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

Supplementary Information for

Effect of $(H_2O)_n$ (n=1 and 2) on HOCl + Cl reaction

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Sl. No. **Contents**

19. **Figure S3**: Comparison of geometrical parameters obtained at MO6-2X/aug-cc-pVTZ level of theory with CCSD/aug-cc-pVDZ level of theory (in parenthesis) for water catalyzed HOCl + Cl $\rightarrow$ HCl + ClO reaction. All bond length are given in Å.
20. **Figure S4**: Gibbs free energy profile for H_2O catalyzed HOCl + $Cl^{\bullet}$ $\longrightarrow$ HCl + $ClO^{\bullet}$ reaction, calculated at CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level of theory.
21. **Figure S5**: Gibbs free energy profile for $(H_2O)_2$ catalyzed HOCl + $Cl^{\bullet}$ $\longrightarrow$ HCl + $ClO^{\bullet}$ reaction , calculated at CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level of theory.

1 Formal proof for same value of termolecular rate constant for different paths of water catalyzed HOCl + $Cl^{\bullet} \longrightarrow$ HCl + $ClO^{\bullet}$ reaction.

$$\text{HOCl+Cl}^{\bullet}\text{+WM} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{HOCl-Cl}^{\bullet} + \text{WM} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{RC}_{d-HAT} \xrightarrow[\text{TS}_{d-HAT}]{k_{uni}} \text{Product} \qquad \text{Path A}_{WM}$$

$$\text{HOCl+Cl}^{\bullet}\text{+WM} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Cl}^{\bullet}\text{-WM} + \text{HOCl} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{RC}_{d-HAT} \xrightarrow[\text{TS}_{d-HAT}]{k_{uni}} \text{Product} \qquad \text{Path B}_{WM}$$

$$\text{HOCl+Cl}^{\bullet}\text{+WM} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Cl}^{\bullet}\text{-WM} + \text{HOCl} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{RC}_{i-HAT} \xrightarrow[\text{TS}_{i-HAT}]{k_{uni}} \text{Product} \qquad \text{Path C}_{WM}$$

$$\text{HOCl+Cl}^{\bullet}\text{+WM} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{HOCl-WM} + \text{Cl}^{\bullet} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{RC}_{i-HAT} \xrightarrow[\text{TS}_{i-HAT}]{k_{uni}} \text{Product} \qquad \text{Path D}_{WM}$$

For path A_{WM},

$$K_{eq1} = \frac{[HOCl - Cl]}{[HOCl][Cl]} \tag{1}$$

and

$$K_{eq2} = \frac{[RC_{d-HAT}]}{[HOCl - Cl][WM]} \tag{2}$$

Therefore,

$$K_{eq1} \times K_{eq2} = \frac{[RC_{d-HAT}]}{[HOCl][Cl][WM]} \tag{3}$$

Similarly, for path B_{WM},

$$K_{eq1} \times K_{eq2} = \frac{[Cl - WM]}{[Cl][WM]} \times \frac{[RC_{d-HAT}]}{[Cl - WM][HOCl]} \tag{4}$$

$$K_{eq1} \times K_{eq2} = \frac{[RC_{d-HAT}]}{[Cl][WM][HOCl]} \tag{5}$$

From the equation 3, and 5 it is clear that, the product of K_{eq1} and K$eq2$ is same for path A_{WM}, and B_{WM}. As the k_{uni} for path A_{WM}, and B_{WM} are also same, it gives same trimolecular rate k_t for d-HAT paths. Similarly, the k_t for i-HAT paths (Path C_{WM} and Path D_{WM}) are also found to be same.

Table S1: Comparison of frequencies obtained at CCSD/aug-cc-pVDZ level of theory with frequencies obtained at higher level of theory (CCSD(T)/cc-pVQZ).

Species	Frequencies (cm^{-1})	
	CCSD/aug-cc-pVDZ	CCSD(T)/cc-pVQZ
HOCl	731 1275 3791	807 1275 3844
TS	108 457 852 809 1390 i4768	126 331 875 1006 1097 i1549
OH	3717	3766
Cl_2	521	575
HCl	2989	2989
ClO	806	903

Table S2: Contribution of post-CCSD(T) corrections (kcal mol^{-1}) to the energy barrier for HOCl + Cl $\rightarrow$ HCl + ClO reaction.

Species	T1-diagnostic	CCSD(T)/CBS	ΔE_T	ΔE_Q	ZPE	Final
TS_{uncat}	0.0743	15.75	-2.12	-6.66	-3.05	3.92
RC_{uncat}	-	-2.76	-1.53	-1.76	0.45	-5.60
PC_{uncat}	-	-7.72	-0.44	-0.03	-1.77	-9.96
TS_{WM}	0.0550	0.10	-0.65	-0.66	0.03	-1.18
RC_{WM}	-	-12.79	-0.08	-0.07	2.81	-10.13
PC_{WM}	-	-14.66	-0.45	-0.68	0.20	-15.59
TS_{WM}^{d-HAT}	-	4.30	-0.34	-0.46	-2.03	1.47
RC_{WM}^{d-HAT}	-	-9.87	-1.10	-0.01	2.26	-8.72
PC_{WM}^{d-HAT}	-	-11.77	-0.29	-0.03	-0.57	-12.66
ClO + HCl	-	-5.60	-0.42	-0.02	-2.86	-8.90
Cl-WM	-	-3.36	-0.02	-0.01	0.71	-2.68
HOCl-WM	-	-7.83	-0.02	-0.01	2.03	-5.80
TS_{WD}	0.0351	-	-	-	-	-

* For the isolated product molecule, we have estimated the CCSD(T)/CBS value using aug-cc-pVnz (n= T, Q, 5) basis set.

Table S3: Contribution of post-CCSD(T) corrections (kcal mol^{-1}) to the energy barrier for HOCl + Cl $\rightarrow$ Cl_2 + OH reaction.

Species	T1-diagnostic	CCSD(T)/CBS	ΔE_T	ΔE_Q	ZPE	Final
TS_{uncat}	0.0312	2.75	-1.49	-0.56	-0.42	0.28
RC_{uncat}	-	-2.76	-1.53	-1.76	0.45	-5.60
PC_{uncat}	-	-1.96	-0.08	0.16	-1.68	-3.56
TS_{WM}	0.0271	-4.47	-1.51	-0.59	1.30	-5.27
RC_{WM}	-	-13.56	-0.09	-0.08	2.90	-10.83
PC_{WM}	-	-9.81	-0.08	0.14	0.54	-9.21
OH + Cl_2	-	-0.70	-0.07	0.17	-2.15	-2.75
TS_{WD}	0.0244	-	-	-	-	-

* For the isolated product molecule, we have estimated the CCSD(T)/CBS value using aug-cc-pVnz (n= T, Q, 5) basis set.

Table S4: Coordinates (in angstrom) and frequencies (in cm^{-1}) of all the important geometries of water catalyzed HOCl + Cl reaction optimized at M062-2X/aug-cc-pVTZ level of theory.

Species	Geometry				Frequencies		
HOCl	O	0.03597	1.08886	0.00000	806.9529	3844.2931	1275.9183
	H	-0.89927	1.32415	0.00000			
	Cl	0.03597	-0.59030	0.00000			
Cl	Cl	0.00000	0.00000	0.00000			
HCl	H	0.00000	0.00000	-1.20783	2989.4506		
	Cl	0.00000	0.00000	0.07105			
ClO	O	0.00000	0.00000	-1.06668	903.0413		
	Cl	0.00000	0.00000	0.50197			
RC_{uncat}^{R1}	O	-1.30337	1.03832	-0.00001	89.6724	158.3457	236.7789

Table S4: Coordinates (in angstrom) and frequencies (in cm^{-1}) of all the important geometries of water catalyzed HOCl + Cl reaction optimized at M062-2X/aug-cc-pVTZ level of theory.

Species	Geometry				Frequencies		
	H	-0.41034	1.41930	0.00004	801.7847	1322.2712	3736.1667
	Cl	-1.01876	-0.60511	0.00000			
	Cl	1.65625	0.03300	0.00000			
TS^{R1}_{uncat}	O	-0.54724	0.89825	-0.02064	126.5087	331.7842	875.078
	H	0.47557	0.50282	0.26728	1006.1816	1097.3497	1549.368i
	Cl	-1.62360	-0.30356	0.00048			
	Cl	1.85315	-0.14872	-0.00649			
PC^{R1}_{uncat}	O	-1.03437	1.03002	0.00010	48.053	66.5963	131.1955
	H	1.00822	0.63556	-0.00140	443.4933	917.1332	2884.7996
	Cl	-1.63255	-0.41684	-0.00002			
	Cl	2.06000	-0.10526	0.00005			
RC^{R2}_{uncat}	O	-1.30334	1.03851	0.00022	89.2268	158.3207	231.5424
	H	-0.41020	1.41926	-0.00163	801.5316	1321.4837	3738.624
	Cl	1.65647	0.03294	0.00003			
	Cl	-1.01901	-0.60514	-0.00004			
TS^{R2}_{uncat}	O	-2.31369	0.24223	-0.12984	165.3625	290.8317	441.6887
	H	-2.41544	0.79203	0.66343	834.7253	3786.0868	393.7563i
	Cl	1.61825	0.15659	-0.01922			
	Cl	-0.38737	-0.31717	0.04130			

Table S4: Coordinates (in angstrom) and frequencies (in cm^{-1}) of all the important geometries of water catalyzed HOCl + Cl reaction optimized at M062-2X/aug-cc-pVTZ level of theory.

Species	Geometry				Frequencies		
PC^{R2}_{uncat}	O	-3.00769	-0.05902	0.00000	241.9625	61.2672	111.6331
	H	-3.23369	0.88736	0.00000	221.578	564.4505	3756.5557
	Cl	-0.19688	-0.06467	0.00000			
	Cl	1.80248	0.04024	0.00000			
WM	O	0.00000	0.00000	0.11626	1618.6983	3867.7173	3971.4479
	H	0.00000	0.76310	-0.46505			
	H	0.00000	-0.76310	-0.46505			
RC^{WM}_{i-HAT}	O	-1.57167	-0.17474	-0.65232	75.863	119.1538	162.842
	H	-1.35064	0.75039	-0.35713	193.9229	215.4617	265.9002
	Cl	-0.63879	-1.11714	0.32219	314.5842	524.6308	811.6569
	O	-0.55584	2.11799	0.14721	880.2559	1464.402	1615.9607
	H	-0.69909	2.49767	1.01751	3186.5943	3746.3714	3921.7235
	H	0.36381	1.81337	0.12573			
	Cl	1.73914	-0.09506	-0.13073			
TS^{WM}_{i-HAT}	O	-1.59609	0.55278	-0.43437	724.3865i	86.2137	161.4383
	H	-0.53686	1.47439	-0.07214	218.3153	426.9676	442.3525
	Cl	-1.16171	-0.82099	0.19292	515.917	662.3547	934.7383
	O	0.41960	1.87079	0.10274	1243.1465	1288.6002	1587.991
	H	0.47455	2.21470	1.00256	1657.58	2380.2727	3853.0955

Table S4: Coordinates (in angstrom) and frequencies (in cm^{-1}) of all the important geometries of water catalyzed HOCl + Cl reaction optimized at M062-2X/aug-cc-pVTZ level of theory.

Species	Geometry				Frequencies		
	H	1.05045	0.95514	0.02515			
	Cl	1.65723	-0.59270	-0.09307			
PC_{i-HAT}^{WM}	O	-1.95958	0.42271	0.55971	20.7306	43.4788	63.6696
	H	-0.53063	1.73118	0.07617	147.5403	176.1524	192.2421
	Cl	-1.46314	-0.82986	-0.23520	285.5938	382.5316	500.5412
	O	0.33869	1.93252	-0.29504	648.2214	929.1171	1620.6561
	H	0.62614	2.75511	0.10761	2572.3806	3773.6635	3929.4796
	H	1.42559	0.50360	-0.09946			
	Cl	2.13644	-0.57201	0.10569			
RC_{d-HAT}^{WM}	O	-1.40607	-1.22044	-0.07470	47.1034	84.0597	134.6117
	H	-0.43237	-1.22656	-0.05279	156.3356	168.7461	216.1457
	Cl	-1.80062	0.40083	0.04330	385.3151	438.7016	571.2986
	Cl	1.78335	-0.72104	0.02834	807.1108	1357.6524	1601.1212
	O	1.27353	1.63839	-0.14502	3657.4664	3751.3029	3889.7934
	H	1.46772	1.84393	0.77614			
	H	0.31851	1.48271	-0.18354			
TS_{d-HAT}^{WM}	O	-0.63135	-0.58041	0.86876	1509.2529i	73.4949	94.471
	H	0.38439	-0.27082	0.52179	112.7289	127.6607	152.1998
	Cl	-1.70336	-0.34092	-0.30102	193.1246	292.8242	376.4326
	Cl	1.77773	-0.66112	-0.14608	883.743	1123.2523	1268.8815

Table S4: Coordinates (in angstrom) and frequencies (in cm^{-1}) of all the important geometries of water catalyzed HOCl + Cl reaction optimized at M062-2X/aug-cc-pVTZ level of theory.

Species	Geometry				Frequencies		
	O	0.23486	2.15388	-0.01339	1615.3166	3835.7536	3947.7022
	H	0.43844	2.91494	0.53428			
	H	1.08473	1.80286	-0.29839			
PC_{d-HAT}^{WM}	O	-0.98912	-0.67324	0.95067	54.743	58.1909	87.7672
	H	0.89600	-0.67006	0.47958	95.4365	124.646	152.3015
	Cl	-1.73109	-0.36084	-0.38775	172.8969	284.0577	479.2661
	Cl	2.03513	-0.55266	-0.12566	524.0061	931.9408	1619.0292
	O	0.07800	2.12606	0.03179	2762.5747	3835.3922	3947.4029
	H	0.31304	2.88030	0.57616			
	H	0.91132	1.69659	-0.18733			
Cl-WM	O	1.62699	0.00001	-0.11797	161.919	271.5042	287.1386
	H	1.73376	0.76614	0.45329	1606.3837	3842.1995	3946.4058
	H	1.73367	-0.76621	0.45324			
	Cl	-0.96961	0.00000	0.00219			
HOCl-WM	O	-0.34887	1.07876	-0.00772	78.1093	96.6376	219.9876
	H	0.59408	0.82228	-0.03818	240.9479	345.3015	638.0965
	Cl	-1.12848	-0.40392	0.01202	804.8815	1417.692	1619.3956
	O	2.11464	-0.16727	-0.07752	3572.4075	3850.4238	3949.349
	H	2.66841	-0.18007	0.70697			
	H	1.79553	-1.06737	-0.19124			

Table S4: Coordinates (in angstrom) and frequencies (in cm^{-1}) of all the important geometries of water catalyzed HOCl + Cl reaction optimized at M062-2X/aug-cc-pVTZ level of theory.

Species	Geometry				Frequencies		
WD	O	1.50493	0.00982	-0.12097	84.5182	126.783	148.4515
	H	0.55662	-0.00559	0.06345	193.5486	355.6011	606.3369
	H	1.93499	-0.06114	0.73249	1618.9862	1635.644	3772.5038
	O	-1.38612	-0.00794	0.11167	3859.7328	3944.091	3958.8595
	H	-1.72382	-0.73758	-0.41341			
	H	-1.71831	0.78930	-0.30811			
HOCl-WD	Cl	-1.33505	-0.63573	-0.09040	18.2803	103.4993	128.9525
	O	-1.26447	1.00579	0.21457	165.7504	214.6606	234.0733
	H	-0.31827	1.23831	0.04037	252.352	292.1205	382.7812
	O	1.33986	1.45708	-0.20659	478.6093	708.7312	795.1208
	H	1.78055	2.05884	0.39695	807.5074	1499.4319	1619.4836
	H	1.76015	0.58536	-0.09233	1637.9569	3299.4881	3613.089
	O	1.94592	-1.20111	0.17655	3801.4269	3923.5747	3931.6017
	H	2.30098	-1.77137	-0.50923			
	H	1.00187	-1.39782	0.22472			
Cl-WD	O	-0.14910	-1.48862	-0.11538	129.209	184.1303	211.7959
	H	0.04676	-1.78675	0.77872	227.4683	236.4189	375.8135
	H	-0.94064	-0.91814	-0.04628	430.7331	442.2501	838.89
	O	-1.94280	0.57675	0.09908	1612.5112	1616.7818	3535.6976
	H	-2.54668	0.87925	-0.58295	3804.1636	3888.5503	3934.6721

Table S4: Coordinates (in angstrom) and frequencies (in cm^{-1}) of all the important geometries of water catalyzed HOCl + Cl reaction optimized at M062-2X/aug-cc-pVTZ level of theory.

Species	Geometry				Frequencies		
	H	-1.17136	1.15582	0.05696			
	Cl	1.25571	0.46852	-0.00447			
RC_{i-HAT}^{WD}	Cl	-0.47063	-1.24336	0.62076	25.8978	57.6396	79.9746
	O	0.56804	-1.75725	-0.53234	120.2476	162.5472	195.4498
	H	1.32779	-1.08958	-0.48882	229.9189	240.1962	287.5002
	O	2.38494	0.04174	-0.29971	322.0224	352.0703	518.0203
	H	2.92006	0.25631	-1.06693	557.909	831.034	836.3702
	H	1.94293	0.87408	-0.01701	942.0089	1584.1732	1618.9837
	O	0.94855	2.19736	0.40783	1649.3538	2889.547	3405.3369
	H	0.90717	2.52361	1.30946	3695.9158	3918.4315	3924.1008
	H	0.04227	1.94502	0.16819			
	Cl	-1.78540	0.75135	-0.41553			
TS_{i-HAT}^{WD}	Cl	0.36368	-1.39899	0.42761	491.2961i	44.7438	67.7795
	O	1.62382	-1.07947	-0.45983	89.8448	139.1645	218.8028
	H	1.84250	0.35468	-0.30075	344.4222	357.0691	432.6861
	O	1.83493	1.38812	-0.17169	527.2556	601.3539	701.8984
	H	2.20156	1.79675	-0.96074	807.7838	941.2957	999.4774
	H	0.67081	1.78277	0.10198	1118.4607	1476.0798	1591.4069
	O	-0.40586	2.09384	0.34731	1659.5166	1754.0663	2338.8197
	H	-0.52421	2.26818	1.28741	2481.5618	3870.4953	3895.9488
	H	-1.04945	1.30738	0.08808			

Table S4: Coordinates (in angstrom) and frequencies (in cm^{-1}) of all the important geometries of water catalyzed HOCl + Cl reaction optimized at M062-2X/aug-cc-pVTZ level of theory.

Species	Geometry				Frequencies		
	Cl	-1.98511	-0.17335	-0.30657			
PC_{i-HAT}^{WD}	Cl	0.54962	-1.23701	0.02509	9.2639	47.3511	79.6002
	O	2.11675	-1.30317	0.04925	105.1728	128.0813	154.8037
	H	2.39376	0.65838	-0.01842	163.7249	191.4608	249.3609
	O	2.09820	1.57953	-0.03623	262.8686	311.6225	402.359
	H	2.65847	2.03456	-0.66832	494.5436	670.6672	747.4139
	H	0.32327	1.86120	-0.01111	885.8035	910.7151	1619.0844
	O	-0.63486	2.04670	0.03223	1645.6292	2179.6272	3566.1657
	H	-0.77087	2.59026	0.81185	3754.4386	3915.0384	3931.5157
	H	-1.63121	0.76416	-0.02690			
	Cl	-2.40928	-0.32141	-0.05151			
RC_{d-HAT}^{WD}	O	-1.27899	0.86180	0.37061	20.2499	33.3182	50.4435
	H	-0.58576	0.49769	0.95127	58.5402	169.833	189.4119
	Cl	-2.19866	-0.45628	-0.10712	212.5124	269.712	281.6673
	Cl	1.44498	-1.40966	-0.28657	356.7602	381.1579	456.1364
	O	1.07565	1.88073	-1.00126	549.2296	786.4796	807.4416
	H	0.12385	1.73040	-0.90966	890.657	1348.0952	1660.1779
	O	1.25705	0.57496	1.35138	1713.5868	3424.1577	3631.3963
	H	2.01149	0.54291	1.94385	3714.8232	3876.3994	3879.0151
	H	1.36644	1.24192	-1.65870			
	H	1.46683	1.16808	0.60003			

Table S4: Coordinates (in angstrom) and frequencies (in cm^{-1}) of all the important geometries of water catalyzed HOCl + Cl reaction optimized at M062-2X/aug-cc-pVTZ level of theory.

Species	Geometry				Frequencies		
TS^{WD}_{d-HAT}	O	1.01197	0.13955	0.92790	1507.8788i	15.716	64.7546
	H	0.12234	0.39874	0.30069	89.4853	124.8363	140.4016
	Cl	2.23497	-0.25445	-0.02341	151.127	159.0258	201.583
	Cl	-0.73096	1.60448	-0.33778	213.9753	230.0117	328.1812
	O	-0.41161	-1.79034	-0.56801	356.2965	425.6384	691.1998
	H	-0.54326	-1.83960	-1.51696	890.7141	1160.7769	1319.7806
	H	-1.29663	-1.64254	-0.19966	1614.4975	1647.9451	3705.1439
	O	-2.85527	-0.75469	0.39461	3786.7537	3927.1341	3937.8895
	H	-3.29492	-0.76507	1.24709			
	H	-2.51637	0.14186	0.27305			
PC^{WD}_{d-HAT}	O	2.34481	-0.00347	0.62357	22.7745	43.821	54.2518
	H	-1.66705	0.07949	-0.50975	79.4669	97.2976	163.0378
	Cl	1.58546	0.70115	-0.54964	175.1614	232.1637	265.7934
	Cl	-1.94054	1.01007	0.40308	302.2786	358.4864	398.4555
	O	-1.10487	-1.21617	-1.37750	525.5505	615.9203	749.2695
	H	-1.76146	-1.85282	-1.67017	925.8244	939.2896	1623.3585
	H	-0.64302	-1.61136	-0.61080	1631.0446	2262.0501	3537.4767
	O	-0.01825	-1.69588	1.08422	3788.0832	3865.135	3911.5969
	H	0.89175	-1.38270	1.16214			
	H	-0.55741	-0.99919	1.47767			

Table S4: Coordinates (in angstrom) and frequencies (in cm^{-1}) of all the important geometries of water catalyzed HOCl + Cl reaction optimized at M062-2X/aug-cc-pVTZ level of theory.

Species	Geometry				Frequencies		
RC_{WM}	O	-1.57070	0.10802	0.52510	55.9664	108.1918	134.8802
	H	-1.06857	0.91411	0.21793	186.709	207.6774	272.6783
	Cl	1.68546	-0.31299	0.11462	384.9775	496.8982	791.4066
	Cl	-0.79200	-1.12731	-0.24196	823.9843	1522.3402	1615.5672
	O	-0.24715	2.23268	-0.28426	3129.9548	3765.3707	3917.6847
	H	0.65026	1.87030	-0.30534			
	H	-0.22775	2.97491	0.32551			
TS_{WM}	O	1.46071	1.37220	0.27222	i456.5402	37.4218	64.4879
	H	2.00104	0.55691	0.18176	91.285	162.2598	212.4587
	Cl	-0.33201	0.61398	-0.23223	237.3565	279.5358	427.6918
	O	2.65805	-1.14980	-0.07788	661.6207	996.3597	1618.484
	H	2.91948	-1.65797	0.69390	3543.7461	3854.8696	3953.8345
	H	2.00741	-1.68571	-0.53949			
	Cl	-2.01376	-0.55472	0.12100			
PC_{WM}	O	-2.22582	-1.39909	0.01975	55.9664	108.1918	134.8802
	H	-2.49932	-0.45634	-0.02231	186.709	207.6774	272.6783
	Cl	0.36719	-0.50187	-0.00632	384.9775	496.8982	791.4066
	O	-2.38520	1.39668	-0.07334	823.9843	1522.3402	1615.5672
	H	-2.82831	2.07120	0.44595	3129.9548	3765.3707	3917.6847
	H	-1.44090	1.55904	0.01384			
	Cl	2.20084	0.31631	0.00580			

Table S4: Coordinates (in angstrom) and frequencies (in cm^{-1}) of all the important geometries of water catalyzed HOCl + Cl reaction optimized at M062-2X/aug-cc-pVTZ level of theory.

Species	Geometry				Frequencies		
RC_{WD}	O	-0.56766	-1.75743	-0.53271	25.9748	57.5569	79.929
	H	-1.32755	-1.09005	-0.48878	120.1433	162.6103	195.1653
	Cl	0.47096	-1.24375	0.62050	229.7592	240.0485	287.079
	O	-2.38494	0.04122	-0.29901	321.4055	351.6481	517.4211
	H	-2.92242	0.25505	-1.06477	557.365	831.0823	835.691
	H	-1.94375	0.87408	-0.01692	941.1577	1583.9811	1618.8323
	Cl	1.78533	0.75191	-0.41514	1649.0544	2890.7104	3406.8051
	O	-0.94905	2.19770	0.40721	3696.5068	3918.6845	3924.3913
	H	-0.90717	2.52533	1.30830			
	H	-0.04296	1.94508	0.16728			
TS_{WD}	O	1.27586	-1.92809	0.10367	456.1179i	33.4038	80.9132
	H	1.87869	-1.13507	0.10823	120.5342	135.893	141.5645
	Cl	-0.45862	-0.96694	-0.24599	169.1356	208.7464	237.3289
	O	2.61698	0.40333	0.09006	263.8643	285.0603	398.9102
	H	3.19178	0.65385	0.81598	413.3015	449.2164	742.5789
	H	1.93817	1.10090	0.02239	779.1155	1091.4544	1621.785
	Cl	-2.07832	0.28859	0.19216	1645.5119	3246.55	3588.0664
	O	0.59325	2.30169	-0.09262	3800.8694	3926.2288	3927.3052
	H	0.50421	2.78489	-0.91753			
	H	-0.27351	1.91210	0.07710			

Table S4: Coordinates (in angstrom) and frequencies (in cm^{-1}) of all the important geometries of water catalyzed HOCl + Cl reaction optimized at M062-2X/aug-cc-pVTZ level of theory.

Species	Geometry				Frequencies		
PC_{WD}	O	-1.98909	-1.92815	0.04832	24.6979	57.8359	59.8256
	H	-2.30207	-0.98939	0.02318	76.7187	109.1178	119.7159
	Cl	0.46548	-0.94942	0.03384	147.7149	189.3566	206.8126
	O	-2.57860	0.74497	-0.03064	222.8287	258.024	337.866
	H	-3.21390	1.15788	-0.61817	417.9453	492.851	539.3948
	H	-1.78540	1.30927	-0.03844	705.9786	822.4079	1618.9271
	Cl	2.22873	0.02489	-0.05002	1645.2621	3402.9243	3635.7951
	O	-0.29243	2.37443	0.01186	3830.6343	3931.5923	3934.1674
	H	-0.13861	2.81825	0.84952			
	H	0.51950	1.89110	-0.17727			
OH	O	0.00000	0.00000	0.10800	3766.227		
	H	0.00000	0.00000	-0.86397			
Cl_2	Cl	0.00000	0.00000	0.99755	575.8253		
	Cl	0.00000	0.00000	-0.99755			

Table S5: Zero curvature tunneling (ZCT) correction for uncatalyzed, water and water dimer catalyzed for HOCl + Cl → Cl_2 + OH reaction

Temp (K)	κ_{uncat}^{ZCT}	κ_{WM}^{ZCT}	κ_{WD}^{ZCT}
213	1.40	1.33	1.51
216	1.38	1.32	1.49
219	1.37	1.31	1.48
224	1.35	1.29	1.45
235	1.31	1.26	1.40
250	1.27	1.23	1.34
259	1.25	1.21	1.31
280	1.21	1.18	1.26
290	1.19	1.16	1.24
298	1.18	1.15	1.23
300	1.18	1.15	1.22
310	1.17	1.14	1.21
320	1.15	1.13	1.19

Table S6: Comparison of energy barrier barrier obtained for TS_{uncat} using different methods.

Method	Barrier (kcal mol^{-1})
CCSD(T)/cc-pVQZ	15.00
CCSD(T)/aug-cc-pVTZ//CCSD/aug-cc-pVDZ	15.62
CCSD(T)/aug-cc-pVQZ//CCSD/aug-cc-pVDZ	15.70
CCSD(T)/aug-cc-pVTZ//M062X/aug-cc-pVTZ	10.16
CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ	10.92
CCSD(T)/aug-cc-pVTZ//wB97XD/aug-cc-pVTZ	10.53
CCSD(T)/aug-cc-pVTZ//LC-wHPBE/aug-cc-pVTZ	10.24

Table S7: Bimolecular rate constant k_{bi} (in cm^3 $molecule^{-1}$ s^{-1}) for H_2O catalyzed and uncatalyzed HOCl + $Cl^{\bullet}$ → $ClO^{\bullet}$ + HCl reaction within temperature range 213-320 K.

Temp (K)	Path A	Path B	Path C	Path D	Uncat
213	1.65×10^{-17}	2.48×10^{-15}	5.19×10^{-15}	1.45×10^{-13}	4.98×10^{-14}
216	1.57×10^{-17}	2.15×10^{-15}	4.62×10^{-15}	1.16×10^{-13}	4.67×10^{-14}
219	1.49×10^{-17}	1.88×10^{-15}	4.15×10^{-15}	9.45×10^{-14}	4.40×10^{-14}
224	1.38×10^{-17}	1.51×10^{-15}	3.54×10^{-15}	6.85×10^{-14}	4.03×10^{-14}
235	1.20×10^{-17}	9.88×10^{-16}	2.66×10^{-15}	3.69×10^{-14}	3.47×10^{-14}
250	1.05×10^{-17}	6.11×10^{-16}	2.01×10^{-15}	1.88×10^{-14}	3.06×10^{-14}
259	9.98×10^{-18}	4.79×10^{-16}	1.79×10^{-15}	1.34×10^{-14}	2.94×10^{-14}
280	9.42×10^{-18}	3.05×10^{-16}	1.50×10^{-15}	7.15×10^{-15}	2.87×10^{-14}
290	9.43×10^{-18}	2.58×10^{-16}	1.42×10^{-15}	5.62×10^{-15}	2.92×10^{-14}
298	9.53×10^{-18}	2.30×10^{-16}	1.38×10^{-15}	4.74×10^{-15}	2.99×10^{-14}
300	9.56×10^{-18}	2.24×10^{-16}	1.37×10^{-15}	4.55×10^{-15}	3.01×10^{-14}
310	9.84×10^{-18}	1.99×10^{-16}	1.34×10^{-15}	3.78×10^{-15}	3.12×10^{-14}
320	1.02×10^{-17}	1.81×10^{-16}	1.32×10^{-15}	3.20×10^{-15}	3.27×10^{-14}

Table S8: Bimolecular rate constant k_{bi} (in cm^3 $molecule^{-1}$ s^{-1}) for H_2O, and $(H_2O)_2$ catalyzed and uncatalyzed $HOCl + Cl^{\bullet} \rightarrow OH^{\bullet} + Cl_2$ reaction within temperature range 213-320 K.

Temp (K)	H_2O		$(H_2O)_2$		Uncat
	Path A	Path B	Path A	Path B	
213	1.10×10^{-10}	2.44×10^{-13}	8.03×10^{-11}	4.03×10^{-13}	4.35×10^{-13}
216	1.02×10^{-10}	2.56×10^{-13}	6.70×10^{-11}	4.22×10^{-13}	4.35×10^{-13}
219	9.53×10^{-11}	2.68×10^{-13}	5.62×10^{-11}	4.41×10^{-13}	4.36×10^{-13}
224	8.51×10^{-11}	2.90×10^{-13}	4.24×10^{-11}	4.75×10^{-13}	4.38×10^{-13}
235	6.78×10^{-11}	3.42×10^{-13}	2.38×10^{-11}	5.55×10^{-13}	4.44×10^{-13}
250	5.18×10^{-11}	4.21×10^{-13}	1.19×10^{-11}	6.80×10^{-13}	4.55×10^{-13}
259	4.50×10^{-11}	4.73×10^{-13}	8.20×10^{-12}	7.64×10^{-13}	4.62×10^{-13}
280	3.40×10^{-11}	6.11×10^{-13}	3.80×10^{-12}	9.90×10^{-13}	4.83×10^{-13}
290	3.03×10^{-11}	6.84×10^{-13}	2.76×10^{-12}	1.11×10^{-12}	4.94×10^{-13}
298	2.79×10^{-11}	7.46×10^{-13}	2.17×10^{-12}	1.22×10^{-12}	5.03×10^{-13}
300	2.74×10^{-11}	7.62×10^{-13}	2.05×10^{-12}	1.25×10^{-12}	5.05×10^{-13}
310	2.49×10^{-11}	8.45×10^{-13}	1.55×10^{-12}	1.39×10^{-12}	5.18×10^{-13}
320	2.29×10^{-11}	9.33×10^{-13}	1.20×10^{-12}	1.54×10^{-12}	5.31×10^{-13}

Table S9: Values of rate constants k_{HL}^{TST} in cm^3 $molecule^{-1}$ s^{-1}, transmission coefficient (Γ_{LL}), and ZCT nand SCT tunneling correction for bare HOCl + Cl → HCl + ClO reaction.

Temp (K)	k_{HL}^{TST}	Γ_{LL}	κ_{LL}^{ZCT}	κ_{LL}^{SCT}
213	2.13×10^{2}	0.88	1.72×10^{3}	2.04×10^{3}
216	2.16×10^{2}	0.88	1.53×10^{3}	1.81×10^{3}
219	2.19×10^{2}	0.88	1.37×10^{3}	1.62×10^{3}
224	2.24×10^{2}	0.88	1.14×10^{3}	1.35×10^{3}
235	2.35×10^{2}	0.88	7.83×10^{2}	9.25×10^{2}
250	2.50×10^{2}	0.88	4.96×10^{2}	5.84×10^{2}
259	2.59×10^{2}	0.88	3.86×10^{2}	4.55×10^{2}
280	2.80×10^{2}	0.88	2.30×10^{2}	2.70×10^{2}
290	2.90×10^{2}	0.88	1.85×10^{2}	2.16×10^{2}
298	2.98×10^{2}	0.88	1.57×10^{2}	1.83×10^{2}
300	3.00×10^{2}	0.88	1.50×10^{2}	1.76×10^{2}
310	3.10×10^{2}	0.88	1.24×10^{2}	1.45×10^{2}
320	3.20×10^{2}	0.88	1.04×10^{2}	1.21×10^{2}
320	3.20×10^{2}	1.15	1.04×10^{2}	1.21×10^{2}

Table S10: Comparison of energetics obtained at different level of theory for HOCl + Cl → HCl + ClO reaction.

Species	CCSD(T)/CBS//M062X/aug-cc-pVTZ	CCSD(T)/CBS//CCSD/aug-cc-pVDZ	CCSDT(Q)/CBS//CCSD/aug-cc-pVDZ
TS_{uncat}	9.94	15.75	6.97
TS_{WM}	-1	0.10	-1.21
RC_{uncat}	-3.34	-2.76	-6.05
RC_{WM}	-14.8	-12.79	-12.94
PC_{uncat}	-8.33	-7.72	-8.19
PC_{WM}	-15.3	-14.66	-15.79

Table S11: Bimolecular rate constant k_{bi} (in cm^3 $molecule^{-1}$ s^{-1}) for $(H_2O)_2$ catalyzed and uncatalyzed $HOCl + Cl^{\bullet} \rightarrow ClO^{\bullet} + HCl$ reaction within temperature range 213-320 K.

Temp (K)	Path A	Path B	Path C	Uncat
213	1.87×10^{-17}	1.20×10^{-16}	4.91×10^{-15}	4.98×10^{-14}
216	1.71×10^{-17}	1.34×10^{-16}	4.77×10^{-15}	4.67×10^{-14}
219	1.58×10^{-17}	1.50×10^{-16}	4.63×10^{-15}	4.40×10^{-14}
224	1.40×10^{-17}	1.79×10^{-16}	4.42×10^{-15}	4.03×10^{-14}
235	1.16×10^{-17}	2.58×10^{-16}	4.01×10^{-15}	3.47×10^{-14}
250	1.02×10^{-17}	4.04×10^{-16}	3.58×10^{-15}	3.06×10^{-14}
259	9.94×10^{-18}	5.16×10^{-16}	3.37×10^{-15}	2.94×10^{-14}
280	1.06×10^{-17}	8.76×10^{-16}	3.02×10^{-15}	2.87×10^{-14}
290	1.13×10^{-17}	1.09×10^{-15}	2.86×10^{-15}	2.92×10^{-14}
298	1.20×10^{-17}	1.29×10^{-15}	2.75×10^{-15}	2.99×10^{-14}
300	1.22×10^{-17}	1.34×10^{-15}	2.72×10^{-15}	3.01×10^{-14}
310	1.34×10^{-17}	1.62×10^{-15}	2.60×10^{-15}	3.12×10^{-14}
320	1.48×10^{-17}	1.95×10^{-15}	2.50×10^{-15}	3.27×10^{-14}

Table S12: Termolecular rate constant (cm^6 $molecule^{-2}$ s^{-1}) for water catalyzed HOCl + $Cl^{\bullet} \longrightarrow$ HCl + $ClO^{\bullet}$ reaction within temperature range of 213 K - 320 K.

Temp (K)	WM		WD	
	i-HAT	d-HAT	i-HAT	d-HAT
213	8.56×10^{-34}	3.62×10^{-37}	1.68×10^{-34}	1.32×10^{-37}
216	6.69×10^{-34}	3.02×10^{-37}	1.35×10^{-34}	1.09×10^{-37}
219	5.28×10^{-34}	2.53×10^{-37}	1.09×10^{-34}	9.02×10^{-38}
224	3.63×10^{-34}	1.92×10^{-37}	7.69×10^{-35}	6.78×10^{-38}
235	1.72×10^{-34}	1.11×10^{-37}	3.79×10^{-35}	3.98×10^{-38}
250	7.25×10^{-35}	5.99×10^{-38}	1.60×10^{-35}	2.30×10^{-38}
259	4.63×10^{-35}	4.37×10^{-38}	9.98×10^{-36}	1.79×10^{-38}
280	1.90×10^{-35}	2.41×10^{-38}	3.77×10^{-36}	1.19×10^{-38}
290	1.33×10^{-35}	1.93×10^{-38}	2.49×10^{-36}	1.04×10^{-38}
298	1.03×10^{-35}	1.65×10^{-38}	1.83×10^{-36}	9.61×10^{-39}
300	9.64×10^{-36}	1.60×10^{-38}	1.70×10^{-36}	9.44×10^{-39}
310	7.19×10^{-36}	1.36×10^{-38}	1.19×10^{-36}	8.77×10^{-39}
320	5.51×10^{-36}	1.19×10^{-38}	8.50×10^{-37}	8.31×10^{-39}
320	5.51×10^{-36}	1.19×10^{-38}	8.50×10^{-37}	8.31×10^{-39}

Table S13: Termolecular rate constant (cm^6 $molecule^{-2}$ s^{-1}) for water catalyzed HOCl + $Cl^{\bullet} \longrightarrow Cl_2 + OH^{\bullet}$ reaction within temperature range of 213 K - 320 K.

Temp (K)	WM	WD
213	6.89×10^{-33}	5.47×10^{-31}
216	6.10×10^{-33}	4.10×10^{-31}
219	5.44×10^{-33}	3.10×10^{-31}
224	4.52×10^{-33}	1.98×10^{-31}
235	3.11×10^{-33}	7.94×10^{-32}
250	2.00×10^{-33}	2.63×10^{-32}
259	1.59×10^{-33}	1.45×10^{-32}
280	9.98×10^{-34}	4.27×10^{-33}
290	8.25×10^{-34}	2.56×10^{-33}
298	7.19×10^{-34}	1.75×10^{-33}
300	6.95×10^{-34}	1.59×10^{-33}
310	5.95×10^{-34}	1.03×10^{-33}
320	5.17×10^{-34}	6.82×10^{-34}

Table S14: Values of rate constants k_{HL}^{TST} in s^{-1}, transmission coefficient (Γ_{LL}), and ZCT and SCT tunneling correction for water monomer catalyzed HOCl + Cl → HCl + ClO reaction.

Temp (K)	k_{HL}^{TST}	Γ_{LL}	κ_{LL}^{ZCT}	κ_{LL}^{SCT}
213	7.71×10^{3}	0.89	5.07	1.78×10^{1}
216	9.84×10^{3}	0.89	4.78	1.57×10^{1}
219	1.25×10^{4}	0.89	4.51	1.40×10^{1}
224	1.83×10^{4}	0.89	4.14	1.17×10^{1}
235	3.98×10^{4}	0.89	3.51	8.41
250	1.03×10^{5}	0.90	2.93	5.95
259	1.71×10^{5}	0.90	2.68	5.05
280	4.96×10^{5}	0.90	2.27	3.74
290	7.76×10^{5}	0.90	2.13	3.34
298	1.09×10^{6}	0.90	2.04	3.09
300	1.18×10^{6}	0.90	2.02	3.03
310	1.74×10^{6}	0.90	1.92	2.79
320	2.50×10^{6}	0.91	1.83	2.59
320	3.20×10^{6}	1.15	1.04	1.21

Table S15: Values of rate constants k_{HL}^{TST} in s^{-1}, transmission coefficient (Γ_{LL}), and ZCT and SCT tunneling correction for water dimer catalyzed HOCl + Cl → HCl + ClO reaction.

Temp (K)	k_{HL}^{TST}	Γ_{LL}	κ_{LL}^{ZCT}	κ_{LL}^{SCT}
213	3.51	0.90	1.25	1.39
216	4.98	0.90	1.24	1.38
219	6.99	0.90	1.24	1.37
224	1.21×10^{1}	0.90	1.23	1.35
235	3.69×10^{1}	0.91	1.20	1.32
250	1.44×10^{2}	0.91	1.18	1.28
259	3.00×10^{2}	0.91	1.17	1.26
280	1.38×10^{3}	0.91	1.14	1.22
290	2.64×10^{3}	0.91	1.13	1.20
298	4.29×10^{3}	0.91	1.12	1.19
300	4.82×10^{3}	0.92	1.12	1.19
310	8.45×10^{3}	0.92	1.11	1.17
320	1.43×10^{4}	0.92	1.11	1.16
320	3.20×10^{4}	1.15	1.04	1.21

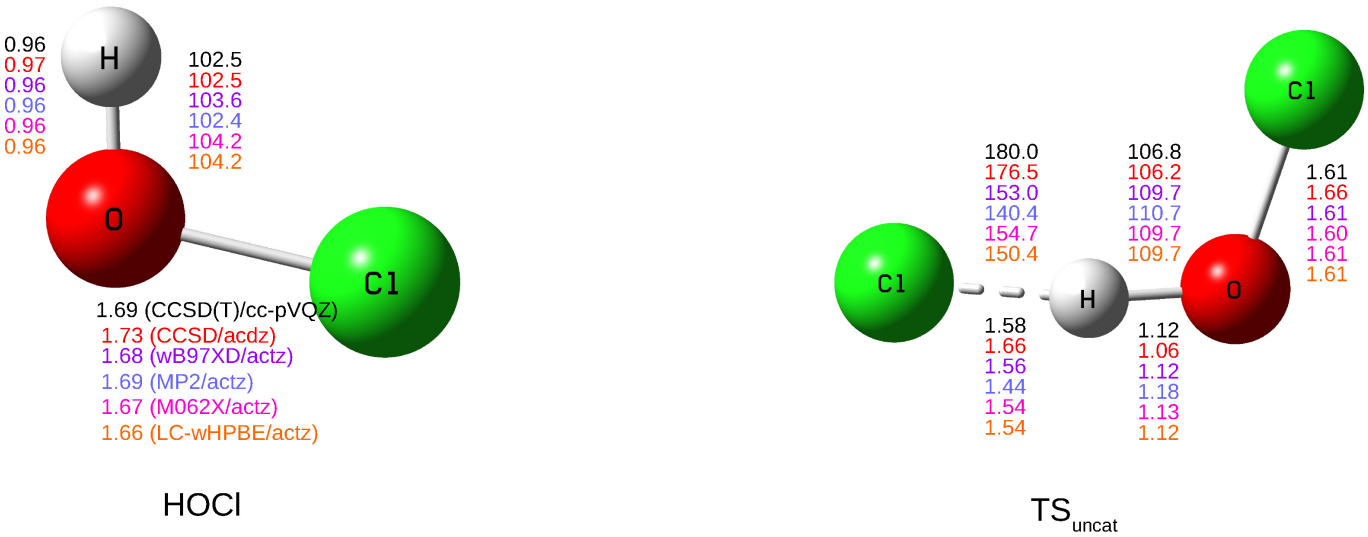

Figure S1: Comparison of geometrical parameters obtained at CCSD/aug-cc-pVDZ level of theory with others level of theory. All bond length are given in Å.

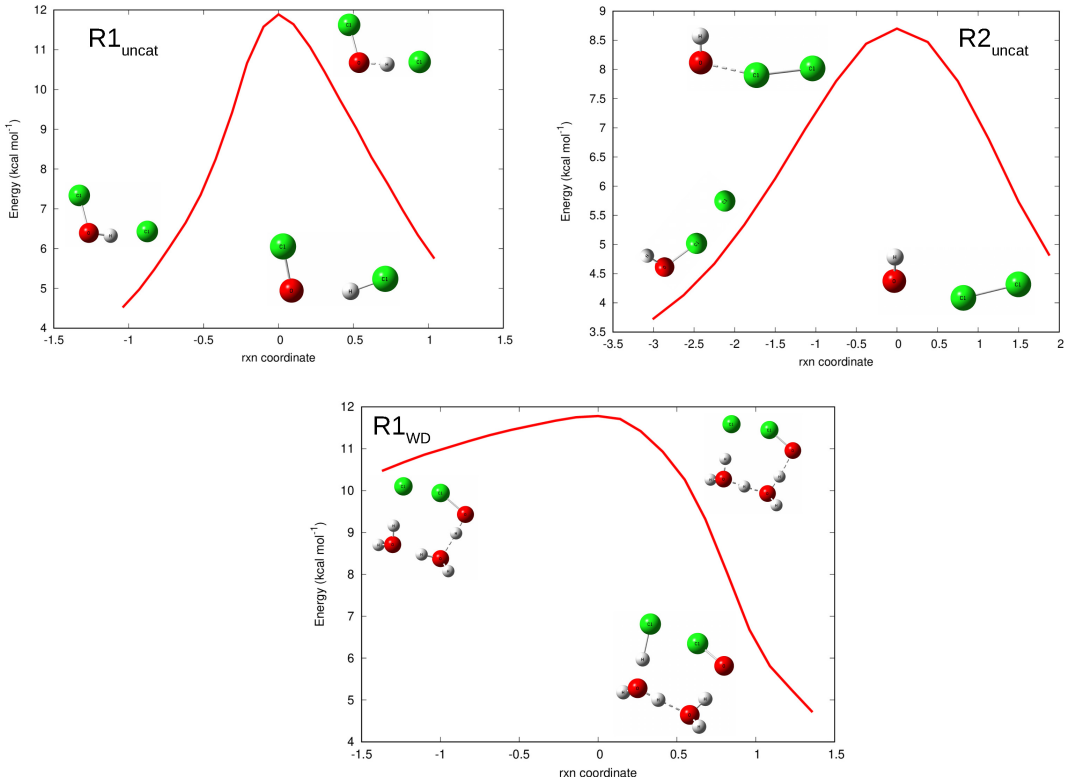

Figure S2: IRC calculation for HOCl + Cl reaction at M062X/aug-cc-pVTZ level of theory.

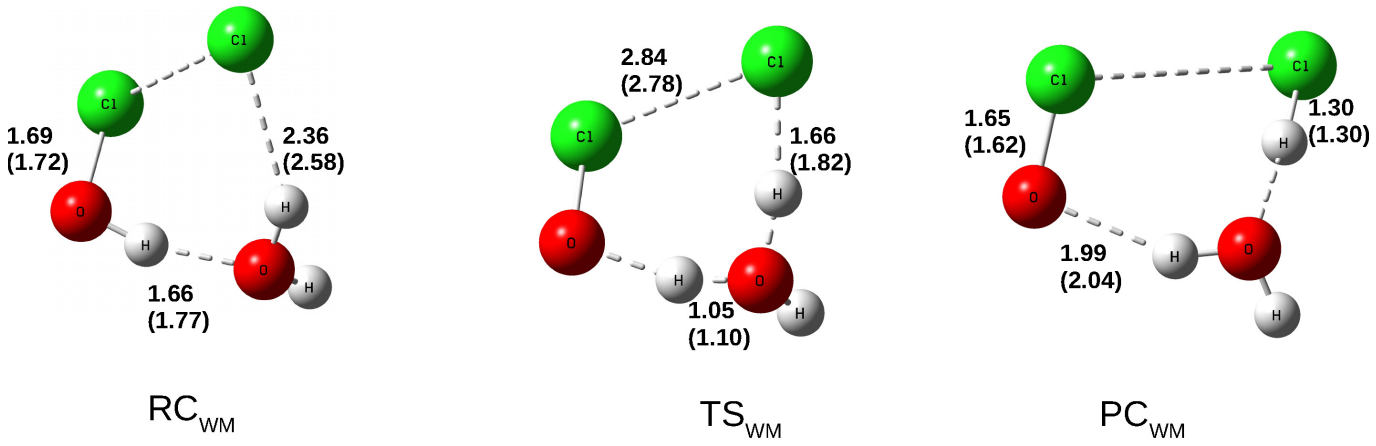

Figure S3: Comparison of geometrical parameters obtained at MO6-2X/aug-cc-pVTZ level of theory with CCSD/aug-cc-pVDZ level of theory (in parenthesis) for water catalyzed HOCl + HCl → HCl + ClO reaction. All bond length are given in Å.

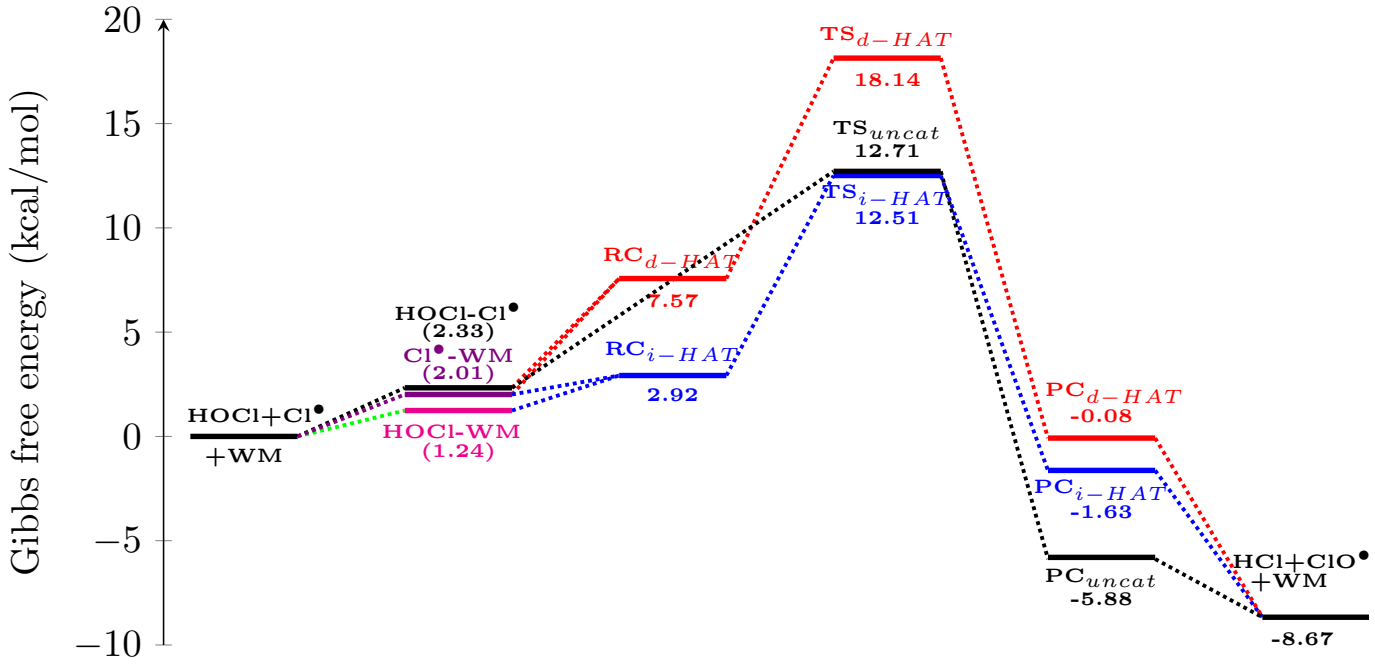

Figure S4: Gibbs free energy profile for H_2O catalyzed HOCl + Cl$^\bullet$ $\longrightarrow$ HCl + ClO$^\bullet$ reaction, calculated at CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level of theory.

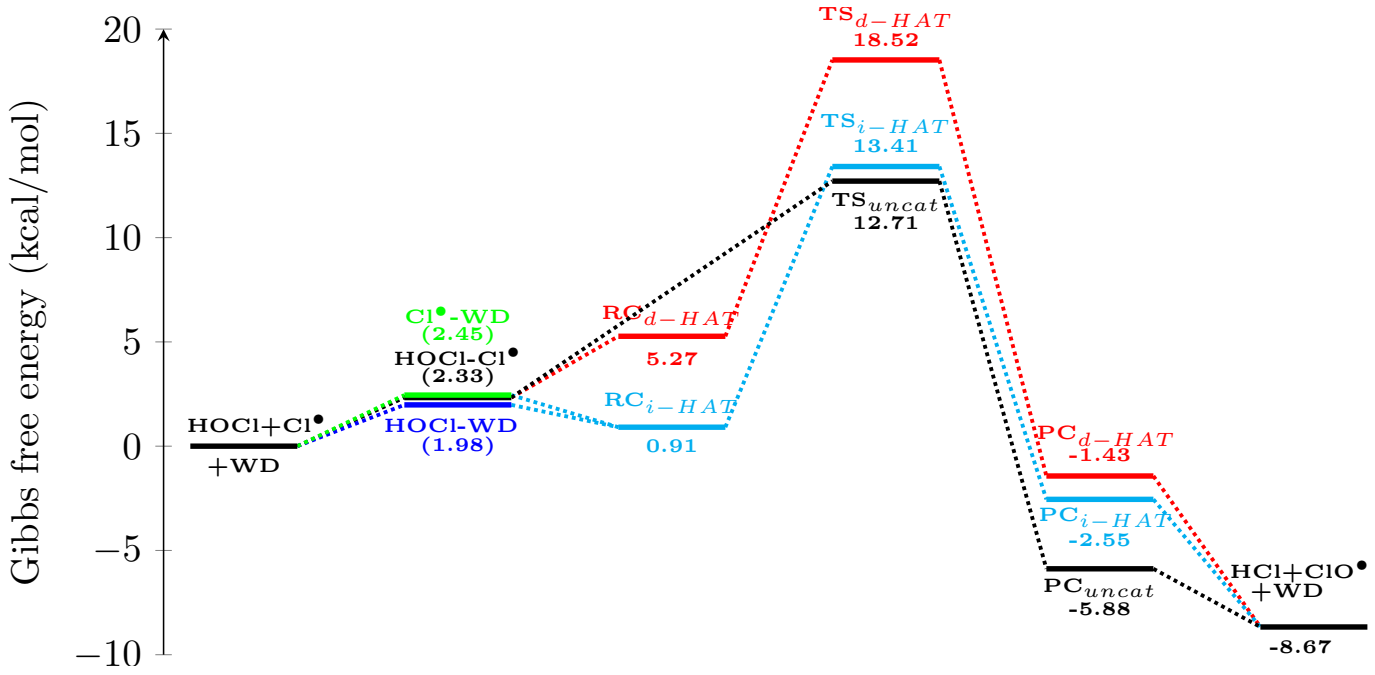

Figure S5: Gibbs free energy profile for $(H_2O)_2$ catalyzed HOCl + Cl$^\bullet$ $\longrightarrow$ HCl + ClO$^\bullet$ reaction , calculated at CCSD(T)/CBS//M06-2X/aug-cc-pVTZ level of theory.