FIGURE S1. The energy profile [kcal/mol] and geometrical parameters for Cl· + H$_2$O → HCl + OH· reaction obtained by CCSD(T)/cc-pVQZ//ωB97XD/cc-pVTZ and CCSD(T)/aug-cc-pVQZ//ωB97XD/aug-cc-pVTZ calculations.
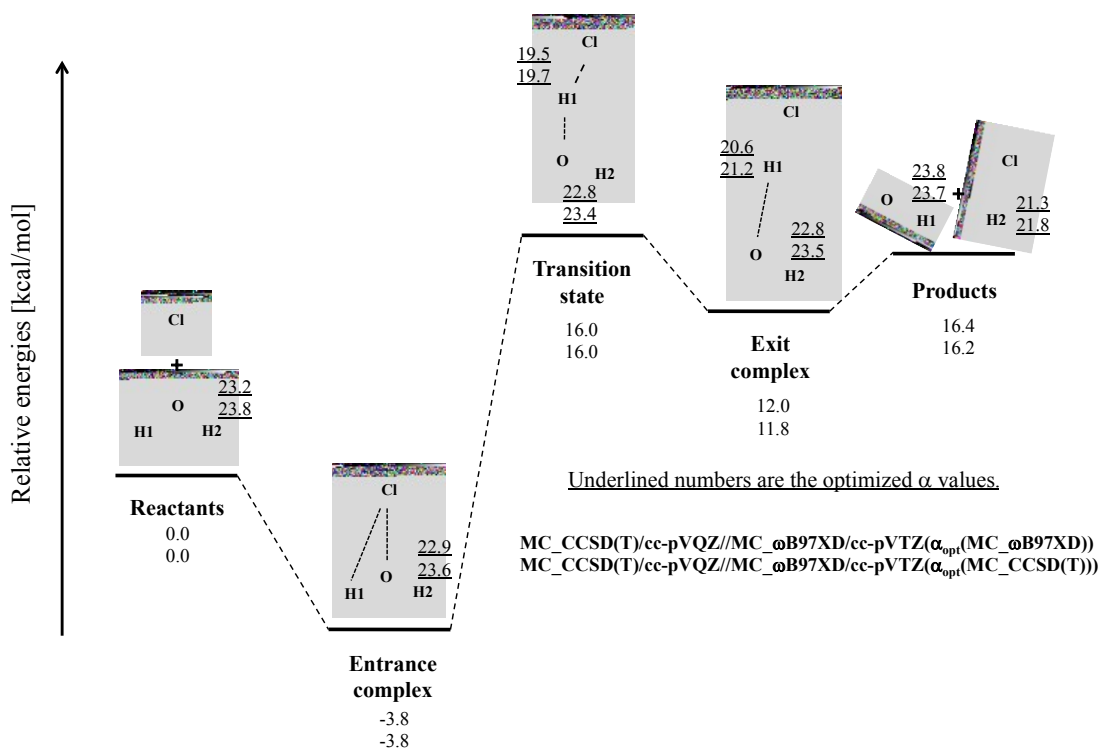
Relative energies [kcal/mol]

Transition state
16.0
16.0

Cl
<u>19.5</u>
<u>19.7</u>
H1
O   H2
<u>22.8</u>
<u>23.4</u>

Cl
+
O   <u>23.2</u>
<u>23.8</u>
H1   H2

Reactants
0.0
0.0

Cl
H1 O   <u>22.9</u>
<u>23.6</u>
H2

Entrance complex
-3.8
-3.8

Cl
<u>20.6</u>
<u>21.2</u> H1
O   <u>22.8</u>
<u>23.5</u>
H2

Exit complex
12.0
11.8

Cl
O   <u>23.8</u>
<u>23.7</u>   +   H2   <u>21.3</u>
H1   <u>21.8</u>

Products
16.4
16.2

Underlined numbers are the optimized α values.

MC_CCSD(T)/cc-pVQZ//MC_ωB97XD/cc-pVTZ(α_opt(MC_ωB97XD))
MC_CCSD(T)/cc-pVQZ//MC_ωB97XD/cc-pVTZ(α_opt(MC_CCSD(T)))

FIGURE S2. The potential energy profile [kcal/mol] for Cl· + H_2O → HCl + OH· reaction by MC_CCSD(T)/cc-pVQZ//MC_ωB97XD/cc-pVTZ calculations with the optimized $α_{opt}$ values by MC_ωB97XD/MC_cc-pVQZ//MC_ωB97XD/cc-pVTZ($α_{opt}$(MC_ωB97XD)) and MC_CCSD(T)/cc-pVQZ//MC_ωB97XD/cc-pVTZ($α_{opt}$(MC_CCSD(T))) calculations.
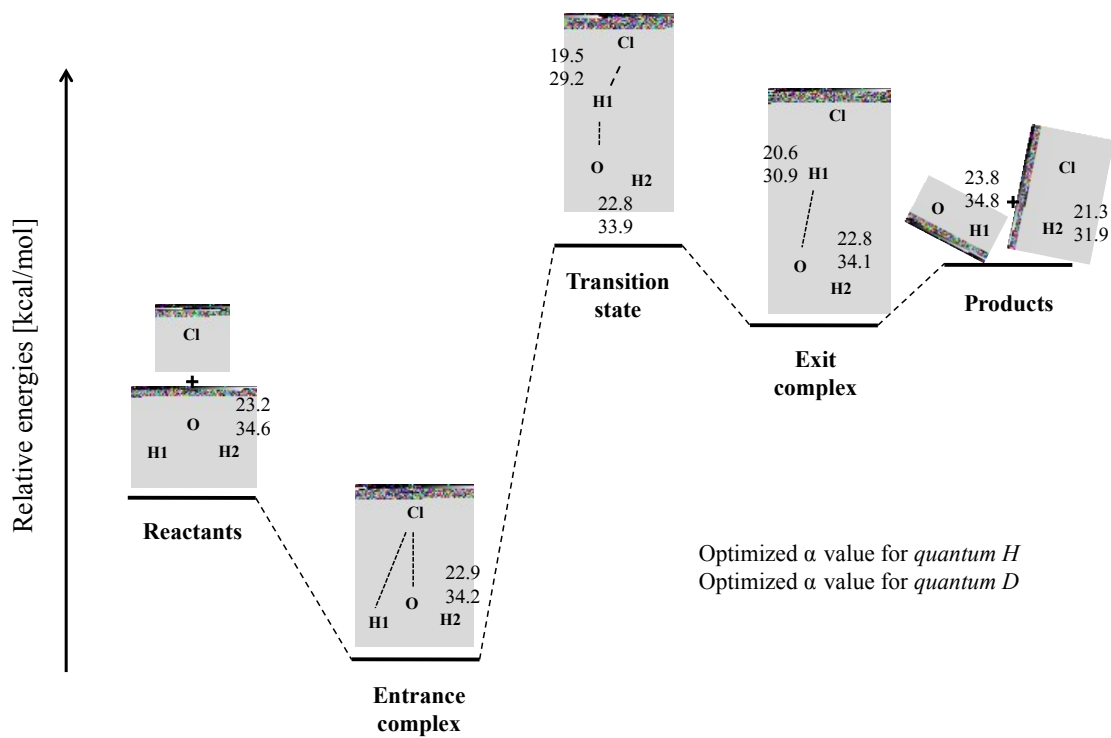
FIGURE S3. The exponent α_{opt} value of nuclear basis function obtained by MC_ωB97XD/cc-pVQZ//MC_ωB97XD/cc-pVTZ calculation for Cl· + H$_2$O → HCl + OH· and Cl· + D$_2$O → DCl + OD· reaction.
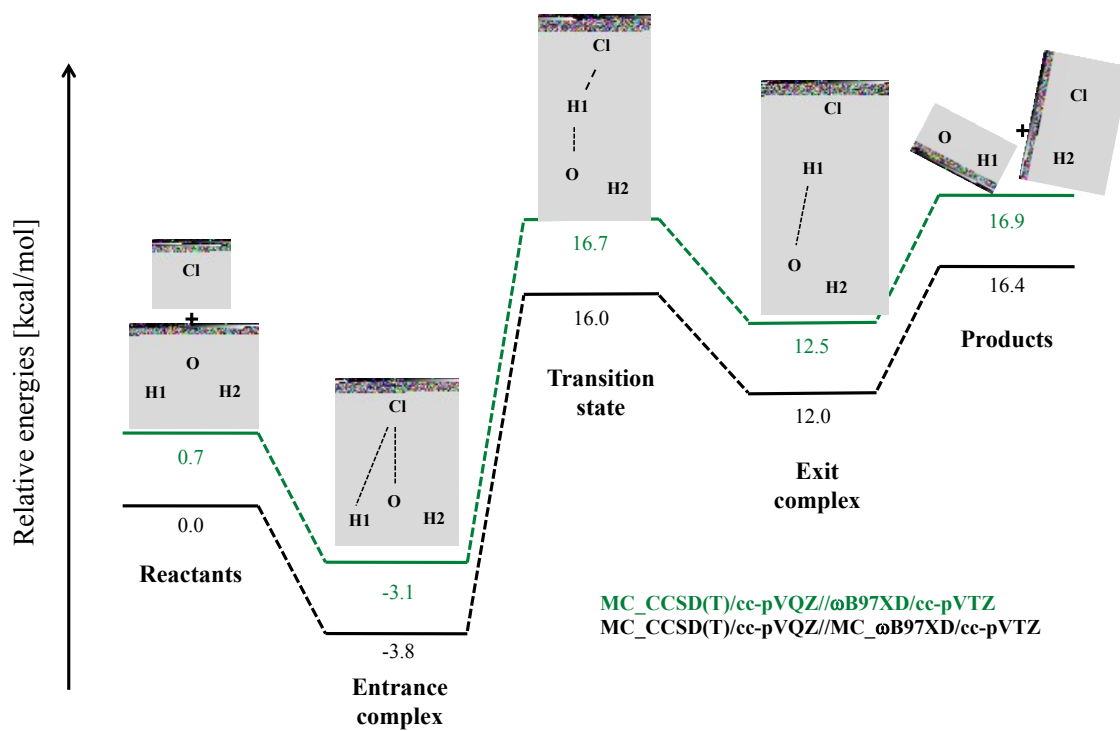
FIGURE S4. The potential energy profile [kcal/mol] for Cl· + H$_2$O → HCl + OH· reaction obtained by MC_CCSD(T)/cc-pVQZ//ωB97XD/cc-pVTZ and MC_CCSD(T)/cc-pVQZ//MC_ωB97XD/cc-pVTZ methods.
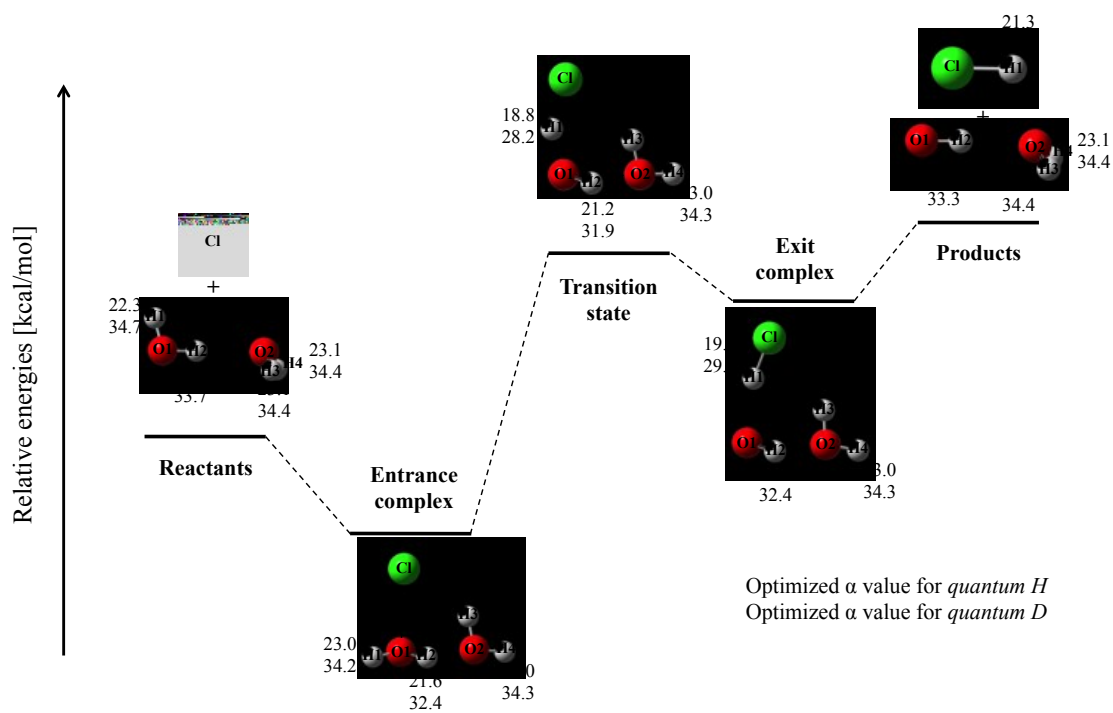
FIGURE S5. The exponent α_{opt} value of nuclear basis function obtained by MC_ωB97XD.cc-pVQZ//MC_ωB97XD/cc-pVTZ calculation for Cl· + $(H_2O)_2 \rightarrow$ HCl + OH·(H_2O) and Cl· + $(D_2O)_2 \rightarrow$ DCl + OD·(D_2O) reaction.
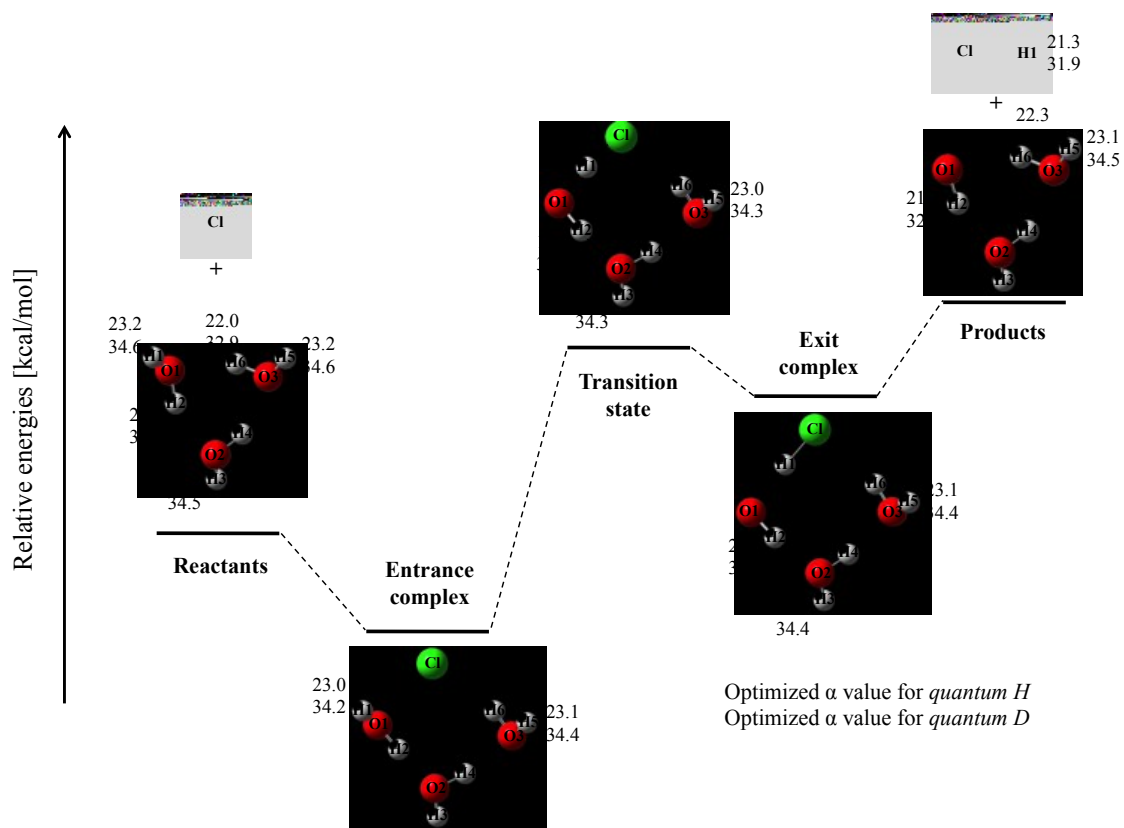
FIGURE S6. The exponent α_{opt} value of nuclear basis function obtained by MC_ωB97XD/cc-pVQZ//MC_ωB97XD/cc-pVTZ calculation for Cl· + $(H_2O)_3 \to$ HCl + OH·$(H_2O)_2$ and Cl· + $(D_2O)_3 \to$ DCl + OD·$\overline{(D_2O)_2}$ reaction.

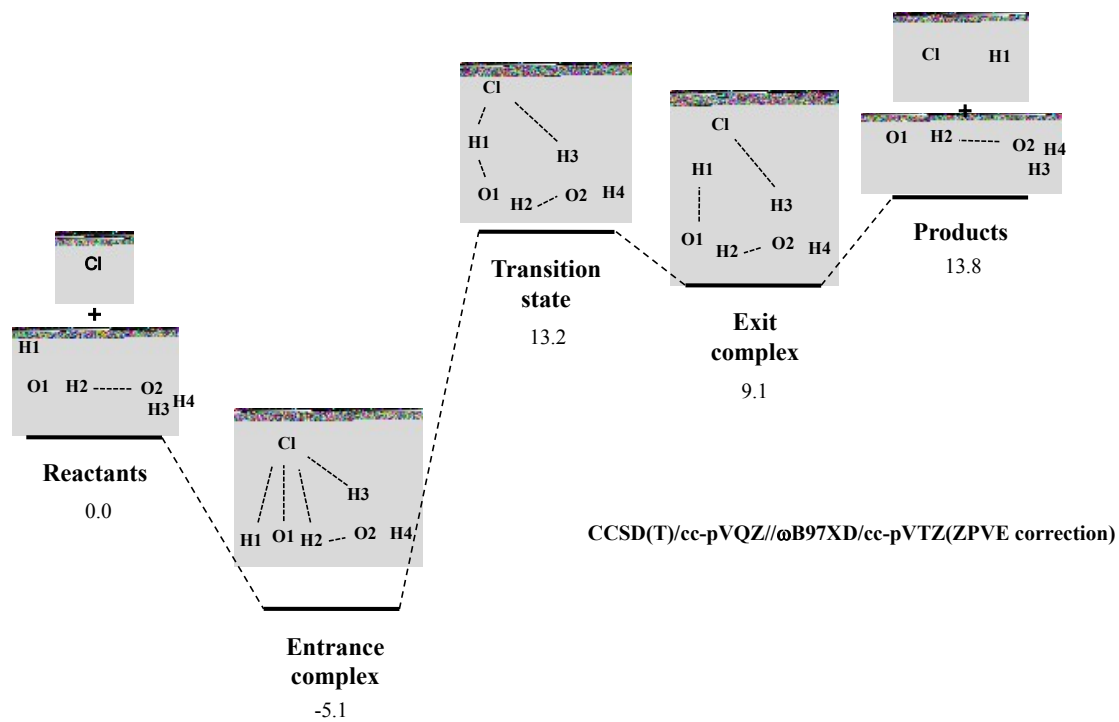FIGURE S7. The potential energy profile (kcal/mol) and the optimized geometrical parameters (Å) for $Cl\cdot + (H_2O)_2 \rightarrow HCl + OH\cdot (H_2O)$ reaction obtained by CCSD(T)/cc-pVQZ//ωB97XD/cc-pVTZ calculations. Relative energies are calculated as the energy difference between the energy of each stationary point structure and sum of energies of Cl radical and $(H_2O)_2$ (**Reactants**).

FIGURE S8. The potential energy profile (kcal/mol) and stationary point structures for Cl· + (H₂O)₃ → HCl + OH· (H₂O)₂ reaction obtained by CCSD(T)/cc-pVQZ//ωB97XD/cc-pVTZ calculations. Relative energies are calculated as the energy difference between the energy of each stationary point structure and sum of energies of Cl radical and (H₂O)₃ (**Reactants**).

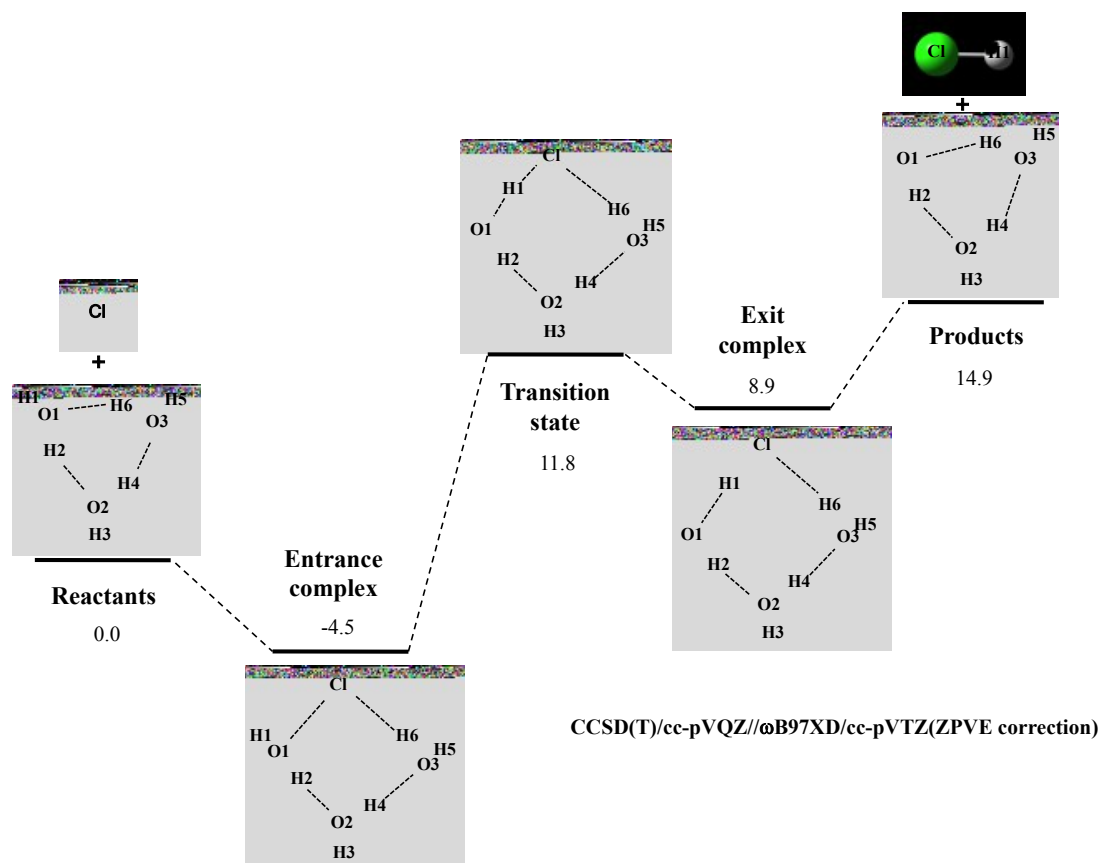TABLE S1. Optimized geometrical parameter (Å) of **Reactants** for Cl· + $(H_2O)_2 \rightarrow$ HCl + OH·(H_2O) reaction obtained by DFT/cc-pVTZ methods.

Method	R(O1-H1)	R(O1-H2)	R(O2-H3)	R(O2···H2)
B3LYP	0.960	0.968	0.962	1.948
CAM-B3LYP	0.959	0.967	0.961	1.906
M06	0.957	0.966	0.959	1.936
ωB97XD	0.956	0.965	0.958	1.936
MPW1K	0.950	0.958	0.951	1.933
CCSD(T)/cc-pVQZ[a]	0.957	0.964	0.959	1.953

[a]Ref. 7

TABLE S2. Optimized geometrical parameter (Å) of **Exit complex** for Cl· + $(H_2O)_2 \rightarrow$ HCl + OH·(H_2O) reaction obtained by DFT/cc-pVTZ methods.

Method	R(O1-H2)	R(O2-H3)	R(O2-H4)	R(O1···H1)	R(O2···H2)	R(Cl···H1)	R(Cl···H3)
B3LYP	0.994	0.967	0.962	1.818	1.788	1.318	2.649
CAM-B3LYP	0.993	0.966	0.960	1.810	1.761	1.313	2.582
M06	0.989	0.965	0.958	1.877	1.809	1.311	2.514
ωB97XD	0.988	0.962	0.957	1.844	1.800	1.311	2.640
MPW1K	0.981	0.955	0.951	1.813	1.779	1.304	2.661
CCSD(T)/ cc-pVQZ[a]	0.983	0.962	0.968	1.916	1.835	1.298	2.616

[a]Ref. 7

TABLE S3. Optimized geometrical parameter (Å) of **Products** for Cl· + $(H_2O)_2 \rightarrow$ HCl + OH·(H_2O) reaction obtained by DFT/cc-pVTZ methods.

Method	OH·(H_2O)			HCl
	R(O1-H2)	R(O2-H3)	R(O2···H2)	R(Cl-H2)
B3LYP	0.983	0.962	1.881	1.283
CAM-B3LYP	0.982	0.960	1.848	1.280
M06	0.980	0.958	1.886	1.283
ωB97XD	0.979	0.957	1.882	1.280
MPW1K	0.971	0.951	1.871	1.273
CCSD(T)/cc-pVQZ[a]	0.976	0.958	1.903	1.277

[a]Ref. 7

TABLE S4. Optimized geometrical parameters (Å) of **Reactants** for Cl· + (H₂O)₃ → HCl + OH·(H₂O)₂ reaction obtained by DFT/cc-pVTZ methods.

Method	R(O1-H1)	R(O1-H2)	R(O2-H3)	R(O2-H4)	R(O3-H5)	R(O3-H6)	R(O1···H6)	R(O2···H2)	R(O3···H4)
B3LYP	0.961	0.977	0.961	0.977	0.961	0.977	1.894	1.877	1.876
CAM-B3LYP	0.959	0.977	0.959	0.977	0.959	0.976	1.856	1.841	1.837
M06	0.957	0.974	0.957	0.974	0.957	0.974	1.891	1.882	1.876
ωB97XD	0.956	0.972	0.957	0.973	0.956	0.972	1.896	1.882	1.877
MPW1K	0.950	0.966	0.950	0.966	0.950	0.965	1.882	1.862	1.859

TABLE S5. Optimized geometrical parameters (Å) of **Entrance complex** for Cl· + (H₂O)₃ → HCl + OH·(H₂O)₂ reaction obtained by DFT/cc-pVTZ methods.

Method	R(O1-H1)	R(O1-H2)	R(O2-H3)	R(O2-H4)	R(O3-H5)	R(O3-H6)	R(O1···Cl)	R(O2···H2)	R(O3···H4)	R(Cl···H6)
B3LYP	0.965	1.000	0.961	0.984	0.962	0.973	2.419	1.660	1.752	2.311
CAM-B3LYP	0.963	0.997	0.960	0.982	0.960	0.971	2.371	1.649	1.730	2.295
M06	0.962	0.990	0.958	0.978	0.958	0.969	2.433	1.706	1.776	2.331
ωB97XD	0.960	0.991	0.957	0.978	0.957	0.968	2.386	1.676	1.761	2.313
MPW1K	0.953	0.984	0.951	0.971	0.951	0.961	2.356	1.664	1.749	2.320

TABLE S6. Optimized geometrical parameters (Å) of **Transition state** for Cl· + $(H_2O)_3 \rightarrow$ HCl + OH·$(H_2O)_2$ reaction obtained by DFT/cc-pVTZ methods.

Method	R(O1-H2)	R(O2-H3)	R(O2-H4)	R(O3-H5)	R(O3-H6)	R(O1···H1)	R(O2···H2)	R(O3···H4)	R(Cl···H1)	R(Cl···H6)
B3LYP	1.017	0.961	0.985	0.962	0.973	1.379	1.611	1.739	1.418	2.324
CAM-B3LYP	1.022	0.960	0.986	0.960	0.972	1.289	1.563	1.700	1.452	2.273
M06	1.001	0.958	0.980	0.958	0.970	1.374	1.631	1.754	1.420	2.289
ωB97XD	1.013	0.957	0.981	0.957	0.969	1.295	1.598	1.733	1.446	2.297
MPW1K	1.018	0.951	0.978	0.951	0.964	1.197	1.532	1.694	1.503	2.255

TABLE S7. Optimized geometrical parameters (Å) of **Exit complex** for Cl· + $(H_2O)_3 \rightarrow$ HCl + OH·$(H_2O)_2$ reaction obtained by DFT/cc-pVTZ methods.

Method	R(O1-H2)	R(O2-H3)	R(O2-H4)	R(O3-H5)	R(O3-H6)	R(Cl-H1)	R(O1···H1)	R(O2···H2)	R(O3···H4)	R(Cl···H6)
B3LYP	1.008	0.961	0.983	0.962	0.971	1.341	1.668	1.659	1.760	2.361
CAM-B3LYP	1.007	0.960	0.982	0.960	0.970	1.335	1.662	1.636	1.732	2.326
M06	0.998	0.957	0.978	0.958	0.968	1.325	1.752	1.701	1.783	2.343
ωB97XD	1.000	0.957	0.977	0.958	0.966	1.332	1.690	1.671	1.764	2.343
MPW1K	0.994	0.950	0.971	0.951	0.960	1.326	1.661	1.652	1.751	2.350

TABLE S8. Optimized geometrical parameters (Å) of **Products** for Cl· + $(H_2O)_3 \rightarrow$ HCl + OH·$(H_2O)_2$ reaction obtained by DFT/cc-pVTZ methods

| Method | OH·$(H_2O)_2$ | | | | | | | | HCl |
	R(O1-H2)	R(O2-H3)	R(O2-H4)	R(O3-H5)	R(O3-H6)	R(O1···H6)	R(O2···H2)	R(O3···H4)	R(Cl-H1)
B3LYP	0.994	0.961	0.977	0.961	0.973	2.018	1.808	1.878	1.283
CAM-B3LYP	0.994	0.959	0.976	0.959	0.972	1.977	1.775	1.838	1.280
M06	0.989	0.957	0.973	0.957	0.970	2.006	1.822	1.877	1.283
ωB97XD	0.988	0.957	0.972	0.957	0.968	2.032	1.817	1.881	1.280
MPW1K	0.980	0.950	0.965	0.950	0.961	2.018	1.799	1.865	1.273