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

Supporting Information

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Effect of a single water molecule on the HO_2 + ClO reaction

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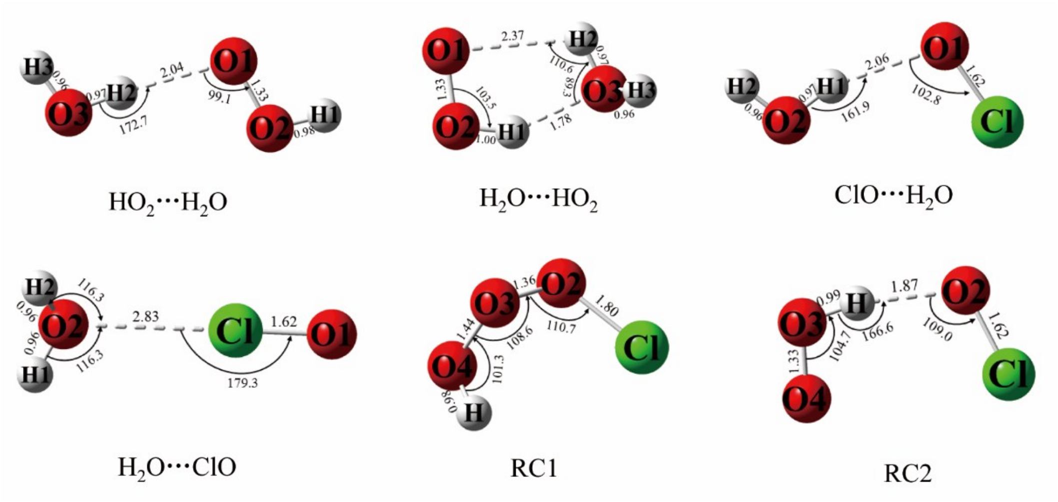

$HO_2\cdots H_2O$ $H_2O\cdots HO_2$ $ClO\cdots H_2O$

$H_2O\cdots ClO$ RC1 RC2

Figure S1 Geometrical parameters for the binary complexes optimized at the B3LYP-D3/aug-cc-pVDZ level of theory.

Table S1 Equilibrium constants (K_{eq} in units of cm^3 molecule^{-1}**)** for the formation of $HO_2{\bullet}{\bullet}{\bullet}H_2O$, $H_2O{\bullet}{\bullet}{\bullet}HO_2$, $ClO{\bullet}{\bullet}{\bullet}H_2O$ and $H_2O{\bullet}{\bullet}{\bullet}ClO$ complexes at different heights in the Earth atmosphere

H (km)	T (K)	$[H_2O]^a$	$K_{eq}(HO_2{\bullet}{\bullet}{\bullet}H_2O)$	$K_{eq}(H_2O{\bullet}{\bullet}{\bullet}HO_2)$	$K_{eq}(ClO{\bullet}{\bullet}{\bullet}H_2O)$	$K_{eq}(H_2O{\bullet}{\bullet}{\bullet}ClO)$
0	298.15	7.72×10^{17}	1.74×10^{-24}	1.04×10^{-22}	1.86×10^{-23}	2.51×10^{-23}
0	288.19	4.03×10^{17}	1.71×10^{-24}	1.35×10^{-22}	1.91×10^{-23}	2.65×10^{-23}
2	275.21	1.86×10^{17}	1.67×10^{-24}	1.93×10^{-22}	1.99×10^{-23}	2.87×10^{-23}
4	262.23	7.34×10^{16}	1.63×10^{-24}	2.89×10^{-22}	2.09×10^{-23}	3.13×10^{-23}
6	249.25	2.60×10^{16}	1.60×10^{-24}	4.50×10^{-22}	2.20×10^{-23}	3.45×10^{-23}
8	236.27	8.02×10^{15}	1.56×10^{-24}	7.40×10^{-22}	2.35×10^{-23}	3.87×10^{-23}
10	223.29	2.11×10^{15}	1.53×10^{-24}	1.29×10^{-21}	2.53×10^{-23}	4.40×10^{-23}
12	216.69	9.98×10^{14}	1.51×10^{-24}	1.76×10^{-21}	2.64×10^{-23}	4.74×10^{-23}

[a] Water concentrations are taken from Ref 1.[1]

[b] U.S. standard atmosphere.[2]

Table S2 Rate constant (cm^3 molecule^{-1} s^{-1}) for the HO_2 + ClO reaction and effective rate constants (cm^3 molecule^{-1} s^{-1}) for reactions with water at different altitudes in the Earth atmosphere

H (km)	T (K)	k'_{RC1W1}	k'_{RC1W2}	k'_{RC2W1}	k'_{RC2W2}
0	298.15	1.09×10^{-25}	1.07×10^{-23}	2.61×10^{-23}	7.06×10^{-29}
0	288.19	3.88×10^{-26}	4.66×10^{-24}	1.14×10^{-23}	1.96×10^{-29}
2	275.21	9.01×10^{-27}	1.43×10^{-24}	3.55×10^{-24}	3.21×10^{-30}
4	262.23	1.80×10^{-27}	3.87×10^{-25}	9.71×10^{-25}	4.34×10^{-31}
6	249.25	3.04×10^{-28}	9.15×10^{-26}	2.32×10^{-25}	4.81×10^{-32}
8	236.27	4.11×10^{-29}	1.80×10^{-26}	4.63×10^{-26}	4.05×10^{-33}
10	223.29	4.34×10^{-30}	2.89×10^{-27}	7.55×10^{-27}	2.52×10^{-34}
12	216.69	1.24×10^{-30}	1.04×10^{-27}	2.75×10^{-27}	5.39×10^{-35}

k'_{RC1W1}, k'_{RC1W2}, k'_{RC2W1} and k'_{RC2W2} are effective rate constants of Paths RW1, RW2, RW3 and RW4, respectively.

Table S3 Ratios of effective rate constants (cm^3 molecule^{-1} s^{-1}) to corresponding rate constants for the HO_2 + ClO reaction with and without water at different heights in the Earth atmosphere

H (km)	T (K)	k'_{RC1W1}/ k_{R1}	k'_{RC1W2}/k_{R2}	k'_{RC2W1}/k_{R2}	k'_{RC2W2}/k_{R2}
0	298.15	1.02×10^{-5}	4.69×10^{-7}	1.14×10^{-6}	3.10×10^{-12}
0	288.19	5.91×10^{-6}	2.56×10^{-7}	6.26×10^{-7}	1.08×10^{-12}
2	275.21	2.71×10^{-6}	1.08×10^{-7}	2.69×10^{-7}	2.43×10^{-13}
4	262.23	1.15×10^{-6}	4.16×10^{-8}	1.04×10^{-7}	4.67×10^{-14}
6	249.25	4.40×10^{-7}	1.44×10^{-8}	3.65×10^{-8}	7.56×10^{-15}
8	236.27	1.48×10^{-7}	4.32×10^{-9}	1.11×10^{-8}	9.71×10^{-16}
10	223.29	4.30×10^{-8}	5.12×10^{-9}	2.89×10^{-9}	9.66×10^{-17}
12	216.69	2.16×10^{-8}	5.15×10^{-10}	1.36×10^{-9}	2.67×10^{-17}

The values of k_{R1} and k_{R2} are given in Table 4 in the main manuscript.

Table S4 Vibrational frequencies of the reactant complexes and transition states predicted at the B3LYP-D3/aug-cc-pVDZ level.

species	Frequencies (cm^{-1})
RC1	161, 310, 400, 530, 590, 758, 925, 1390, 3688
RC2	28, 49, 147, 183, 404, 857, 1163, 1500, 3386
TS1	i1032, 196, 368, 455, 735, 888, 1033, 1251, 1543
TS2	i543, 205, 260, 452, 491, 830, 1213, 1523, 2365
RC1W1	72, 104, 128, 156, 258, 277, 357, 391, 511, 584, 763, 844, 935, 1517, 1614, 3346, 3764, 3876
RC1W2	68, 152, 189, 241, 263, 272, 335, 409, 466, 683, 869, 962, 995, 1575, 1635, 3153, 3555, 3857
TS1W1	i925, 31, 64, 87, 128, 155, 191, 304, 354, 460, 740, 922, 1050, 1261, 1505, 1618, 3778, 3890
TS1W2	i897, 50, 87, 111, 136, 182, 207, 255, 335, 458, 481, 814, 1281, 1495, 1615, 1983, 3786, 3895
RC2W1	97, 128, 179, 226, 269, 324, 335, 441, 493, 642, 864, 1052, 1162, 1601, 1626, 2997, 3509, 3859
RC2W2	44, 99, 131, 152, 236, 269, 350, 381, 521, 590, 757, 823, 918, 1526, 1617, 3390, 3773, 3882
TS2W1	i882, 51, 73, 106, 116, 179, 208, 250, 278, 462, 487, 817, 1275, 1497, 1614, 2003, 3789, 3898
TS2W2	i984, 47, 91, 97, 120, 142, 195, 217, 290, 327, 480, 768, 1359, 1553, 1616, 2216, 3786, 3892

Table S5 Quantum mechanical tunneling coefficient for different paths at 298 K.

TS	Frequencies (cm^{-1})	κ
TS1	i1032	2.04
TS2	i543	1.29
TS1W1	i925	1.83
TS1W2	i897	1.78
TS2W1	i882	1.76
TS2W2	i984	1.94

Details of the rate constants calculation of the barrierless path

For the barrierless reaction, a semi-empirical equation is used to obtain the rate constant, in which some experimental data were used to fit in the theoretical calculation:

$$k(T) = A(T/298K)^{n} e^{-Ea/RT}$$

where n is the order of the reaction, it is 2 here because our title reaction is a second order reaction. *Ea* is the activation energy barrier of the reaction, for this barrierless path, it is 0. A is the pre-exponential factor, determined by experiments. According to the experimental research of Leck et al, the value of A is 4.53×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.[3] Different values of the rate constant of this barrierless path (k_{R4}) are listed in Table 4.

References

1. P. R. Lowe, *J. Appl. Meteorol.*, 1977, **16**, 100-103.
2. J. H. Seinfeld and S. N. Pandis, *Atmospheric chemistry and physics: from air pollution to climate change*, John Wiley & Sons, 2016.
3. T. J. Leck, J. E. L. Cook and J. W. Birks, *J. Chem. Phys.*, 1980, **72**, 2364-2373.