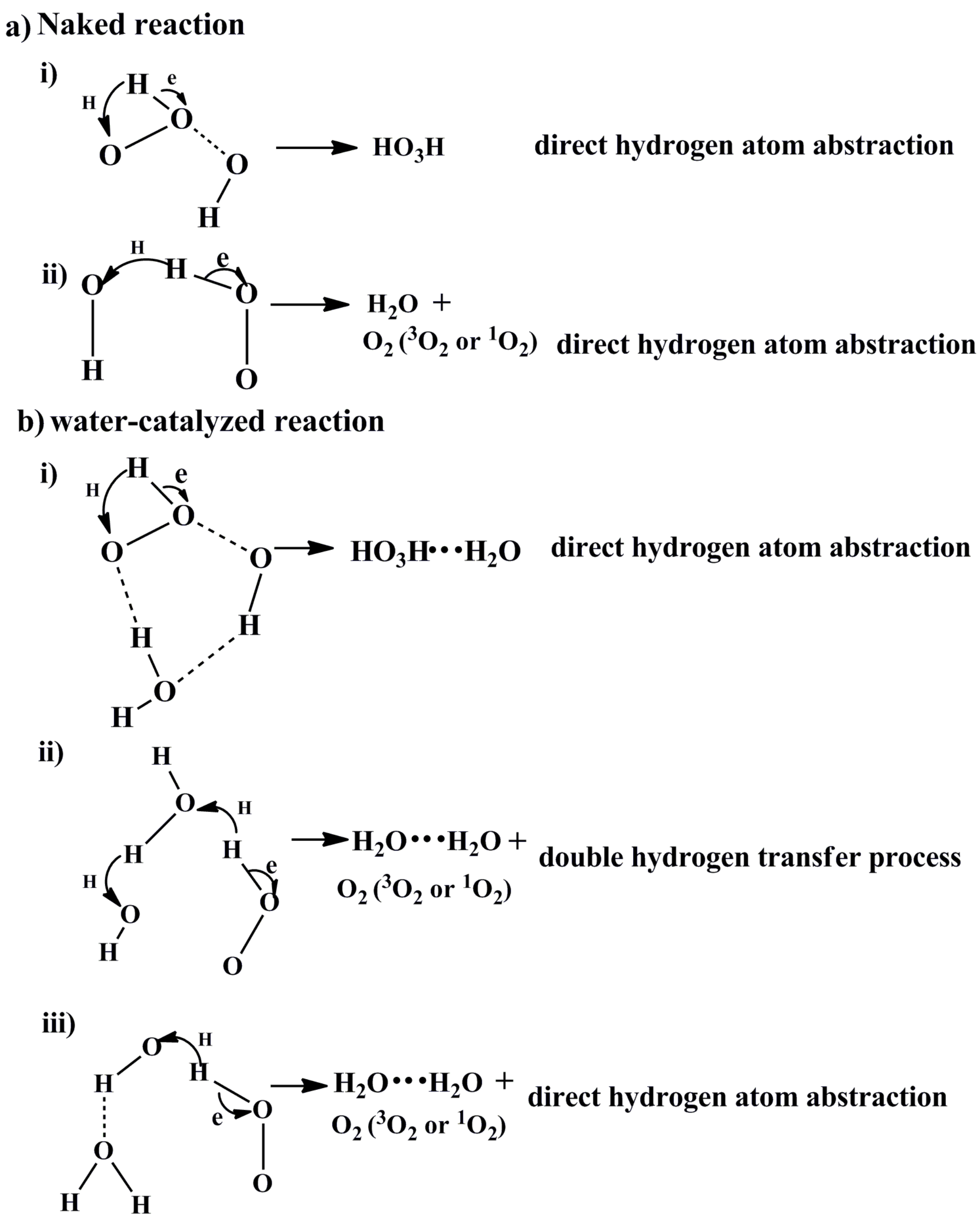


Fig. S3 Pictorial representation of (a) naked processes of HO_3H, $^1O_2$ and $^3O_2$ formation; (b) water-catalyzed processes of HO_3H, $^1O_2$ and $^3O_2$ formation in the HO_2 + OH reaction

Table S1 T_1 diagnostic values and spin contamination for the species that involved in the HO_2 + HO reaction without and with a water molecule

Species	T_1(<S^2>)	Species	T_1(<S^2>)	Species	T_1(<S^2>)
HO_2	0.030(0.7501)	OH	0.010 (0.7500)	H_2O	0.010(0.0000)
$^1O_2$	0.015(0.0000)	$^3O_2$	0.017 (2.0006)	$HO_2\cdots H_2O$	0.029 (0.7500)
$HO\cdots H_2O$	0.010(0.7500)	$H_2O\cdots H_2O$	0.010(0.0000)	HO_3H	0.011(0.0000)
IM1	0.028(0.0000)	TS1	0.020(0.0000)	IM2	0.018(0.0000)
TS2	0.022(0.0000)	TS2a	0.022(0.0000)	IM3	0.037(2.0000)
TS3	0.035(2.0000)	TS3a	0.035(2.0000)	IMW1	0.020(0.0000)
TSW1	0.019(0.0000)	IMW2	0.020(0.0000)	TSW2	0.019(0.0000)
IMW3	0.015(0.0000)	IMW3a	0.015(0.0000)	TSW3	0.020(0.0000)
TSW3a	0.020(0.0000)	TSW4	0.019(0.0000)	TSW4a	0.019(0.0000)
TSW5	0.019(0.0000)	IMW6	0.024(2.0000)	TSW6	0.024(2.0000)
IMW7	0.026(2.0000)	IMW7a	0.026(2.0000)	TSW7	0.040(2.0000)
TSW7a	0.041(2.0000)	IMW8	0.027(2.0000)	IMW8a	0.027(2.0000)
TSW8	0.039(2.0000)	TSW8a	0.039(2.0000)		

The values with and without parentheses were the T_1 diagnostic values and spin contamination, respectively.

Table S2 The electronic energies (E) and relative energies (ΔE) (in kcal·mol^{-1}) for the HO_2 + OH reaction at the CASSCF/aug-cc-pV5Z//CCSD/6-311G(d,p) level

Species	E(a.u.)	ΔE(a.u.)	ΔE(kcal·mol^{-1})
HO_2 + OH	-225.751411	0.00	0.00
IM1	-225.734933	0.016478	10.34
TS1	-225.714487	0.036924	23.17
$^1HO_3H$	-225.806119	-0.05471	-34.33
IM2	-225.751204	0.000207	0.13
TS2	-225.749307	0.002104	1.32
TS2a	-225.748574	0.002837	1.78
H_2O + $^1O_2$	-225.835378	-0.08397	-52.69
IM3	-225.762216	-0.0108	-6.78
TS3	-225.748447	0.002964	1.86
TS3a	-225.748447	0.002964	1.86
H_2O + $^3O_2$	-225.869911	-0.118500	-74.36

Table S3 Rate constants ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$) for the process of HO_3H formation without and with a water molecule

T (K)	k_{RW1}	k_{R1}	k_{RW1}/k_{R1}
298.2	1.324E-36	8.747E-33	1.51E-04
288.2	2.147E-36	1.221E-32	1.76E-04
275.2	5.745E-36	1.645E-31	3.49E-05
262.2	1.601E-35	1.606E-30	9.97E-06
249.3	4.618E-35	1.187E-29	3.89E-06
236.3	1.358E-35	6.816E-28	1.99E-08
223.3	4.009E-34	3.088E-27	1.30E-07
216.7	9.131E-34	4.932E-26	1.85E-08

k_{RW1} and k_{R1} was the rate constants of Channel RW1 and Channel R1, respectively.

Table S4 Kinetic results for water-catalyzed $^1O_2$ formation occurring through $HO_2 \cdots H_2O$ + OH and HO_2 + $HO \cdots H_2O$ reactions

T(K)	Keq(IMW2)	k_{IMW3}	k_{IMW3a}	k(TSW3)	k(TSW3a)	k_2(RW2a)	k_{RW2a}
298.2	4.06E-25	8.43E+11	1.24E+12	1.18E+11	1.13E+11	2.08E+11	8.46E-14
288.2	3.96E-25	8.18E+11	1.05E+12	7.26E+10	4.53E+10	1.11E+11	4.39E-14
275.2	3.90E-25	8.09E+11	8.82E+11	4.92E+10	3.99E+10	8.46E+10	3.30E-14
262.2	3.76E-25	7.88E+11	7.22E+11	3.80E+10	3.77E+10	7.21E+10	2.71E-14
249.3	3.66E-25	7.73E+11	5.61E+11	2.91E+10	1.76E+10	4.51E+10	1.65E-14
236.3	3.53E-25	7.36E+11	4.38E+11	2.09E+10	1.66E+10	3.63E+10	1.28E-14
223.3	3.39E-25	7.20E+11	3.91E+11	1.85E+10	1.53E+10	3.27E+10	1.11E-14
T(K)	k_{RW2b1}	k_{RW2b2}	k_{RW2b3}	k_{RW2b}			
298.2	3.16E-19	2.11E-19	1.34E-19	6.61E-19			
288.2	2.15E-19	1.56E-19	9.77E-20	4.69E-19			
275.2	1.25E-19	1.03E-19	6.27E-20	2.91E-19			
262.2	6.98E-20	6.56E-20	3.89E-20	1.74E-19			
249.3	4.03E-20	3.70E-20	2.32E-20	1.00E-19			
236.3	2.38E-20	1.85E-20	1.32E-20	5.55E-20			
223.3	1.34E-20	8.74E-21	7.19E-21	2.93E-20			

K_{eq}(IMW2) was the equilibrium constant for the process of $HO_2 \cdots H_2O$ + OH → IMW2 ; k(IMW3) and k(IMW3a) was the rate constant for the process of IMW2 →TSW2 →IMW3 and IMW2 →TSW2 →IMW3a, respectively; k(TSW3) and k(TSW3a) was the rate constant for the process of IMW3 →TSW3 →$H_2O \cdots H_2O$ + $^1O_2$ and IMW3a →TSW3a →$H_2O \cdots H_2O$ + $^1O_2$, respectively; $k_{RW2b1,}$ k_{RW2b2} and k_{RW2b3} was the rate constant for the process of $HO_2 \cdots H_2O$ + OH → $H_2O \cdots H_2O$ + $^1O_2$ via TSW4, TSW4a and TSW5, respectively.

Table S5 Kinetic results for water-catalyzed $^3O_2$ formation occurring through $HO_2 \cdots H_2O$ + OH and HO_2 + $HO \cdots H_2O$ reactions

T(K)	Keq(IMW6	k_{IMW7}	k_{IMW7a}	k_{TSW7}	k_{TSW7a}	k_2(RW3a	k_{RW3a}
298.	4.51E-25	9.92E+11	5.28E+11	8.44E+09	2.03E+10	2.82E+10	1.27E-1
288.	4.66E-25	1.01E+12	5.92E+11	8.26E+09	2.02E+10	2.80E+10	1.30E-1
275.	4.88E-25	1.05E+12	7.29E+11	8.03E+09	2.00E+10	2.76E+10	1.35E-1
262.	5.15E-25	1.08E+12	8.80E+11	7.79E+09	1.98E+10	2.72E+10	1.40E-1
249.	5.47E-25	1.12E+12	1.05E+1	7.55E+09	1.95E+10	2.67E+10	1.46E-1
236.	5.88E-25	1.15E+12	1.23E+1	7.31E+09	1.93E+10	2.63E+10	1.55E-1
223.	6.39E-25	1.18E+12	1.42E+1	7.07E+09	1.91E+10	2.59E+10	1.66E-1
216.	6.77E-25	1.21E+12	1.58E+1	6.96E+09	1.89E+10	2.56E+10	1.73E-1
T(K)	Keq(IMW8	Keq(IMW8a	k(TSW8)	k(TSW8a	k_2(RW3b	k_{RW3b}	
298.	2.84E-23	1.25E-23	3.02E+1	4.48E+12	7.50E+12	1.42E-10	
288.	4.02E-23	1.75E-23	2.98E+1	4.60E+12	7.58E+12	2.00E-10	
275.	6.53E-23	2.81E-23	2.92E+1	4.82E+12	7.74E+12	3.26E-10	
262.	1.11E-22	4.72E-23	2.85E+1	5.03E+12	7.88E+12	5.54E-10	
249.	2.01E-22	8.37E-23	2.79E+1	5.24E+12	8.03E+12	9.99E-10	
236.	3.88E-22	1.58E-22	2.71E+1	5.43E+12	8.14E+12	1.91E-09	
223.	8.06E-22	3.21E-22	2.64E+1	5.62E+12	8.26E+12	3.93E-09	
216.	1.28E-21	5.02E-22	2.60E+1	5.76E+12	8.36E+12	6.22E-09	

K_{eq}(IMW6) was the equilibrium constant for the process of $HO_2 \cdots H_2O$ + OH → IMW6; k_{IMW7} and k_{IMW7a} was the rate constant for the process of IMW6 →TSW6 →IMW7 and IMW6 →TSW7 →IMW7a respectively; k_{TSW7} and k_{TSW7a} was the rate constant for the process of IMW7 →TSW7→$H_2O \cdots H_2O$ +$^3O_2$ and IMW7a →TSW7a →$H_2O \cdots H_2O$ +$^3O_2$ respectively; k_2(RW3a) was the rate constant for the process of IMW6 →$H_2O \cdots H_2O$ +$^3O_2$; K_{eq}(IMW8) and K_{eq}(^{3}IMW8a) was the equilibrium constant for the process of $HO_2 \cdots H_2O$ + HO → IMW8 and $HO_2 \cdots H_2O$ + HO → IMW8a, respectively;
k(TSW8) and k(TSW8a) was the rate constant for the process of IMW8 →TSW8 → $H_2O \cdots H_2O$ + $^3O_2$ and IMW8a →TSW8a→ $H_2O \cdots H_2O$ + $^3O_2$, respectively.

References

1 C. Gonzalez, J. Theisen, L. Zhu, H. B. Schlegel, W. L. Hase and E. W. Kaiser, *J. Phys. Chem.*, 1991, **95**, 6784-6792.

2 C. Gonzalez, J. Theisen, H. B. Schlegel, W. L. Hase and E. W. Kaiser, *J Phys Chem*, 1992, **96**, 1767-1774.