Supporting Information

Theoretical Study of the Reactions of Hydroperoxy (HO_2) with Hydroxymethylperoxy ($HOCH_2O_2$) and Methoxymethylperoxy ($CH_3OCH_2O_2$)

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Table S1. Zero-point energies (ZPE), relative energies (ΔE), and Gibbs free energies (ΔG) at 298.15 K for various product channels in the HO_2 + $HOCH_2O_2$ reaction.

Species	ZPE	[a] ΔE_1	[a] ΔG_1	[a] ΔE_2	[a] ΔG_2	[a] ΔE_3	[a] ΔG_3	Exptl.[b]
HO_2+$HOCH_2O_2$(*cis*)	39.37	0	0	0		0		
HO_2+$HOCH_2O_2$(*trans*)	39.13	1.68	–1.72	1.77	–1.63	1.71	–1.69	
$^3O_2$+$HOCH_2OOH$ (A)	40.41	–34.54	–39.09	–38.59	–43.14	–38.74	–43.29	–40.3
$HOCHO_2$ + H_2O_2	38.46	16.93	10.83	14.13	8.03	14.09	7.99	
CH_2O + $^3O_2$ + H_2O_2	35.57	–20.25	–34.64	–23.16	–37.55	–22.81	–37.2	–21.4
CH_2O + 2 HO_2	34.35	13.56	–2.53	14.84	–1.25	15.47	–0.62	16.9
HCOOH + HO_3H	40.27	–67.9	–91.25	–74.21	–97.56	–75.87	–99.22	–75.1
HCOOH + OH + HO_2	35.41	–40.14	–54.86	–43.63	–58.35	–42.32	–57.04	–41.5
HCOOH + H_2O + $^1O_2$	36.94	–66.91	–80.04	–82.63	–95.76	–83.67	–96.8	–88.6
HCOOH + H_2 + O_3	32.12	–9.19	–21.49	–16.73	–29.03	–20.59	–32.89	–20.1
$^1O_2$+$HOCH_2OOH$ (A)	40.39	4.46	0.56	–8.78	–12.68	–10.41	–14.31	
$CH_2(OH)_2$ + O_3	40.29	–3.51	–9.24	–16.74	–22.47	–16.49	–22.22	
CH_2O + H_2O + O_3	34.55	2.82	–11.4	–10.87	–25.09	–12.99	–27.21	–13.6
$HOCH_2O$ + OH + $^3O_2$	33.39	4.34	–13.15	0.92	–16.57	4.98	–12.51	3.8

[a] Subscripts 1, 2, and 3 represent B3LYP/6-311G(d,p), CCSD(T)/CBS, and CBS-QB3 levels of theory, respectively. All energies are in kcal/mol.

[b] Experimental enthalpies of formation (ref 38) for various specious are as follows (in kcal/mol): HO_2 (3.64), $HOCH_2O_2$ (–38.3), $HOCH_2OOH$ (–75), H_2O_2 (–31), HCOOH (–88.7), H_2O (–57.1), OH (8.9), CH_2O (–25.1), HO_3H (–21.1), HO_3 (7.1), O_3 (33.9), $^1O_2$ (22.5), $HOCH_2O$ (–39.8), $CH_2(OH)_2$ (–93.5).

Table S2. Zero-point energies (ZPE), relative energies (ΔE), and Gibbs free energy (ΔG) at 298.15 K for various conformations of the $HOCH_2O_4H$ adducts and the isomerization transition states with respect to the $HO_2 + HOCH_2O_2$ asymptote.

Species	ZPE	[a] ΔE_1	[a] ΔG_1	[a] ΔE_2	[a] ΔG_2	[a] ΔE_3	[a] ΔG_3
IM-S1A	41.94	–6.91	–1.54	–13.42	–8.05	–12.42	–7.05
IM-S1B	42.23	–8.76	–2.84	–14.72	–8.80	–13.71	–7.79
IM-S1C	42.24	–9.18	–3.31	–15.13	–9.26	–14.22	–8.35
IM-S1D	42.02	–7.24	–1.81	–14.11	–8.68	–13.09	–7.66
IM-S1E	42.14	–6.15	–0.45	–12.85	–7.15	–12.02	–6.32
IM-S1F	42.01	–6.88	–1.44	–12.86	–7.42	–11.96	–6.52
IM-S1G	42.16	–7.74	–2.32	–14.18	–8.76	–13.29	–7.87
IM-S1H	41.94	–5.91	–0.58	–12.65	–7.32	–11.51	–6.18
TS (S1A ↔ S1B)	41.66	–1.43	4.86	–7.88	–1.59	–10.93	–4.64
TS (S1A ↔ S1D)	41.30	–3.08	2.39	–10.17	–4.70	–12.42	–6.95
TS (S1A ↔ S1H)	42.08	–1.25	4.65	–6.90	–1.00	–4.56	1.34
TS (S1B ↔ S1G)	41.81	0.11	6.21	–5.63	0.47	–7.29	–1.19
TS (S1C ↔ S1D)	41.72	–4.22	1.83	–11.04	–4.99	–10.4	–4.35
TS (S1C ↔ S1F)	42.04	–1.75	4.33	–6.49	–0.41	–5.94	0.14
TS (S1D ↔ S1E)	41.89	–2.42	8.21	–3.53	7.10	–0.83	9.80
TS (S1E ↔ S1F)	41.15	–3.39	2.99	–9.15	–2.77	–12.01	–5.63
TS (S1F ↔ S1G)	41.39	–2.95	2.55	–9.67	–4.17	–8.75	–3.25
TS (S1G ↔ S1H)	41.70	–4.30	1.75	–11.19	–5.14	–10.51	–4.46

[a] Subscripts 1, 2, and 3 represent B3LYP/6-311G(d,p), CCSD(T)/CBS, and CBS-QB3 levels of theory, respectively. All energies are in kcal/mol.

Table S3. Zero-point energies (ZPE), relative energies (ΔE), and Gibbs free energies (ΔG) at 298.15 K for various species involved in the HO_2 + $CH_3OCH_2O_2$ reaction.

Species	ZPE	[a] ΔE_1	[a] ΔG_1	[a] ΔE_2	[a] ΔG_2	[a] ΔE_3	[a] ΔG_3
HO_2 + $CH_3OCH_2O_2$	56.81	0	0	0	0	0	0
IM-T1	58.30	−7.30	−1.91	−6.72	−1.33	−5.33	0.06
IM-T2	58.46	−7.78	−2.09	−7.97	−2.28	−6.29	-0.60
TS-T1	55.83	−6.66	−1.15	0.45	5.96	1.31	6.82
TS-T2	57.29	−6.64	−0.38	−4.22	2.04	−2.24	4.02
TS-T3	56.27	15.89	21.09	29.07	34.27	28.31	33.51
IM-S1	59.62	−8.60	−0.02	−12.08	−3.50	−13.24	−4.66
TS-S1[b]	59.76	*n/a*	*n/a*	44.08	*n/a*	40.23	*n/a*
TS-S2	54.76	34.62	51.99	19.23	36.60	21.43	38.80
TS-S3	55.51	18.76	47.87	14.93	44.04	13.23	42.34
TS-S4	55.67	7.77	36.88	4.58	33.69	2.62	31.73
TS-S5	55.75	16.56	43.20	11.29	37.93	9.11	35.75
TS-S6	52.32	34.59	63.70	31.58	60.69	32.83	61.94
TS-S7	56.19	11.87	40.98	12.92	42.03	13.32	42.43
TS-S8	57.56	25.24	54.35	9.02	38.13	10.56	39.67
TS-S9	57.36	14.47	22.59	8.02	16.14	8.33	16.45
CH_3OCH_2O + HO_3	54.59	3.32	−1.03	5.48	1.13	5.50	1.15
CH_3OCH_2O + HO + $^3O_2$	51.19	2.99	−8.61	−1.33	−12.93	6.46	−5.14
CH_3OCH_2OOH + $^3O_2$	57.56	−33.58	−33.86	−38.55	−38.83	−36.16	−36.44
CH_3OCHO + HO_3H	57.33	−63.53	−84.85	−65.01	−86.33	−67.01	−88.33
CH_3OCHO + HO_2 + OH	52.47	−35.77	−48.47	−39.10	−51.80	−38.30	−51.00
CH_3OCH_2OH + O_3	57.68	−4.19	−7.32	−13.61	−16.74	−14.83	−17.96
CH_3OCHO + H_2 + O_3	49.18	−4.82	−15.09	−13.52	−23.79	−14.81	−25.08
CH_3OH + CH_2O + O_3	53.26	4.64	−8.59	−5.36	−18.59	−8.19	−21.42
CH_3OCHO + H_2O + $^1O_2$	54.00	−62.54	−73.65	−75.08	−86.19	−79.97	−91.08

[a] Subscripts 1, 2, and 3 represent B3LYP/6-311G(d,p), CCSD(T)/cc-pVDZ, and CBS-QB3 levels of theory, respectively. All energies are in kcal/mol.

[b] Geometries and ZPE were calculated at the CISD/cc-pVDZ level of theory.

Table S4. Cartesian coordinates (in Ångstroms) of various stationary points optimized at the B3LYP/6-311G(d,p) level for the HO_2 + $HOCH_2O_2$ reaction.

$HOCH_2O_2$, *cis*

C	-0.616567	0.569924	0.238086
O	0.759162	0.536336	-0.294575
O	1.366966	-0.554776	0.127703
O	-1.349965	-0.511005	-0.181482
H	-0.504379	0.638338	1.325094
H	-1.039024	1.476603	-0.190253
H	-0.966499	-1.298926	0.223479

$HOCH_2O_2$, trans

C	-0.496898	0.507707	-0.045751
O	0.607323	-0.466410	-0.199112
O	1.759253	0.072663	0.142203
O	-1.682853	-0.181749	-0.002149
H	-0.251467	1.082898	0.851433
H	-0.496557	1.132770	-0.938239
H	-1.740375	-0.657937	0.833771

IM-T1:

O	-1.126731	1.016451	-0.099193
C	-1.129109	-0.420250	0.337235
O	0.076791	1.534715	-0.132339
H	1.626722	0.638939	0.154325
O	2.435789	0.069146	0.191191
O	2.036854	-1.119478	-0.239183
O	-2.326279	-0.962357	-0.034517
H	-1.075624	-0.396231	1.425237
H	-0.238728	-0.866468	-0.113570
H	-2.309115	-1.162549	-0.977073

TS-T1:

O	-0.446874	0.162588	0.793231
C	-1.337170	-0.714585	0.003142
O	-0.042223	1.181044	0.035978
H	1.451395	0.842783	-0.146610
O	2.319313	0.323680	-0.297718

O	2.055228	-0.921185	-0.016702
H	-1.574424	-1.517090	0.698020
O	-2.491775	-0.067765	-0.353580
H	-0.729846	-1.057665	-0.837832
H	-2.273456	0.592588	-1.022105

IM-T2:

O	0.624665	-0.214540	-0.324145
C	2.028845	-0.292526	0.179403
O	-0.128185	-1.124242	0.250200
H	-1.835484	-0.634702	-0.177579
O	-2.711254	-0.200614	-0.307682
O	-2.593165	0.981675	0.286838
H	2.493411	-1.130811	-0.337817
O	2.668796	0.858522	-0.177766
H	1.931040	-0.473979	1.252752
H	2.351109	1.588242	0.366673

TS-T2:

O	-0.692904	0.448251	-0.600351
C	-1.936627	0.580987	0.166389
O	0.050081	-0.530568	-0.056742
H	1.344814	-0.028878	0.237377
O	2.296430	0.326329	0.512763
O	3.142307	-0.254828	-0.272729
H	-2.448566	1.403984	-0.328719
O	-2.716224	-0.545177	0.082876
H	-1.630661	0.836334	1.186271
H	-2.283347	-1.249426	0.580199

IM-T3:

O	-1.982213	-0.681643	0.042418
O	-2.051143	0.637016	0.113219
H	-1.116505	0.958705	-0.010509
O	0.549313	1.449879	-0.218761
O	1.625391	0.727663	-0.031783
C	1.318567	-0.665938	0.464298
H	2.324877	-1.050288	0.622517
H	0.776742	-0.509418	1.402445
O	0.659460	-1.401460	-0.459876

H	-0.302980	-1.255020	-0.361970

TS-T3:

O	1.787602	0.917895	0.108525
O	1.995615	-0.327477	-0.116075
H	1.044116	-0.880317	0.014608
O	-0.085193	-1.490324	0.219693
O	-1.098790	-0.891906	-0.431727
C	-1.578315	0.296509	0.306433
H	-2.649387	0.300674	0.108396
H	-1.343358	0.092777	1.355001
O	-1.035285	1.445030	-0.199627
H	-0.093073	1.482061	0.037085

TS-T4:

C	-0.731850	0.748981	0.493808
O	-1.563281	-0.436872	0.275416
O	-0.929409	-1.388816	-0.389571
H	-1.253836	1.336138	1.246679
H	0.500643	0.245206	0.937636
H	0.300239	0.968200	-1.074165
O	-0.431257	1.432606	-0.615900
O	1.573339	-0.155239	0.859712
O	1.778334	-0.197962	-0.542480
H	1.422239	-1.073163	-0.770414

TS-T5:

C	-0.442958	0.480643	0.505639
O	-1.510117	-0.510973	0.647806
O	-1.962171	-0.857676	-0.545913
H	-0.179746	0.819736	1.506086
H	0.681718	-0.260224	0.068249
H	-1.168197	1.083577	-1.115519
O	-0.761202	1.485952	-0.329135
O	1.619083	-0.804521	-0.254729
O	2.668988	0.058226	0.132656
H	2.887320	0.504991	-0.698133

IM-T4:

C	-1.196958	0.814100	0.442090
O	-1.827771	-0.393542	-0.007269
O	-1.021383	-1.451275	0.066625
H	-1.943365	1.447684	0.907431
H	2.051630	0.895384	0.681409
H	0.286394	0.778474	-0.757656
O	-0.390697	1.418859	-0.434412
O	2.394363	0.001258	0.533469
O	1.570881	-0.440336	-0.576304
H	0.983949	-1.085849	-0.140607

IM-T5:

C	-1.605035	-0.589208	0.279285
O	-1.633832	0.803843	-0.234127
O	-0.533762	1.442616	0.106040
O	-0.714002	-1.368702	-0.398579
H	-1.397589	-0.489214	1.349154
H	-2.618262	-0.937298	0.082490
H	0.185108	-1.149029	-0.098060
O	1.782054	-0.389134	0.590834
O	2.405738	0.171983	-0.435491
H	3.011379	0.825938	-0.038714

TS-T6:

C	-1.491788	-0.924216	0.209206
O	-1.620782	0.932055	-0.138103
O	-0.478185	1.446762	-0.034206
O	-0.438915	-1.324898	-0.376235
H	-1.487812	-0.745007	1.287709
H	-2.447794	-1.183723	-0.244117
H	0.477915	-0.858454	0.091069
O	1.379770	-0.120492	0.615739
O	2.349581	0.013966	-0.362716
H	2.876671	0.753340	-0.025740

TS-T7:

C	-0.184010	0.425256	0.110156
H	-0.203878	0.079580	1.128942
O	-0.180022	1.736870	-0.041157
H	0.047652	-0.234408	-0.708324

O	-2.112786	-0.025602	-0.094495
O	-2.365263	-1.240140	0.059802
O	2.005129	0.127027	0.369407
O	2.473115	-0.942853	-0.349817
H	2.683049	-1.608275	0.324719
H	0.015856	1.969154	-0.956193

IM-T6:

C	-1.130486	0.893863	0.241124
O	-0.910076	-0.506420	-0.282110
O	-1.819321	-1.350404	0.157891
O	-0.182781	1.688995	-0.314783
H	-2.121167	1.184515	-0.102078
H	-1.084468	0.783595	1.328756
H	0.687362	1.441000	0.048915
O	1.851378	-0.988527	-0.202999
H	0.887543	-0.973988	-0.422796
O	2.112506	0.181569	0.354558

TS-T8:

C	-0.508557	1.515642	0.235616
O	-1.060321	-0.302553	-0.338350
O	-2.099303	-0.918997	0.178882
O	0.650415	1.568647	-0.250817
H	-1.305738	2.076301	-0.253164
H	-0.678207	1.216846	1.274057
H	1.334081	0.627684	0.059369
O	1.078519	-1.418217	-0.081183
H	-0.066234	-0.941006	-0.294130
O	1.901620	-0.438090	0.216490

IM-S1C

O	0.552774	-1.000317	-0.475552
C	1.599541	-0.214491	0.084920
O	-0.560233	-0.975865	0.476866
O	-1.623647	-0.330633	-0.132253
O	-1.460022	1.095149	0.012513
H	-0.944238	1.301477	-0.785719
H	1.774671	-0.542547	1.114664
H	2.449208	-0.464181	-0.552248

O	1.386280	1.159676	-0.003549
H	0.761907	1.408116	0.689581

TS-S1:

O	1.109160	-0.798342	0.758357
C	1.704756	-0.289607	-0.263673
O	-0.645163	-0.429382	-0.276126
O	-1.916946	-0.501654	-0.234322
O	-2.534261	0.784912	0.178364
H	-1.777367	1.201754	0.626832
H	0.854541	-0.221872	-1.086006
O	2.265508	0.993919	-0.163955
H	2.430404	-0.956764	-0.774013
H	2.037494	1.318897	0.716679

TS-S2:

O	0.967204	-1.217957	-0.310717
C	1.233779	-0.221283	0.395884
O	-1.178392	-1.073921	-0.311523
O	-1.249733	-0.150800	0.519758
O	-1.357762	1.293052	-0.149707
H	-0.544924	1.275929	-0.695700
H	0.100622	-0.009212	0.930833
H	1.840193	-0.352421	1.312605
O	1.502692	0.992307	-0.283626
H	1.729373	1.671957	0.363483

TS-S3:

O	0.272556	-0.889632	0.714612
C	1.225397	0.094545	0.511806
O	-0.793539	-0.818752	-0.489587
O	-1.868476	-0.387254	-0.101708
O	-0.794974	1.482624	0.098910
H	-0.942752	2.444740	0.060364
H	0.536274	1.084264	0.549757
H	1.925617	0.028673	1.350349
O	1.915331	0.070444	-0.677045
H	1.281294	0.215613	-1.392761

TS-S4:

O	0.789934	0.921650	0.590162
C	1.114511	-0.068835	-0.060722
O	-1.429213	1.076220	-0.115359
O	-1.487078	-0.090837	-0.573322
O	-1.545892	-1.093706	0.403233
H	-0.473013	-1.276692	0.708852
H	0.588327	-1.288351	0.714799
H	0.436262	-0.440161	-0.867528
O	2.396057	-0.403569	-0.354236
H	2.970897	0.140154	0.204384

TS-S5:

O	-0.495886	-0.532742	-0.618947
C	-1.694734	-0.524971	0.144989
O	0.387508	0.306568	0.005782
O	1.800000	-0.394277	0.566089
O	2.494258	0.370471	-0.240341
H	1.268105	0.644749	-0.636092
O	-2.365737	0.664732	0.074603
H	-2.293400	-1.295027	-0.340639
H	-1.441401	-0.815405	1.170353
H	-1.926050	1.297495	0.638956

TS-S6:

O	0.385198	-0.859901	-0.677177
C	1.319773	-0.562046	0.307248
O	-1.512644	-0.843122	0.099360
O	-1.424573	0.337274	0.559130
O	-0.900780	1.148466	-0.451770
H	-0.227578	0.297766	-0.856443
H	2.098411	-1.332462	0.269982
O	1.953788	0.671184	0.101792
H	0.831723	-0.606790	1.297685
H	1.370902	1.382548	0.394616

TS-S7:

O	0.960899	-1.209386	-0.350294
C	1.355939	-0.318335	0.442126
O	-1.017279	-1.106202	-0.259980
O	-1.338934	-0.131419	0.480155

O	-1.303861	1.097629	-0.162090
H	-0.015342	1.263978	-0.335505
O	1.109977	1.236501	-0.281539
H	0.768595	-0.141490	1.361527
H	2.441971	-0.248908	0.586187
H	1.382724	1.939450	0.325017

TS-S8:

O	0.300650	-1.372521	-0.320194
C	1.593010	-0.193784	0.279548
O	-0.850894	-1.029480	0.355369
O	-1.568200	-0.183890	-0.258568
O	-0.873252	1.558196	0.017810
H	-1.124006	1.724685	0.938212
H	1.326973	-0.339821	1.335499
H	2.397598	-0.836720	-0.087183
O	1.438343	0.934705	-0.268731
H	0.268196	1.358472	-0.069302

TS-S9:

O	-0.854623	-1.129822	-0.397512
O	-1.687050	-0.613245	0.465400
H	-1.756412	0.411429	0.151719
O	-0.789453	1.409040	-0.010538
O	0.163611	0.679356	-0.582854
C	1.262079	0.390670	0.408836
H	1.914003	1.263085	0.381926
H	0.733308	0.292612	1.360681
O	1.942308	-0.702064	-0.022071
H	1.338291	-1.457264	0.033251

TS-S10:

O	0.766312	0.593302	-0.391203
C	1.555920	-0.345005	0.408595
O	-0.343157	0.933457	0.293955
H	-1.611964	0.544862	-0.645816
O	-1.895340	-0.381382	-0.394052
O	-3.015584	-0.347939	0.239706
H	1.040276	-1.306476	0.384119
O	2.783484	-0.491385	-0.191724

H	1.578423	0.065746	1.423195
H	3.292025	0.317478	-0.066524

IM-S2:

C	-1.129161	0.895140	0.241254
O	-0.909478	-0.507008	-0.276594
O	-1.827069	-1.346409	0.154465
O	-0.180275	1.687493	-0.316713
H	-2.119356	1.185373	-0.103636
H	-1.083897	0.788952	1.329365
H	0.689524	1.439682	0.047933
O	1.852364	-0.990245	-0.202703
H	0.888354	-0.975668	-0.421341
O	2.114501	0.180022	0.354064

TS-S11:

C	-0.497348	1.523179	0.239738
O	-1.057353	-0.300127	-0.310698
O	-2.121640	-0.911049	0.155843
O	0.655702	1.564188	-0.261162
H	-1.297953	2.081957	-0.245713
H	-0.656032	1.235633	1.283105
H	1.339082	0.620886	0.047518
O	1.076765	-1.424906	-0.074389
H	-0.065027	-0.948863	-0.272233
O	1.904529	-0.444191	0.209018

HOCH2OOH-A:

O	-1.357649	-0.600551	-0.020301
C	-0.612532	0.550405	0.287346
H	-1.656166	-0.528191	-0.933924
H	-0.449893	0.533299	1.365604
H	-1.105899	1.476803	-0.029949
O	0.618659	0.593386	-0.393503
O	1.466491	-0.436312	0.173237
H	1.067138	-1.236525	-0.201261

HOCH2OOH-D:

C	0.525199	0.499093	-0.031820

O	-0.467806	-0.534265	-0.122059
O	-1.739194	0.099478	0.178844
O	1.758234	-0.132795	-0.039066
H	0.485885	1.147160	-0.912453
H	0.325101	1.077506	0.878763
H	1.815818	-0.677510	0.754373
H	-2.187872	-0.001063	-0.671509

SR1-TS1:

C	0.671334	-0.621619	0.535686
O	1.021728	0.703122	0.739359
O	1.009539	1.343419	-0.578479
H	0.664020	-1.083885	1.523027
H	-0.617925	-0.649223	0.091121
H	1.431595	-0.853112	-1.183967
O	1.445069	-1.330224	-0.343273
O	-1.723020	-0.722548	-0.308639
O	-2.316605	0.519863	-0.004117
H	1.806613	1.884419	-0.490444
H	-2.805991	0.322454	0.807335

SR1-TS2:

C	-0.395236	0.505540	0.507095
O	-1.506515	-0.278265	0.751952
O	-1.872047	-0.876576	-0.540304
H	-0.076296	0.901950	1.471310
H	0.632970	-0.291316	0.133936
H	-0.938322	1.092451	-1.208874
O	-0.549607	1.501265	-0.423544
O	1.607278	-0.877224	-0.199863
O	2.664857	-0.000909	0.123562
H	-2.829683	-0.929509	-0.414877
H	2.831020	0.446853	-0.718482

SR1-TS3:

C	1.300675	-0.694996	-0.111749
O	0.440282	0.032060	0.804076
O	0.025048	1.187905	0.175157
O	2.501497	-0.049028	-0.319231
H	1.497613	-1.630432	0.410680
H	0.723289	-0.851699	-1.027537

H	2.321926	0.747939	-0.831841
H	-1.086318	0.935597	-0.135038
O	-2.121366	0.439778	-0.434308
O	-1.980913	-0.880161	-0.055889
H	-2.176941	-0.875863	0.895793

SR1-TS4:

C	-1.860454	-0.430946	0.436394
O	-0.855808	-0.677248	-0.566880
O	0.036372	0.379646	-0.534917
O	-2.642811	0.671834	0.151073
H	-2.490025	-1.319161	0.394971
H	-1.335324	-0.349742	1.395677
H	-2.079616	1.451954	0.216809
H	1.077067	-0.118697	-0.292096
O	2.032023	-0.516437	0.277136
O	3.015463	0.423082	0.018415
H	3.308700	0.674302	0.907657

SR1-TS5:

C	0.988686	-0.220862	0.416804
O	0.925336	0.905045	-0.404897
O	-0.059220	1.800673	0.162448
H	1.156220	0.020305	1.469958
H	-0.187588	-0.776706	0.327684
H	1.797339	-1.206309	-0.999962
O	1.933316	-1.082326	-0.050864
O	-1.302071	-1.251609	0.012254
O	-2.142732	-0.125569	-0.186021
H	-0.881038	1.416118	-0.197778
H	-2.654083	-0.097952	0.635913

SR1-TS6:

C	0.866778	-0.415892	0.379468
O	1.279217	0.774677	-0.210337
O	0.323378	1.796505	0.146304
H	0.732416	-0.357731	1.463736
H	-0.364637	-0.555949	-0.112503
H	1.923821	-1.342104	-0.906802
O	1.704317	-1.430036	0.030620

O	-1.428014	-0.270002	-0.659782
O	-2.408631	-0.311895	0.362238
H	-0.474606	1.476054	-0.324263
H	-2.779797	-1.198906	0.250680

SR1-TS7:

C	-1.380596	0.02184500	0.516987
O	-0.487604	0.48112700	-0.549589
O	0.369101	1.428118	-0.035274
O	-2.366099	-0.738519	-0.071249
H	-0.807724	-0.615500	1.188937
H	-1.737097	0.923840	1.024041
H	-2.946217	-0.157871	-0.576204
H	1.373089	0.835109	0.091678
O	2.237403	0.020237	0.217987
O	1.600977	-1.176898	-0.039525
H	1.571299	-1.229171	-1.009184

SR1-TS8:

C	-1.761845	-0.173387	0.498528
O	-0.857545	0.354224	-0.509939
O	0.245672	0.877910	0.131837
O	-2.963082	-0.449352	-0.117287
H	-1.349368	-1.112449	0.873280
H	-1.816500	0.576633	1.295257
H	-3.373317	0.382559	-0.379094
H	1.143272	0.226318	-0.232924
O	1.992350	-0.608266	-0.307630
O	3.149321	0.015145	0.126865
H	3.433258	-0.550023	0.861541

SR2-TS1:

C	-0.385677	0.553050	0.408252
O	-1.203394	-0.467046	0.794307
O	-1.753586	-1.047100	-0.457830
H	0.174228	0.903890	1.274381
H	0.894022	-0.065562	-0.315854
H	-1.513539	1.135242	-0.990607
O	-0.928992	1.549619	-0.339993
O	1.861471	-0.418597	-0.619545

O	2.691090	-0.101313	0.333253
H	-2.573362	-1.416373	-0.098980

SR2-TS2:

C	0.986295	-0.224658	0.398974
O	0.823576	0.880791	-0.413106
O	-0.114307	1.772196	0.232260
H	1.146846	-0.000182	1.455469
H	-0.414457	-0.872757	0.363945
H	1.844667	-1.081029	-1.071450
O	1.915231	-1.071446	-0.106942
O	-1.465186	-1.185516	0.195711
O	-2.101162	-0.156469	-0.290806
H	-0.960040	1.385463	-0.078745

SR2-TS3:

C	0.800142	-0.464107	0.364800
O	1.352634	0.643136	-0.268715
O	0.627947	1.809766	0.172215
H	0.632183	-0.346491	1.436448
H	-0.758600	-0.453436	-0.196178
H	1.722971	-1.570328	-0.883875
O	1.486612	-1.587659	0.053270
O	-1.713027	-0.268329	-0.605154
O	-2.553801	-0.193983	0.399875
H	-0.000323	1.931454	-0.557123

SR3-TS1:

C	-0.542619	0.273079	0.416970
O	0.276358	0.900349	-0.356866
O	1.604436	-0.459232	0.047411
H	0.289643	-0.450111	0.930885
H	-0.940411	0.850761	1.267387
H	2.536510	-0.662684	-0.173989
O	-1.549212	-0.521651	-0.127307
H	-1.282683	-0.732168	-1.032008

Table S5. Cartesian coordinates (in Ångstroms) of various stationary points optimized at the B3LYP/6-311G(d,p) level for the HO_2 + $CH_3OCH_2O_2$ reaction.

$CH_3OCH_2O_2$

O	1.232288	0.291426	-0.377583
C	0.101258	0.903207	0.334241
O	1.538690	-0.891933	0.126622
O	-1.099773	0.576770	-0.240881
H	0.255800	1.973286	0.204043
H	0.194563	0.576186	1.375671
C	-1.558982	-0.753289	0.018479
H	-1.587354	-0.951084	1.096304
H	-2.565737	-0.811267	-0.392078
H	-0.920562	-1.496739	-0.465528

IM-T1

O	-0.544440	1.334240	-0.055248
C	-0.720611	0.030497	0.680522
O	0.702277	1.573211	-0.380132
H	2.100557	0.466477	-0.076029
O	2.812146	-0.216523	0.014098
O	2.182791	-1.380352	-0.070712
O	-2.030883	-0.315672	0.605845
H	-0.467507	0.245446	1.718655
H	-0.019588	-0.667868	0.210743
C	-2.434952	-0.862302	-0.657567
H	-1.817960	-1.729525	-0.916107
H	-3.470932	-1.172280	-0.537910
H	-2.366315	-0.110646	-1.447896

IM-T2

O	0.444966	-1.192268	-0.389190
C	1.823025	-0.710957	-0.090921
O	-0.315487	-1.158790	0.686615
H	-1.986114	-0.732109	0.150461
O	-2.783040	-0.211531	-0.115718
O	-2.364213	1.044288	-0.197739
H	2.458895	-1.323740	-0.727461
O	1.962077	0.590329	-0.461914
H	1.958828	-0.900253	0.979330
C	1.283286	1.543540	0.374094

H	1.613425	2.523617	0.035820
H	0.199048	1.461040	0.263001
H	1.563635	1.399720	1.423388

TS-T1

O	0.210295	-0.709565	-0.494556
C	1.440824	-0.963461	0.257675
O	-0.446940	0.351382	0.014047
H	-1.789451	-0.001416	0.231421
O	-2.794352	-0.244060	0.453605
O	-3.525016	0.500128	-0.308180
H	1.636503	-2.018969	0.073805
O	2.500353	-0.245514	-0.230786
H	1.206339	-0.745794	1.305623
C	2.520224	1.141503	0.123712
H	3.478100	1.527186	-0.221081
H	1.706573	1.686812	-0.360992
H	2.440928	1.264955	1.209869

TS-T2

O	0.031697	0.298454	-0.556029
C	0.797770	-0.643636	0.285673
O	-0.541896	1.245174	0.180503
H	-2.058649	0.812798	0.109206
O	-2.899017	0.243962	0.086035
O	-2.509801	-0.975707	-0.174056
H	0.875136	-1.518847	-0.369398
O	2.006042	-0.128770	0.665267
H	0.199804	-0.828951	1.174111
C	2.969828	-0.017742	-0.386369
H	3.900902	0.293544	0.083167
H	3.115759	-0.984716	-0.882822
H	2.665271	0.729530	-1.123840

TS-T3

C	0.217180	0.009696	-0.382907
H	0.242116	-0.604927	-1.267321
O	0.169026	1.300019	-0.594163
H	-0.000865	-0.403884	0.588982
O	2.164535	-0.309224	-0.049223

O	2.436766	-1.489276	0.264609
O	-2.008815	-0.363164	-0.476514
O	-2.467196	-1.217250	0.493221
H	-2.662411	-2.037797	0.012980
C	-0.114678	2.111269	0.562092
H	0.654010	1.959080	1.323275
H	-0.099717	3.142776	0.219163
H	-1.102670	1.850124	0.944380

TS-S1

O	-0.036614	0.245987	0.687115
C	-1.123097	0.934358	0.084177
O	0.835082	-0.120680	-0.306189
O	2.346052	0.490498	-0.118030
O	2.842288	-0.720218	0.039407
H	1.516468	-0.958949	-0.008792
O	-1.941898	0.119418	-0.638744
H	-1.616638	1.380056	0.955664
H	-0.731713	1.699293	-0.585985
C	-2.686076	-0.791297	0.138944
H	-3.309503	-0.262148	0.871279
H	-3.328974	-1.342843	-0.546585
H	-2.033880	-1.493819	0.667219

TS-S2

O	0.180781	-1.240576	-0.387061
C	-0.755826	-0.390747	-0.937348
O	1.083788	-0.524651	0.805398
O	2.160293	-0.149743	0.392807
O	1.028806	1.392105	-0.604708
H	1.088804	2.304504	-0.941517
H	-0.131959	0.620960	-1.091249
H	-1.022107	-0.831240	-1.905150
O	-1.914818	-0.143485	-0.242359
C	-1.756187	0.561414	0.990921
H	-2.759567	0.773974	1.354402
H	-1.216266	-0.049545	1.722141
H	-1.197628	1.488140	0.827314

TS-S3

O	0.352396	1.503618	-0.534772

C	1.157503	0.778916	0.146024
O	-1.137228	0.430328	0.444792
O	-2.363548	0.075134	0.454995
O	-2.587153	-1.097121	-0.424425
H	-1.860242	-0.971069	-1.061280
H	0.443025	0.271387	0.965192
O	1.790830	-0.268801	-0.536542
H	1.868707	1.336988	0.797377
C	2.610729	-1.086900	0.287342
H	2.017060	-1.636457	1.029094
H	3.103190	-1.800379	-0.371205
H	3.376495	-0.497825	0.808237

TS-S4

O	-0.334189	-1.675400	-0.280139
C	0.533418	-0.977476	0.293538
O	-2.007951	-0.332789	-0.138870
O	-1.439641	0.518333	0.566659
O	-0.790679	1.707740	-0.286079
H	-0.223650	1.177460	-0.882745
H	-0.202724	-0.121174	0.873619
H	1.060531	-1.381853	1.181226
O	1.367505	-0.180820	-0.516664
C	2.336977	0.587644	0.201405
H	2.937641	-0.048830	0.860022
H	2.987564	1.036614	-0.546799
H	1.857914	1.380261	0.785767

TS-S5

O	-0.367059	1.266186	0.452468
C	0.769553	1.055135	-0.271133
O	-2.056872	0.338499	-0.454034
O	-1.518750	-0.808741	-0.458151
O	-0.967634	-1.043734	0.799218
H	-0.645811	0.024453	0.945934
H	1.254816	2.033006	-0.433242
O	1.662774	0.207489	0.414758
H	0.529446	0.627519	-1.265631
C	2.197217	-0.870462	-0.345575
H	2.783768	-0.507692	-1.199002
H	2.853184	-1.426934	0.322315
H	1.404311	-1.535984	-0.704204

TS-S6

O	0.378643	0.882202	0.493160
C	0.614987	-0.139009	-0.148125
O	-1.890886	1.112197	-0.099862
O	-2.011216	-0.062518	-0.530021
O	-2.066496	-1.043117	0.472020
H	-0.994539	-1.259122	0.733867
H	0.071940	-1.313257	0.683653
H	-0.131304	-0.491283	-0.904924
O	1.844658	-0.566964	-0.508490
C	2.944162	0.096127	0.144357
H	2.828269	0.046536	1.229583
H	3.835271	-0.441147	-0.170606
H	2.997842	1.141161	-0.163424

TS-S7

O	0.647952	1.624574	-0.302029
C	-0.364959	1.260624	0.353856
O	1.933278	0.125333	-0.099348
O	1.357150	-0.820015	0.515016
O	0.543850	-1.599317	-0.291133
H	-0.449711	-0.731371	-0.556668
O	-1.217123	0.060006	-0.505160
H	-0.201727	0.685903	1.285928
H	-1.172979	2.000273	0.434166
C	-2.358606	-0.470027	0.187441
H	-3.138680	0.291344	0.213015
H	-2.718786	-1.335986	-0.367860
H	-2.097586	-0.778400	1.204869

TS-S8

O	0.274768	0.482452	-0.394633
C	0.996017	-0.529752	0.388093
O	-0.804773	0.890794	0.297876
H	-2.101172	0.590999	-0.636812
O	-2.442322	-0.317758	-0.393981
O	-3.556996	-0.218828	0.244365
H	0.409903	-1.449344	0.338567
O	2.210463	-0.749484	-0.198384
H	1.049013	-0.139872	1.412127
C	3.161688	0.301346	-0.002039
H	3.318889	0.485726	1.067461

H	4.092500	-0.039016	-0.451943
H	2.835520	1.224541	-0.487664

TS-S9

O	-1.492349	-1.132942	-0.403748
O	-2.377381	-0.447607	0.260802
H	-2.270808	0.527952	-0.131660
O	-1.117437	1.391654	-0.133704
O	-0.185055	0.484449	-0.447053
C	0.689164	0.253796	0.749641
H	1.044774	1.256815	1.011511
H	0.045330	-0.171502	1.516770
O	1.666140	-0.625764	0.416535
C	2.698073	-0.094819	-0.423748
H	3.137949	0.803344	0.025434
H	3.456703	-0.870906	-0.502528
H	2.311289	0.142114	-1.417549

CH_3OCH_2OOH

O	1.187595	0.464611	-0.358824
C	0.039911	0.920480	0.332738
O	1.450710	-0.909486	0.061505
H	2.384928	-0.829449	0.295690
H	0.109125	2.006146	0.235353
O	-1.173435	0.552500	-0.230075
H	0.115402	0.601889	1.381668
C	-1.578309	-0.792879	0.014031
H	-2.608196	-0.873005	-0.333263
H	-0.950494	-1.505205	-0.526886
H	-1.539342	-1.026990	1.085981

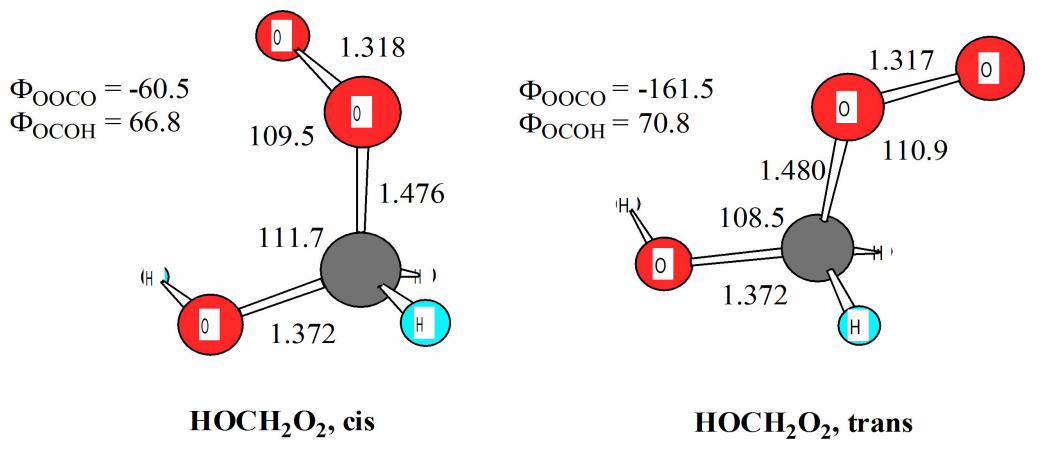

Figure S1. The B3LYP/6-311G(d,p) optimized geometries of two conformations of the $HOCH_2O_2$ radical. Bond distances are in Å and bond angles are in degrees.

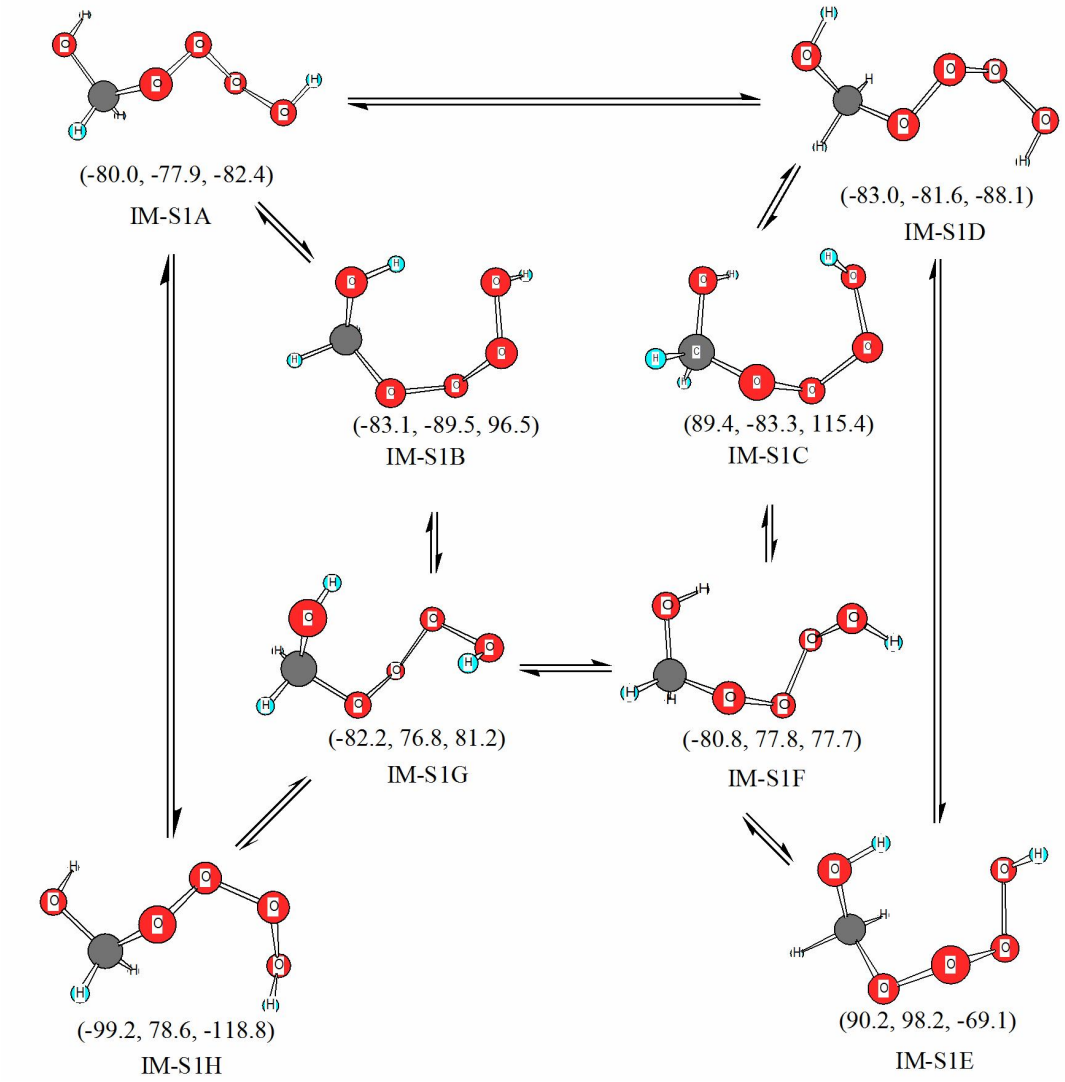

Figure S2. The B3LYP/6-311G(d,p) optimized geometries of eight conformations of the singlet $HOCH_2O_4H$ intermediate (IM-S1) and the relationship of these conformers. The values in parenthesis are three dihedral angles (in degrees) HOOO, OOOO, and OOOC, respectively.

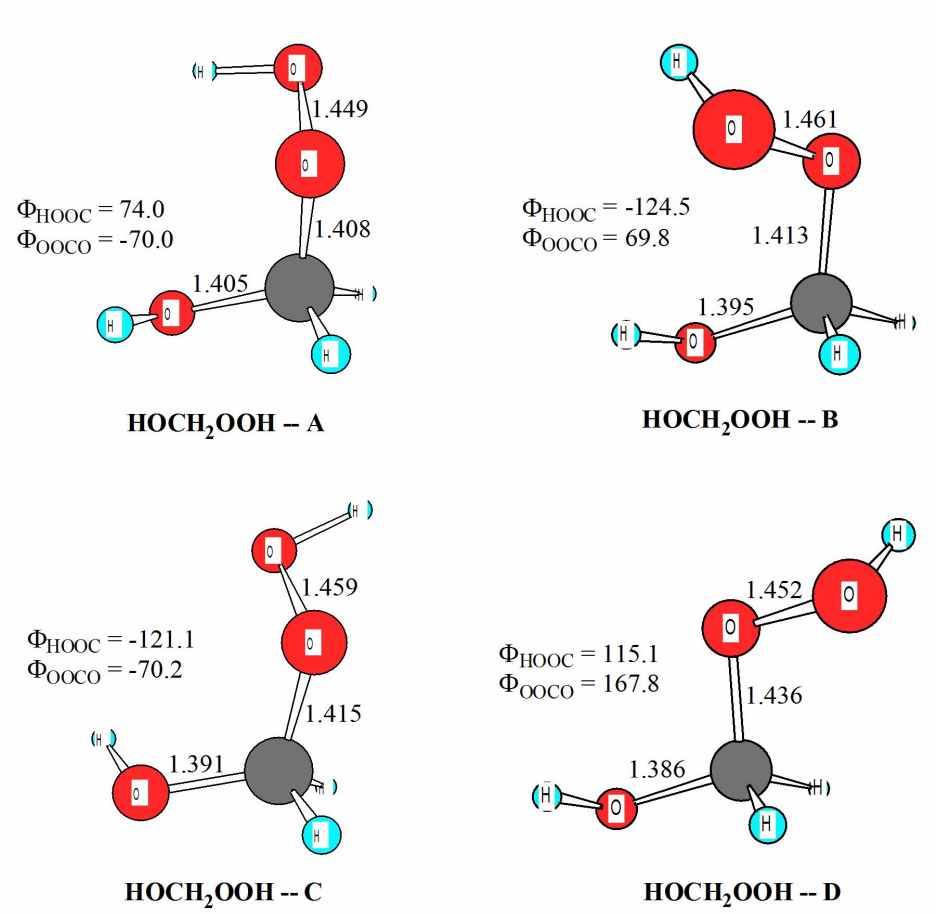

Figure S3. The B3LYP/6-311G(d,p) optimized geometries of four conformations of the $HOCH_2OOH$ molecule. Bond distances are in Å and bond angles are in degrees.

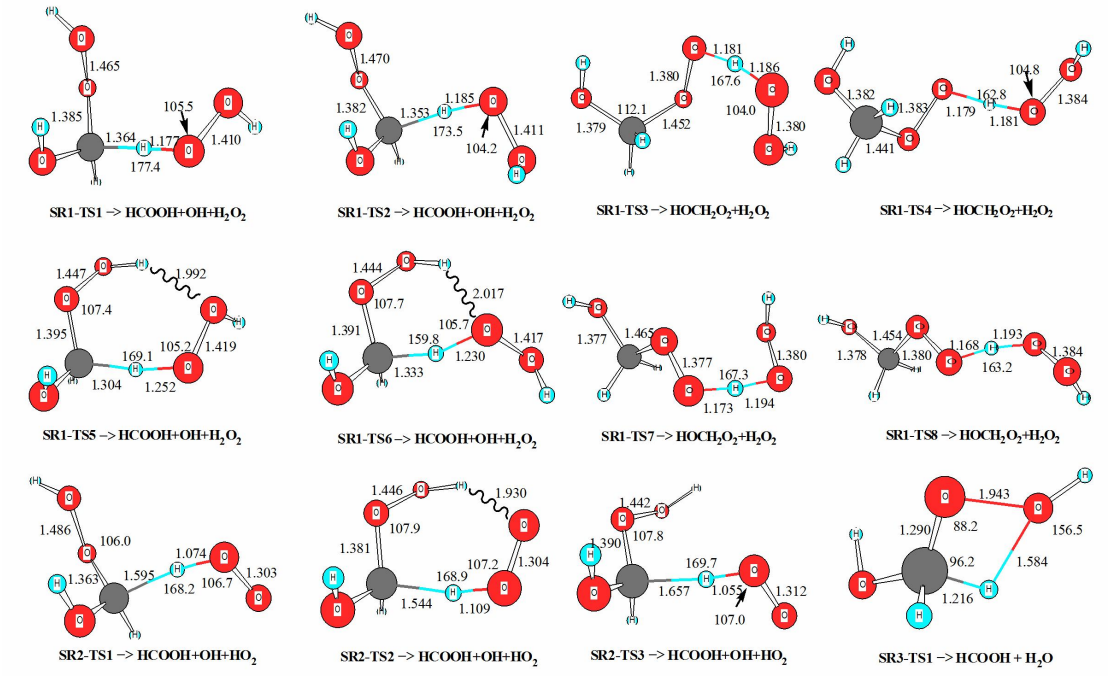

Figure S4. The B3LYP/6-311G(d,p) optimized geometries of the transition states involved in the reactions of $HOCH_2OOH$ with HO_2 (SR1) and O_2 (SR2) reactions. Bond distances are in Å and bond angles are in degrees.

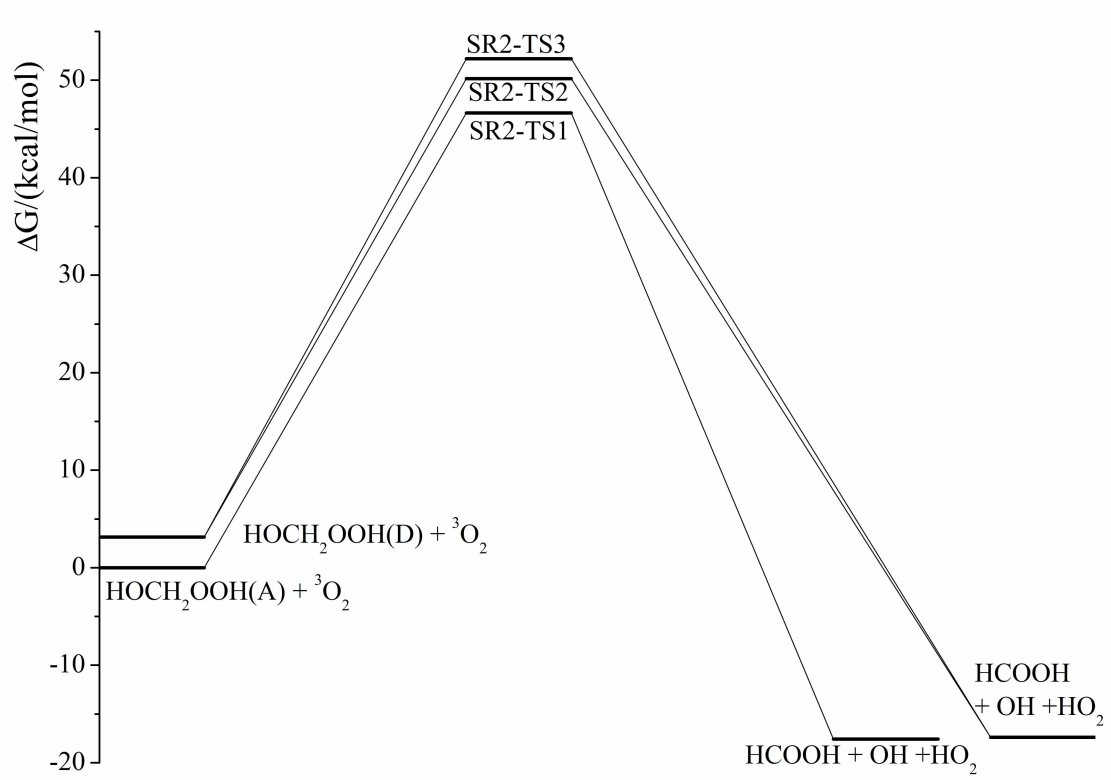

Figure S5. Schematic profile for the potential energy surface of the $^3O_2$ + $HOCH_2OOH$ reaction. The relative energies (ΔG, in kcal/mol) at 298.15 K are calculated at the CCSD(T)/CBS//B3LYP/6-311G(d,p) level.

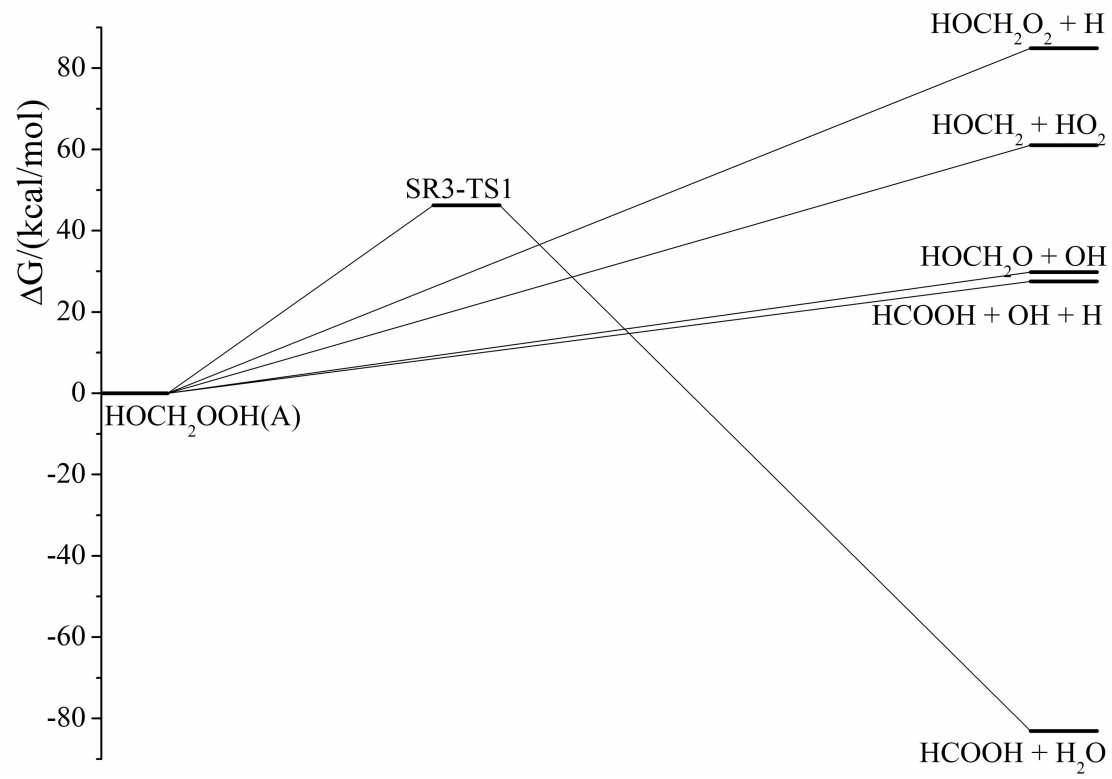

Figure S6. Unimolecular decomposition routes of $HOCH_2OOH$. The relative energies (ΔG, in kcal/mol) at 298.15 K are calculated at the CCSD(T)/CBS // B3LYP/6-311G(d,p) level.

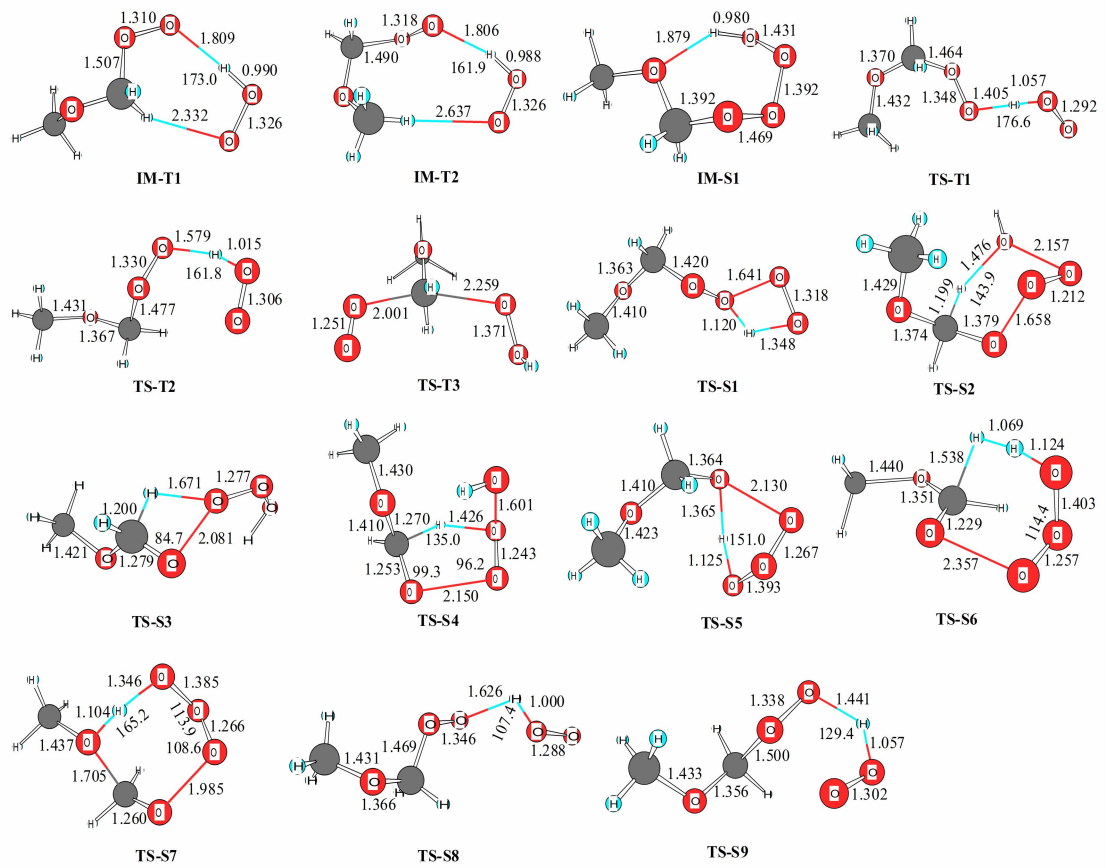

Figure S7. The B3LYP/6-311G(d,p) optimized geometries of the intermediates (IM) and transition states (TS) involved in the HO_2 + $CH_3OCH_2O_2$ reaction. Bond distances are in Å and bond angles are in degrees.