Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting information

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Water-catalyzed gas-phase hydrogen abstraction reactions of CH_3O_2 and HO_2 with HO_2: A computational investigation

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A.The scheme of possible reaction pathways for water-catalyzed reactions of CH_3O_2 and HO_2 with HO_2 along with the corresponding pathways without a water molecule

Fig. S1 The scheme of possible pathways for CH_3O_2 + HO_2 and HO_2+ HO_2 reaction in the presence and absence of a water molecule (a) the reaction of CH_3O_2 with HO_2 in the presence and absence of a water molecule; (b) the reaction of HO_2 with HO_2 in the presence and absence of a water molecule. IMW, TSW and PW are the intermediates, transition states and products for the title reaction in the presence of a water molecule while IM, TS and P denote the intermediates, transition states and products without a water molecule; Channel aw-cw and channel aw'-cw' denote water-catalyzed reaction channels for CH_3O_2 + HO_2 and HO_2 + HO_2 reaction, respectively, while channel a-c, and channel a'-c' denote the corresponding channels without a water molecule for CH_3O_2 + HO_2 and HO_2 + HO_2 reaction, respectively.

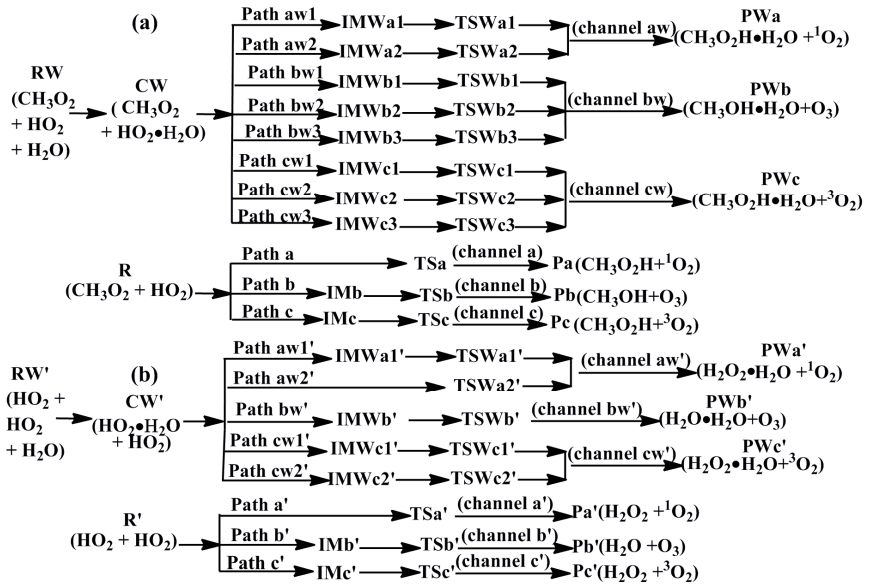

Fig. S1

B. Data from calculations.

Fig. S2 Optimized geometries of all the species in the reaction of CH_3O_2+HO_2 with and without a water molecule. The distance (Å) and angle (°) with and without parentheses were the experimental data from the NIST chemistry webbook(http://webbook.nist.gov/chemistry) and values obtained at the B3LYP/6-311G(2d,2p) level, respectively.

Fig. S3 The optimized geometrical structures for the species of the reactants (HO_2, H_2O) and products (CH_3OH, $^3O_2$, O_3) at several different levels of theory. The values in parentheses are the experimental values. [a] The values obtained at the B3LYP/6-311G(2d,2p) level of theory; [b] The values obtained at the CCSD/6-311G(2d,2p) level of theory; [c] The values obtained at the MP2/6-311G(2d,2p) level of theory; [d] The values obtained at the MPW1PW91/6-311G(2d,2p) level of theory; [e] The values obtained at the MPW1K/6-311G(2d,2p) level of theory; bond length is in angstrom and angle is in degree.

Fig. S4 Optimized geometries of all the species in the reaction of HO_2+HO_2 with and without a water molecule. The distance (Å) and angle (°) with and without parentheses were the experimental data from the NIST chemistry webbook(http://webbook.nist.gov/chemistry) and values obtained at the B3LYP/6-311G(2d,2p) level, respectively.

Fig. S5 Schematic energy diagram for Path aw3 and aw4 that involves in Channel aw. Energies (kcal·mol^{-1}) computed at the CCSD(T)/6-311++G(3d,2p)//B3LYP/6-311G(2d,2p) level include zero-point energy correction. The distances (Å) were optimized at the B3LYP/6-311G(2d,2p) level.

Table S1. T1 diagnostic values for the species that involved in the title reactions of CH_3O_2 + HO_2 and HO_2+ HO_2.

Table S2 The electronic energies(E), zero point energies(ZPE), total energies(E_T) and relative energies(E_R) of the reactants, intermediates, products and transition states for CH_3O_2 + HO_2 reaction in the presence and absence of a water molecule.

Table S3(a) The electronic energies(E), zero point energies(ZPE), total energies(E_T) and relative energies(E_R) of the reactants, intermediates, products and transition states for HO_2 + HO_2 reaction in the presence and absence of a water molecule.

Table S3(b) Relative energy (ΔE, kcal·mol^{-1}) of water-catalyzed transition states and intermediates to the corresponding ones without a water molecule in HO_2 + HO_2 reaction

Table S4 Vibrational frequencies (in cm^{-1}) for the optimized geometries at B3LYP/6-311G(2d,2p) level of theory for CH_3O_2 + HO_2 reaction in the presence and absence of a water molecule.

Table S5 Vibrational frequencies (in cm^{-1}) for the optimized geometries at B3LYP/6-311G(2d,2p) level of theory for HO_2 + HO_2 reaction in the presence and absence of a water molecule

Table S6 The calculated CVT/SCT rate constants for Path a and Path c' along with the available experimental and theoretical values.

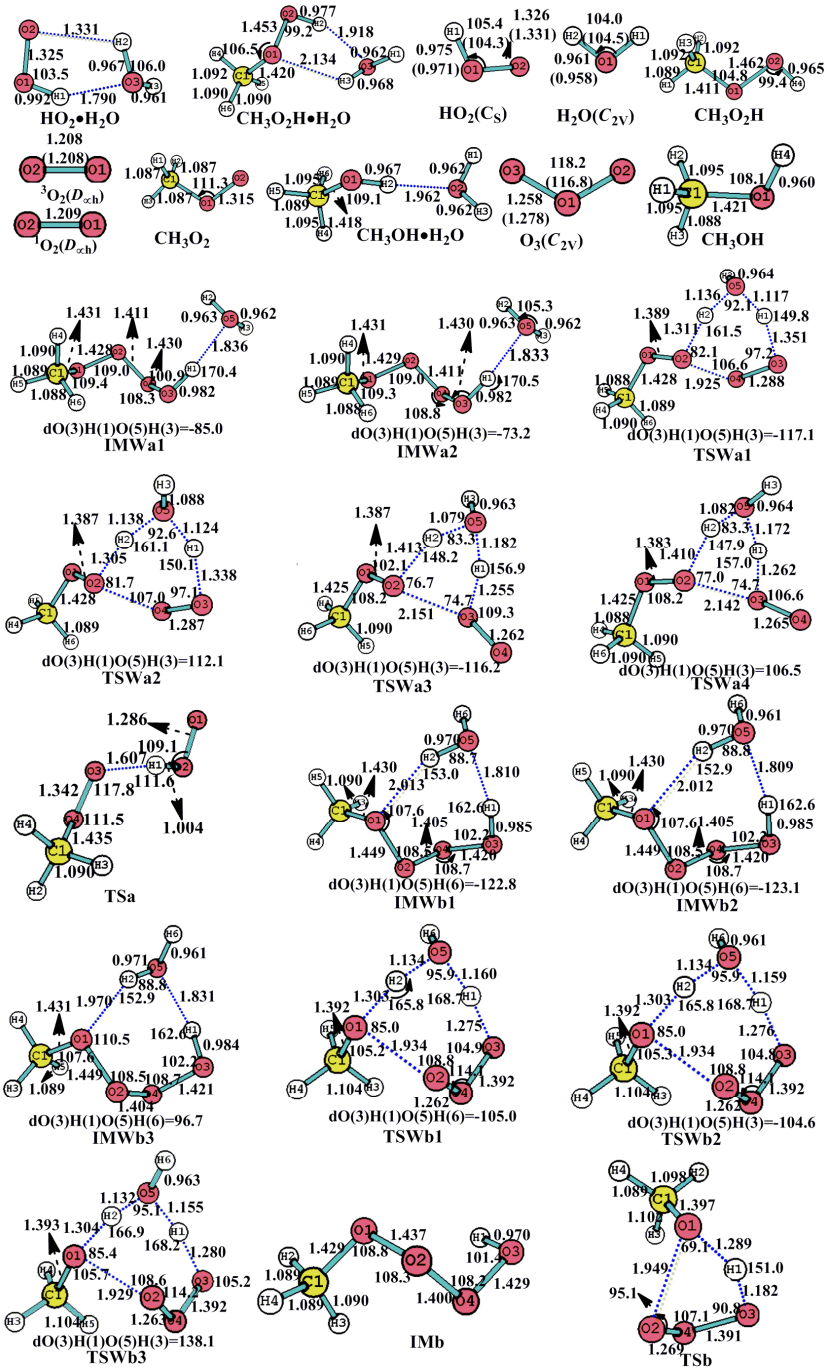

Fig. S2 to be Continued

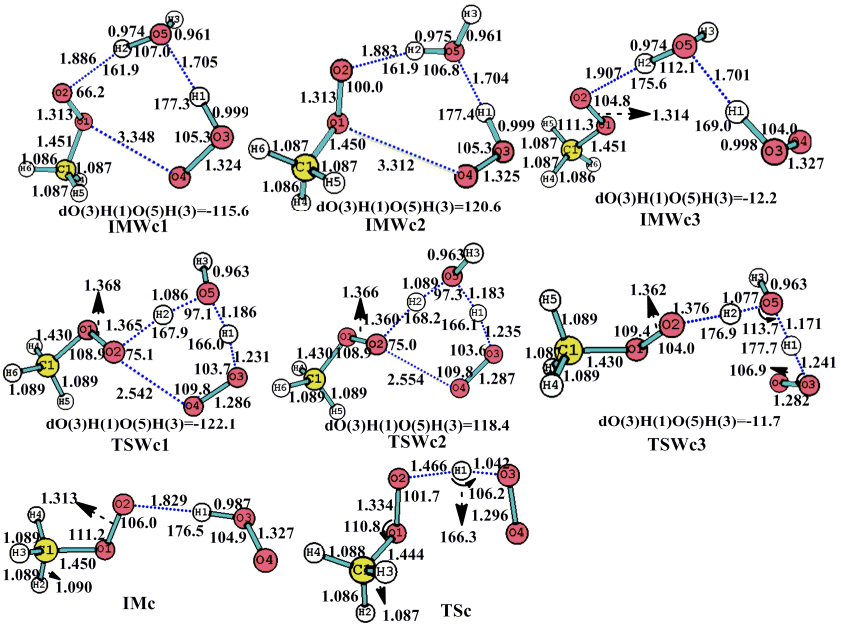
dO(3)H(1)O(5)H(3)=-115.6
IMWc1
dO(3)H(1)O(5)H(3)=120.6
IMWc2
dO(3)H(1)O(5)H(3)=-12.2
IMWc3
dO(3)H(1)O(5)H(3)=-122.1
TSWc1
dO(3)H(1)O(5)H(3)=118.4
TSWc2
dO(3)H(1)O(5)H(3)=-11.7
TSWc3
IMc
TSc

Fig. S2

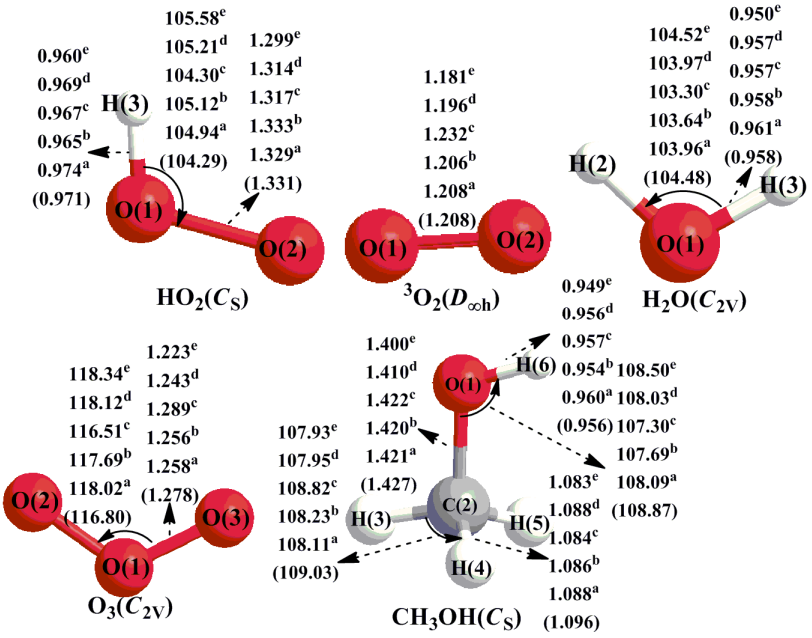

Fig. S3

For the reactants (HO_2, H_2O) and products ($^3O_2$, O_3, CH_3OH), the average absolute deviations between the calculated bond lengths, angles at the B3LYP/6-311G(2d,2p), CCSD/6-311G(2d,2p), MP2/6-311G(2d,2p), MPW1PW91/6-311G (2d,2p), MPW1K/6-311G(2d,2p), levels of theory and the experimental ones are 0.59%, 0.43%, 0.77%, 0.88%, and 1.44%, respectively. It is obvious that the calculated geometrical parameters of the reactants and products for the reaction from the B3LYP/6-311G(2d,2p), CCSD/6-311G(2d,2p), MP2/6-311G(2d,2p) and MPW1PW91/6-311G(2d,2p) methods are more accurate than those from MPW1K/6-311G (2d,2p) method. The calculated geometrical parameters from the B3LYP/6-311G(2d,2p) method are close to those from CCSD/6-311G(2d,2p) method and are in good agreement with the corresponding experimental values. The largest deviations of bond lengths and bond angles at the B3LYP/6-311G(2d,2p) were 0.02Å (O-O bond in O_3) and 1.22° (angle ∠O-O-O in O_3). So the calculated bond lengths and angles at the B3LYP/6-311G(2d,2p) level of theory are acceptable.

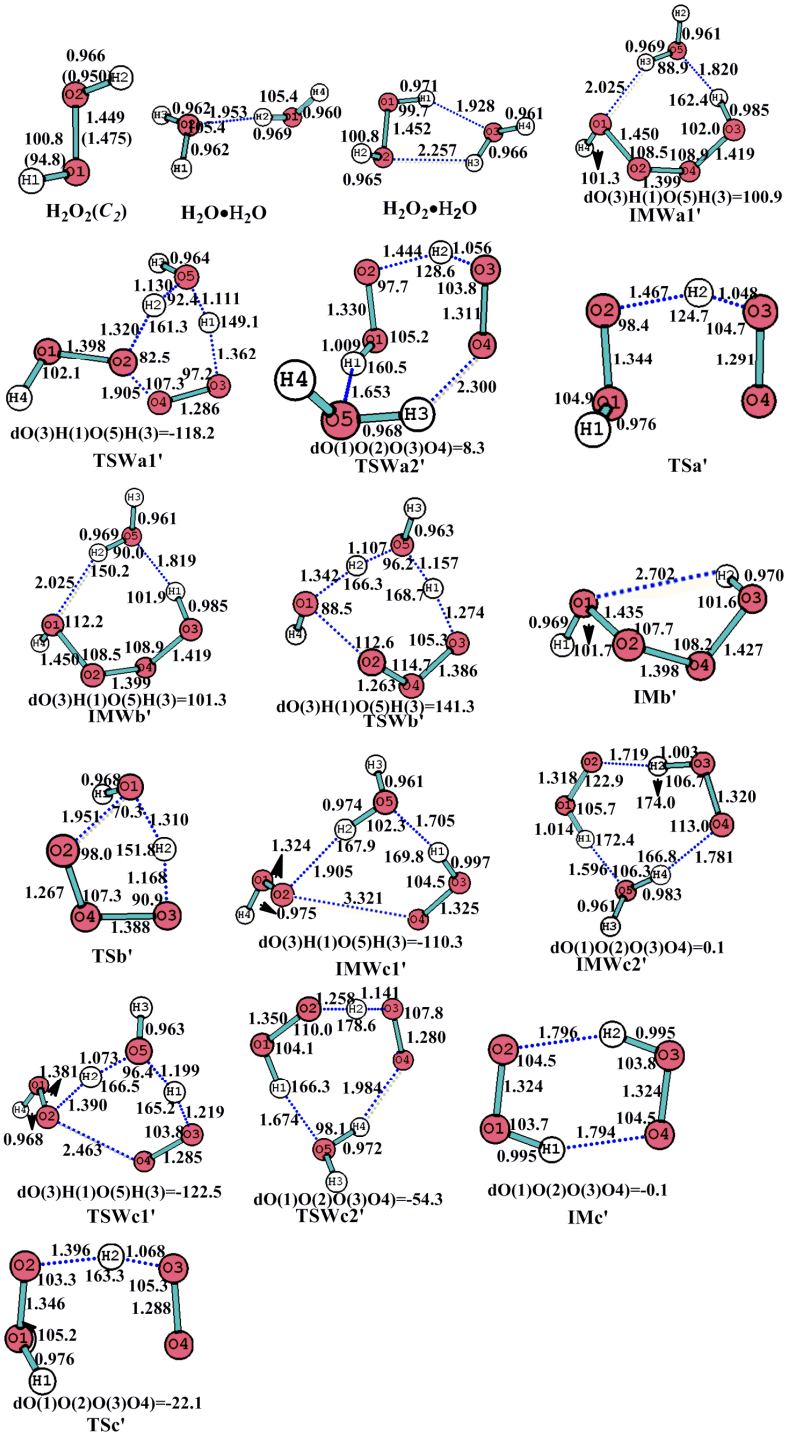
H2O2(C2)
H2O•H2O
H2O2•H2O
dO(3)H(1)O(5)H(3)=100.9
IMWa1'
dO(3)H(1)O(5)H(3)=-118.2
TSWa1'
dO(1)O(2)O(3)O4)=8.3
TSWa2'
TSa'
dO(3)H(1)O(5)H(3)=101.3
IMWb'
dO(3)H(1)O(5)H(3)=141.3
TSWb'
IMb'
TSb'
dO(3)H(1)O(5)H(3)=-110.3
IMWc1'
dO(1)O(2)O(3)O4)=0.1
IMWc2'
dO(3)H(1)O(5)H(3)=-122.5
TSWc1'
dO(1)O(2)O(3)O4)=-54.3
TSWc2'
dO(1)O(2)O(3)O4)=-0.1
IMc'
dO(1)O(2)O(3)O4)=-22.1
TSc'

Fig. S4

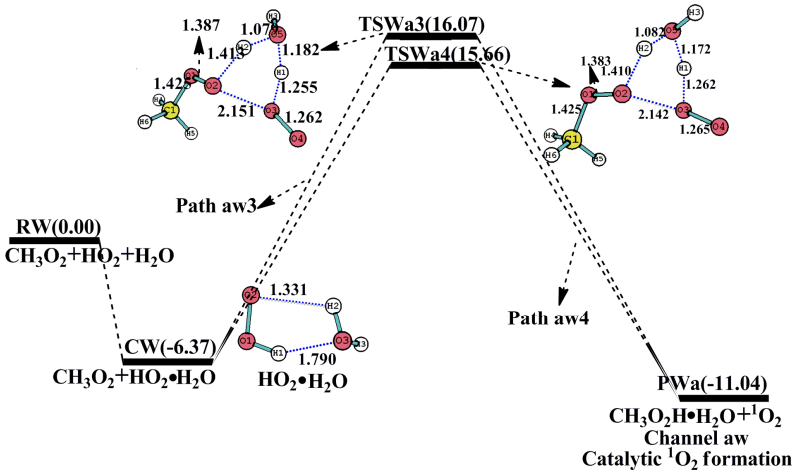

Fig. S5

There are two other pathways (Path aw3 and Path aw4) for water-catalyzed $^1O_2$ formation in CH_3O_2 + HO_2 reaction. The transition states of Path aw3 and Path aw4 have very high energy barrier (TSWa3 and TSWa4 are computed to lie 16.07 and 15.66 kcal·mol^{-1} above the CH_3O_2 +HO_2 + H_2O reactants). Also the calculated results show the singe water molecule in water-catalyzed Path aw3 and Path aw4 cannot reduce the reaction energy barrier because the energy barriers are 5.35 and 4.94 kcal·mol^{-1} higher than that of the non-catalytic route of Path a in Fig 3, respectively. Hence, neither of the two pathways will be of any atmospheric relevance.

Table S1. T1 diagnostic values for the species that involved in the title reactions of CH_3O_2 + HO_2 and HO_2 + HO_2

Species	T1	Species	T1	Species	T1
CH_3O_2	0.029	HO_2	0. 031	H_2O	0.010
HO_2·H_2O	0.027	CH_3O_2H	0. 013	CH_3O_2H·H_2O	0.013
$^1O_2$	0.015	O_3	0. 027	CH_3OH	0.010
CH_3OH·H_2O	0.011	$^3O_2$	0. 018	IMWa1	0.018
IMWa2	0.018	TSWa1	0. 031	TSWa2	0.031
TSa	0.040	IMWb1	0. 017	IMWb2	0.018
IMWb3	0.018	TSWb1	0. 032	TSWb2	0.032
TSWb3	0.032	IMb	0. 018	TSb	0.039
IMWc1	0.029	IMWc2	0. 017	IMWc3	0.029
TSWc1	0.039	TSWc2	0. 031	TSWc3	0.034
IMc	0.030	TSc	0. 036	H_2O_2	0.013
H_2O_2·H_2O	0.013	H_2O·H_2O	0. 011	IMWa1'	0.018
TSWa1'	0.030	TSWa2'	0. 025	TSa'	0.035
IMWb'	0.018	TSWb'	0. 036	IMb'	0.019
TSb'	0.039	IMWc1'	0. 028	IMWc2'	0.030
TSWc1'	0.041	TSWc2'	0. 042	IMc'	0.033
TSc'	0.040				

Table S2. The electronic energies(E), zero point energies(ZPE), total energies(E_T) and relative energies(E_R) of the reactants, intermediates, products and transition states for the reaction of CH_3O_2 + HO_2 in presence and absence of a water molecule.

Species	E^a/a.u.	ZPE^b/a.u.	E_T^c/a.u.	E_R/(kcal·mol^{-1})
RW(CH_3O_2 + HO_2 +H_2O)	-416.864269	0.078416	-416.785853	0
CW(HO_2·H_2O +CH_3O_2)	-416.879268	0.083262	-416.796006	-6.37
IMWa1	-416.897527	0.085696	-416.811831	-16.30
IMWa2	-416.897502	0.085722	-416.811780	-16.27
TSWa1	-416.852023	0.081642	-416.770381	9.71
TSWa2	-416.851028	0.081463	-416.769565	10.22
TSWa3	-416.841498	0.081261	-416.760237	16.07
TSWa4	-416.842118	0.081214	-416.760904	15.66
TSa + H_2O	-416.848334	0.079559	-416.768775	10.72
PWa (CH_3OOH·H_2O +$^1O_2$)	-416.887321	0.083878	-416.803443	-11.04
Pa (CH_3OOH +$^1O_2$) +H_2O	-416.874159	0.079751	-416.794408	-5.37
IMWb1	-416.901354	0.086786	-416.814568	-18.02
IMWb2	-416.901353	0.086791	-416.814562	-18.02
IMWb3	-416.902331	0.086934	-416.815397	-18.54
TSWb1	-416.863130	0.080864	-416.782266	2.25
TSWb2	-416.863120	0.08087	-416.782250	2.26
TSWb3	-416.864789	0.08105	-416.783739	1.32
IMb + H_2O	-416.886706	0.082861	-416.803845	-11.29
TSb + H_2O	-416.845391	0.078095	-416.767296	11.64
PWb (CH_3OH·H_2O+O_3)	-416.899644	0.082766	-416.816878	-19.47
Pb (CH_3OH +O_3) +H_2O	-416.891105	0.079882	-416.811223	-15.92
IMWc1	-416.891448	0.084421	-416.807027	-13.29
IMWc2	-416.891277	0.084337	-416.806940	-13.23
IMWc3	-416.889628	0.084335	-416.805293	-12.20
TSWc1	-416.856187	0.080116	-416.776071	6.14
TSWc2	-416.855672	0.080048	-416.775624	6.42
TSWc3	-416.827615	0.078976	-416.748639	23.35
IMc + H_2O	-416.876189	0.08079	-416.795399	-5.99
TSc + H_2O	-416.867799	0.078383	-416.789416	-2.24
PWc (CH_3OOH·H_2O+$^3O_2$)	-416.936281	0.083895	-416.852386	-41.75
Pc (CH_3OOH +$^3O_2$) +H_2O	-416.923119	0.079768	-416.843351	-36.08

[a] The values obtained at the CCSD(T)/6-311++G(3d,2p)//B3LYP/6-311G(2d,2p) level of theory; [b] The values obtained at the B3LYP/6-311G(2d,2p) level of theory; [c] The values obtained at the CCSD(T)/6-311++G(3d,2p)//B3LYP/6-311G(2d,2p)+ZPE level of theory.

Table S3(a). The electronic energies(E), zero point energies(ZPE), total energies(E_T) and relative energies(E_R) of the reactants, intermediates, products and transition states for the reaction of $HO_2 + HO_2$ in presence and in absence of a water molecule.

Species	E^{a1}/a.u.	E^{a2}/a.u.	ZPE^{b}/a.u.	E_T^{c1}/a.u.	E_T^{c2}/a.u.	E_{R1}/(kcal·mol^{-1})	E_{R2}/(kcal·mol^{-1})	E_{R1}- E_{R2}
RW' ($HO_2 + HO_2 + H_2O$)	-377.647636	-377.795585	0.049826	-377.597810	-377.745759	0	0	0
CW' ($HO_2{\cdot}H_2O + HO_2$)	-377.662636	-377.8104189	0.054672	-377.607964	-377.755747	-6.37	-6.27	-0.1
IMWa1'	-377.686971	-377.8380472	0.059091	-377.627880	-377.778956	-18.87	-20.83	1.96
TSWa1'	-377.635931	-377.785399	0.054062	-377.581869	-377.731337	10.00	9.05	0.95
TSWa2'	-377.654075	-377.803419	0.055556	-377.598519	-377.747863	-0.44	-1.32	0.88
TSa' + H_2O	-377.634911	-377.7839586	0.052203	-377.582709	-377.7317556	9.48	8.79	0.69
PWa' ($H_2O_2{\cdot}H_2O + {}^1O_2$)	-377.672607	-377.8215576	0.055481	-377.617126	-377.7660766	-12.12	-12.75	0.63
Pa'(H_2O_2 + $^1O_2$) + H_2O	-377.661298	-377.8098472	0.051756	-377.609542	-377.7580912	-7.36	-7.74	0.38
IMWb'	-377.686972	-377.8380516	0.059085	-377.627887	-377.7789666	-18.87	-20.84	1.97
TSWb'	-377.646431	-377.7971899	0.053102	-377.593329	-377.7440879	2.81	1.05	1.76
IMb' + H_2O	-377.671992	-377.8230386	0.05514	-377.616852	-377.7678986	-11.95	-13.89	1.94
TSb' + H_2O	-377.627862	-377.7781149	0.050206	-377.577656	-377.7279089	12.65	11.20	1.45
PWb' ($H_2O{\cdot}H_2O + O_3$)	-377.697865	-377.8447576	0.053648	-377.644217	-377.7911096	-29.12	-28.46	-0.66
Pb' ($H_2O + O_3$) + H_2O	-377.689408	-377.8376903	0.05008	-377.639328	-377.7876103	-26.05	-26.26	0.21
IMWc1'	-377.671306	-377.8189263	0.056142	-377.615164	-377.7627843	-10.89	-10.68	-0.21
IMWc2'	-377.683757	-377.8320857	0.059516	-377.624241	-377.7725697	-16.59	-16.82	0.23
TSWc1'	-377.639375	-377.7887755	0.052552	-377.586823	-377.7362235	6.89	5.98	0.91
TSWc2'	-377.661777	-377.8110335	0.052207	-377.609570	-377.7588265	-7.38	-8.20	0.82
IMc' + H_2O	-377.667090	-377.8152852	0.054038	-377.613052	-377.7612472	-9.56	-9.72	0.16
TSc' + H_2O	-377.648250	-377.7972322	0.049396	-377.598854	-377.7478362	-0.66	-1.30	0.64
PWc' ($H_2O_2{\cdot}H_2O + {}^3O_2$)	-377.721567	-377.8692736	0.055498	-377.666069	-377.8137756	-42.83	-42.68	-0.15
Pc' ($H_2O_2 + {}^3O_2$) + H_2O	-377.710258	-377.8575632	0.051773	-377.658485	-377.8057902	-38.07	-37.67	-0.4

[a1, a2] The values obtained at the CCSD(T)/6-311++G(3d,2p)//B3LYP/6-311G(2d,2p) and CCSD(T)/aug-cc-pVTZ//B3LYP/6-311G(2d,2p) level of theory, respectively; [b]The values obtained at the B3LYP/6-311G(2d,2p) level of theory;[c1, c2] The values obtained at the CCSD(T)/6-311++G(3d,2p)//B3LYP/6-311G(2d,2p)+ZPE and CCSD(T)/aug-cc-pVTZ//B3LYP/6-311G(2d,2p)+ZPE level of theory, respectively.; E_{R1}, E_{R2} relative energies(E_R) of the reactants, intermediates, products and transition states for the HO_2 + HO_2 reaction at the CCSD(T)/6-311++G(3d,2p)//B3LYP/6-311G(2d,2p)+ZPE level and CCSD(T)/aug-cc-pVTZ//B3LYP/6-311G(2d,2p)+ZPE level, respectively.; E_{R1}-E_{R2} the energy difference between CCSD(T)/6-311++G(3d,2p)//B3LYP/6-311G(2d,2p)+ZPE and CCSD(T)/aug-cc-pVTZ//B3LYP/6-311G(2d,2p).

Table S3(b). The relative energy (ΔE, kcal·mol^{-1}) of water-catalyzed transition states and intermediates to the corresponding ones without a water molecule in $HO_2 + HO_2$ reaction

ΔE	ΔE^a	ΔE^b	$\Delta E^a - \Delta E^b$
$E_{(TSa' + H2O)} - E_{(TSWa1')}$	-0.52	-0.26	-0.26
$E_{(TSWa2')} - E_{(TSa' + H2O)}$	9.92	10.01	-0.09
$E_{(IMWb')} - E_{(IMb')}$	6.92	6.95	-0.03
$E_{(TSWb')} - E_{(TSb' + H2O)}$	9.84	10.15	-0.31
$E_{(IMc' + H2O)} - E_{(IMWc1')}$	1.33	0.96	0.37
$E_{(IMc' + H2O)} - E_{(IMWc2')}$	7.03	7.10	-0.07
$E_{(TSc' + H2O)} - E_{(TSWc1')}$	7.55	7.28	0.27
$E_{(TSc' + H2O)} - E_{(TSWc2')}$	6.72	6.90	0.18

ΔE^a, ΔE^b The values obtained at the CCSD(T)/6-311++G(3d,2p)//B3LYP/6-311G(2d,2p) and CCSD(T)/aug-cc-pVTZ//B3LYP/6-311G(2d,2p) level of theory, respectively; $\Delta E^a - \Delta E^b$ denotes the energy difference between ΔE^a and ΔE^b.

It can be seen from Table S3(a) that the relative energies to the reactants of intermediates, products and transition states at CCSD(T)/aug-cc-pVTZ//B3LYP/6-311G(2d,2p) level change by 0.10-1.97 kcal·mol^{-1} than the corresponding values at the CCSD(T)/6-311++G(3d,2p)//B3LYP/6-311G(2d,2p) level. Although the single point energy at the aug-cc-pVTZ basis sets can give a more accurate energy, the catalytic effect of water molecule at CCSD(T)/6-311++G(3d,2p)//B3LYP/6-311G (2d,2p) level can be well characterized because, for the relative energy of water-catalyzed transition states and intermediates to the corresponding ones without a water molecule, the energy difference displayed in Table S3(b) between CCSD(T)/aug-cc-pVTZ//B3LYP/6-311G(2d,2p) and CCSD(T)/6-311++G(3d,2p)// B3LYP/6-311G(2d, 2p) level is range from 0.03 to 0.37 kcal·mol^{-1}. From the viewpoint of barrier height reducing and stabilization of intermediates enhancing, the catalytic effect of water molecule at the different basis sets of 6-311G(2d,2p) and aug-cc-pVTZ are in reasonable agreement with each other, revealing that the basis sets effect are not significant. Besides, direct hydrogen abstraction process is still the dominant pahway in Channel aw' and cw', respectively. Therefore, the theoretical methods utilized herein are able to describle the reaction system reliably.

Table S4 Vibrational frequencies (in cm^{-1}) for the optimized geometries at B3LYP/6-311G(2d,2p) level of theory for the reaction of $CH_3O_2 + HO_2$ in the presence and absence of a water molecule.

Species	Frequencies
HO_2[a]	1173, 1449, 3623
HO_2[b]	1156, 1482, 3747
HO_2[c]	1232, 1479, 3727
HO_2[d]	1228, 1479, 3687
HO_2[e]	1266, 1527, 3825
Exp[f]	1098, 1392, 3436
$HO_2 \cdot H_2O$	112, 225, 258, 311, 507, 697, 1193, 1576, 1640, 3333, 3765, 3892
CH_3O_2	136, 495, 911, 1131, 1158, 1224, 1446, 1478, 1488, 3053, 3141, 3153
H_2O[a]	1666, 3810, 3905
H_2O[b]	1709, 3887, 3984
H_2O[c]	1685, 3875, 3988
H_2O[d]	1673, 3876, 3975
H_2O[e]	1700, 3983, 4082
Exp[f]	1595, 3657, 3756
$^1O_2$[a]	1623
$^1O_2$[b]	1573
$^1O_2$[c]	1233
$^1O_2$[d]	1693
$^1O_2$[e]	1796
Exp[f]	1448
$^3O_2$[a]	1638
$^3O_2$[b]	1648
$^3O_2$[c]	1423
$^3O_2$[d]	1709
$^3O_2$[e]	1808
Exp[f]	1580
O_3[a]	745, 1216, 1260
O_3[b]	754, 1258, 1263
O_3[c]	736, 1162, 2282
O_3[d]	774, 1306, 1323
O_3[e]	812, 1408, 1424
Exp[f]	705, 1042, 1110
CH_3OOH	215, 251, 451, 884, 1035, 1172, 1208, 1385, 1452, 1463, 1514, 3011, 3073, 3110, 3771
$CH_3OOH \cdot H_2O$	57, 132, 188, 237, 240, 277, 451, 511, 628, 878, 1028, 1177, 1213, 1455, 1469, 1494, 1514, 1638, 3018, 3088, 3109, 3609, 3742, 3893
CH_3OH[a]	301, 1047, 1087, 1171, 1389, 1485, 1499, 1515, 2990, 3030, 3108, 3842
CH_3OH[b]	300, 1074, 1107, 1196, 1420, 1519, 1530, 1546, 3031, 3081, 3147, 3921
CH_3OH[c]	296, 1095, 1136, 1206, 1410, 1518, 1535, 1548, 3082, 3137, 3202, 4025
CH_3OH[d]	303, 1071, 1107, 1178, 1396, 1487, 1500, 1518, 3014, 3061, 3137, 3909
CH_3OH[e]	306, 1100, 1143, 1207, 1423, 1521, 1534, 1550, 3074, 3125, 3195, 4019
Exp[f]	200, 1033, 1060, 1165, 1345, 1455, 1477, 1477,2844, 2960, 3000, 3681
IMWa1	30, 52, 69, 100, 144, 209, 237, 281, 340, 416, 474, 601, 624, 817, 843, 923, 989, 1173, 1209, 1450, 1474, 1511, 1518, 1644, 3035, 3112, 3128, 3500, 3808, 3904
IMWa2	32, 52, 76, 100, 143, 210, 238, 280, 339, 416, 474, 601, 624, 821, 842, 923, 990, 1173, 1209, 1450, 1474, 1511, 1517, 1644, 3035, 3112, 3128, 3500, 3810, 3905
IMWa3	46, 98, 119, 134, 167, 210, 232, 269, 291, 424, 490, 531, 564, 932, 1030, 1129, 1157, 1209, 1228, 1450, 1473, 1497, 1555, 1637, 2962, 3040, 3119, 3139, 3701, 3878
IMWa4	46, 79, 96, 126, 160, 209, 233, 258, 321, 466, 482, 522, 559, 933, 1033, 1124, 1157, 1208,1217, 1450, 1473, 1496, 1600, 1641, 2927, 3040, 3119, 3140, 3734, 3870
TSWa1	1210*i*, 91, 107, 135, 208, 257, 287, 408, 519, 555, 611, 641, 728, 935, 1040, 1169, 1215, 1248, 1341, 1451, 1468, 1473, 1507, 1607, 1726, 1999, 3035, 3110, 3133, 3835
TSWa2	1252*i*, 93, 111, 133, 208, 256, 282, 404, 525, 570, 597, 629, 725, 939, 1040, 1169, 1211, 1255, 1307, 1454, 1472, 1479, 1506, 1617, 1676, 1972, 3034, 3108, 3134, 3850
TSWa3	1200*i*, 79, 90, 112, 179, 200, 222, 385, 441, 551, 593, 636, 687, 930, 1041, 1141, 1165, 1212, 1325, 1452, 1471, 1503, 1589, 1625, 1667, 2263, 3030, 3102, 3129, 3846
TSWa4	1191*i*, 75, 90, 107, 173, 185, 218, 387, 439, 563, 607, 618, 705, 942, 1038, 1163,

TSa	1181, 1217, 1310, 1449, 1463, 1470, 1502, 1638, 1756, 2253, 3029, 3100, 3130, 3842 532*i*, 72, 97, 109, 197, 212, 470, 510, 928, 1056, 1144, 1203, 1255, 1450, 1475, 1488, 1493, 3031, 3099, 3108, 3143
IMWb1	78, 91, 140, 160, 215, 248, 276, 317, 365, 533, 562, 590, 610, 813, 859, 939, 988, 1176, 1207, 1453, 1475, 1511, 1541, 1652, 3033, 3113, 3120, 3442, 3702, 3886
IMWb2	79, 140, 161, 215, 248, 276, 317, 365, 533, 562, 590, 610, 813, 859, 939, 988, 1178, 1207, 1453, 1475, 1511, 1542, 1652, 3033, 3113, 3120, 3441, 3701, 3886
IMWb3	76, 93, 142, 164, 213, 247, 282, 357, 375, 543, 567, 589, 612, 807, 852, 937, 985, 1176, 1208, 1453, 1475, 1510, 1554, 1641, 3037, 3120, 3123, 3452, 3687, 3882
TSWb1	1327*i*, 94, 151, 207, 228, 288, 381, 510, 518, 557, 593, 672, 742, 942, 1050, 1138, 1165, 1192, 1268, 1377, 1453, 1481, 1486, 1589, 1686, 1889, 2910, 2996, 3076, 3855
TSWb2	1324*i*, 95, 152, 209, 228, 288, 382, 511, 518, 557, 593, 672, 742, 943, 1050, 1139, 1165, 1192, 1268, 1377, 1453, 1481, 1486, 1590, 1687, 1889, 2909, 2995, 3074, 3853
TSWb3	97, 142, 208, 235, 289, 382, 516, 523, 561, 583, 688, 695, 941, 1050, 1140, 1161, 1195, 1327, 1427, 1451, 1481, 1496, 1570, 1693, 1885, 2910, 3005, 3077, 3850
IMb	52, 126, 157, 355, 383, 471, 598, 614, 638, 830, 932, 1009, 1041, 1157, 1297, 1413, 1418, 1481, 3059, 3129, 3737
TSb	1496*i*, 148, 206, 242, 319, 529, 619, 761, 920, 1032, 1121, 1148, 1183, 1372, 1438, 1471, 1487, 1890, 2935, 2986, 3092
IMWc1	6, 12, 25, 47, 62, 72, 103, 120, 134, 227, 280, 413, 510, 696, 910, 1132, 1167, 1193, 1236, 1448, 1477, 1485, 1541, 1657, 3061, 3153, 3168, 3332, 3785, 3905
IMWc2	31, 47, 57, 65, 69, 128, 147, 187, 253, 281, 405, 508, 671, 779, 906, 1130, 1165, 1206, 1238, 1443, 1472, 1490, 1598, 1662, 3060, 3157, 3164, 3209, 3613, 3880
IMWc3	28, 48, 60, 70, 76, 131, 151, 189, 265, 282, 417, 508, 644, 798, 907, 1130, 1165, 1206, 1237, 1444, 1472, 1489, 1597, 1671, 3060, 3155, 3164, 3207, 3607, 3879
IMWc4	6, 10, 39, 60, 70, 80, 132, 162, 286, 342, 459, 508, 626, 839, 908, 1132, 1165, 1197, 1233,1448, 1477, 1486, 1606, 1671, 3060, 3151, 3166, 3210, 3628, 3867
TSWc1	587*i*, 12, 18, 61, 65, 87, 98, 112, 169, 217, 335, 346, 487, 814, 918, 976, 1135, 1190, 1254, 1447, 1475, 1483, 1582, 1649, 1717, 3054, 3141, 3160, 3804, 3911
TSWc2	1562*i*, 55, 89, 92, 145, 158, 228, 257, 405, 521, 614, 636, 715, 946, 1071, 1153, 1165, 1213, 1299, 1385, 1452, 1473, 1499, 1705, 1771, 1982, 3037, 3114, 3138, 3850,
TSWc3	1575*i*, 55, 87, 93, 147, 157, 226, 255, 404, 521, 603, 633, 688, 947, 1074, 1156, 1203, 1228, 1299, 1406, 1451, 1473, 1498, 1684, 1750, 1960, 3037, 3113, 3139, 3849
TSWc4	1756*i*, 14, 24, 49, 99, 128, 172, 190, 373, 454, 560, 660, 721, 942, 1109, 1148, 1173, 1219, 1325, 1429, 1451, 1472, 1493, 1630, 1718, 1973, 3037, 3114, 3144, 3845
IMc	21, 41, 61, 113, 130, 209, 506, 634, 909, 1132, 1167, 1189, 1235, 1448, 1477, 1485, 1542, 3060, 3151, 3166, 3407
TSc	297*i*, 67, 91, 106, 165, 321, 490, 785, 916, 1025, 1134, 1195, 1251, 1447, 1476, 1484, 1619, 2094, 3055, 3142, 3160

[a] The values obtained at the B3LYP/6-311G(2d,2p) level of theory; [b] The values obtained at the CCSD/6-311G(2d,2p) level of theory; [c] The values obtained at the MP2/6-311G(2d,2p) level of theory; [d] The values obtained at the MPW1PW91/6-311G(2d,2p) level of theory; [e] The values obtained at the MPW1K/6-311G(2d,2p) level of theory; [f] the experimental values that taken from the NIST Chemistry Webbook, http://cccbdb.nist.gov/cccbdbindex.asp

The harmonic vibrational frequencies (cm^{-1}) of the reactants, intermediates, transition states and products for the reaction of $CH_3O_2 + HO_2$ in the presence and absence of a water molecule at the B3LYP/6-311G(2d,2p) level of theory along with the available experimental data are listed in Table S3. For the species (HO_2, H_2O, $^3O_2$, O_3 and CH_3OH), the average absolute deviation between the calculated harmonic vibrational frequencies at the B3LYP/6-311G(2d,2p), CCSD/6-311G(2d, 2p), MP2/6-311G(2d,2p), MPW1PW91/6-311G(2d,2p) and MPW1K/6-311G(2d,2p) levels of theory and the corresponding experimental ones are 6.97%, 8.53%, 11.06% , 9.25% and 12.91%, respectively. This further indicates that the calculated data for the title reaction at the B3LYP/6-311G(2d,2p) level of theory is acceptable.

Table S5 Vibrational frequencies (in cm^{-1}) for the optimized geometries at B3LYP/6-311G(2d,2p) level of theory for the reaction of HO_2 + HO_2 in the presence and absence of a water molecule.

Species	Frequencies
$H_2O{\cdot}H_2O$	139, 161, 163, 196, 388, 652, 1639, 1660, 3703, 3816, 3899, 3914
$H_2O_2{\cdot}H_2O$	110, 199, 215, 228, 317, 472, 653, 938, 1356, 1529, 1643, 3598, 3774, 3789, 3900
IMWa1'	96, 137, 176, 240, 263, 359, 417, 473, 562, 596, 633, 814, 864, 947, 1374, 1560, 1640, 3438, 3718, 3748, 3884
IMWa2'	110, 139, 184, 239, 305, 327, 376, 444, 512, 580, 616, 1047, 1114, 1231, 1436, 1598, 1648, 3052, 3645, 3649, 3674
TSWa1'	1147*i*, 138, 163, 249, 293, 378, 527, 561, 581, 631, 726, 997, 1252, 1350, 1418, 1475, 1615, 1749, 2029, 3766, 3831
TSWa2'	651*i*, 82, 102, 202, 227, 269, 337, 441, 458, 497, 594, 1033, 1108, 1214, 1525, 1583, 1640, 2408, 3043, 3746, 3877
TSa'	682*i*, 220, 296, 447, 522, 618, 1060, 1248, 1420, 1549, 2520, 3634
IMWb'	96, 137, 176, 240, 262, 358, 416, 473, 562, 595, 633, 814, 863, 947, 1374, 1561, 1640, 3437, 3718, 3748, 3884
TSWb'	1206*i*, 94, 229, 333, 435, 489, 542, 570, 608, 685, 739, 786, 971, 1164, 1289, 1432, 1661, 1695, 1934, 3808, 3846
IMb'	176, 373, 395, 509, 625, 650, 869, 940, 1394, 1416, 3735, 3741
TSb'	1456*i*, 347, 456, 538, 621, 763, 792, 934, 1153, 1351, 1915, 3787
IMWc1'	23, 34, 40, 75, 132, 183, 259, 272, 296, 414, 660, 789, 1174, 1198, 1460, 1603, 1667, 3220, 3628, 3634, 3881
IMWc2'	70, 82, 153, 188, 232, 281, 305, 354, 489, 724, 818, 910, 1222, 1234, 1611, 1644, 1688, 2924, 3156, 3456, 3876
TSWc1'	1477*i*, 76, 120, 148, 209, 276 , 378, 505, 566, 637, 706, 1032, 1142, 1300, 1377, 1414, 1705, 1790, 2096, 3744, 3848
TSWc2'	1669*i*, 51, 126, 143, 184, 272, 287, 322, 368, 604, 607, 889, 1105, 1170, 1345, 1550, 1587, 1648, 3118, 3666, 3875
IMc'	111, 218, 274, 296, 609, 726, 1199, 1208, 1566, 1591, 3224, 3316
TSc'	787*i*, 122, 157, 260, 358, 857, 957, 1240, 1458, 1502, 1758, 3632

Table S6 The calculated CVT/SCT rate constants for Path a and Path c' along with the available experimental and theoretical values.

T(K)	k_a		$k_{c'}$	Exp[b]	Exp[c]
225	2.30E-15	3.42 E-16[a]	5.08E-11	7.36E-11[b]	
250	2.18E-15	1.51E-16[a]	1.30E-11	7.26E-12[b]	2.77E-12[c]
275	1.20E-15	8.31E-17[a]	4.55E-12	4.21E-12[b]	2.17E-12[c]
295	9.05E-16		2.32E-12		
298	6.18E-16		2.12E-12		
300	5.19E-16	5.41E-17[a]	2.00E-12	2.67E-12[b]	1.77E-12[c]
309	5.04E-16		1.55E-12	2.31E-12[b]	
325	4.83E-16	4.01 E-17[a]	1.03E-12		1.49E-12[c]
350	4.77E-16	3.29 E-17[a]	6.01E-13		1.29E-12[c]
375	3.76E-16	2.92 E-17[a]	3.85E-13		
420	3.70E-16		2.05E-13		
600	3.57E-16		9.57E-14		
800	2.96E-16		5.36E-14		
1000	2.80E-16		3.07E-14		
1200	2.46E-16		2.71E-14		
1400	1.97E-16		2.53E-14		

[a] the calculated rate constant of $^1O_2$ formation in $CH_3O_2 + HO_2$ reaction by Anglada et al [J. M. Anglada, S. Olivella and A. Sole, *J. Phys. Chem. A.*, 2006, **110**, 6073-6082.]; [b] the experimental values of $^3O_2$ formation in $HO_2 + HO_2$ reaction by Stone et al [D. Stone and D. M. Rowley, *Phys. Chem. Chem. Phys.*, 2005, **7**, 2156-2163]; [c] the experimental values of $^3O_2$ formation in $HO_2 + HO_2$ reaction by Kanno et al [N. Kanno, K. Tonokura and M. Koshi, *J. Geophys. Res.*, 2006, **111**, 7.]