Supplementary Materials

Effect of a Single Water Molecule on $^{\bullet}CH_2OH + {}^3O_2$ Reaction Under Atmospheric and Combustion Conditions

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Table S1: Redundant internal coordinates of reactants, complexes, products and transition states obtained using ωB97XD /6-311++G(3df,3pd) taken from Gaussian checkpoint file.

CH_2OH

C	0.0000000000	-0.0479873592	-0.1680771006	0.0781764968
H	0.0000000000	0.0448843049	0.3020170625	1.0433913037
H	0.0000000000	0.7521442963	-0.1296883463	-0.6483320063
O	0.0000000000	-1.3292810800	-0.2757552508	-0.3579257849
H	0.0000000000	-1.3423365585	-0.6335930447	-1.2453100093

O_2

O	0.0000000000	0.0000000000	0.0000000000	0.0010162690
O	0.0000000000	0.0000000000	0.0000000000	1.1962557310

Int-1

C	0.0000000000	-0.0136173982	-0.0018612394	-0.0065157207
H	0.0000000000	-0.0362616134	-0.0057103923	1.0845884939
H	0.0000000000	1.0005688338	-0.0034840193	-0.3941850512
O	0.0000000000	-0.7014806529	1.0386106156	-0.5658053046
H	0.0000000000	-1.5813501252	1.0657771913	-0.1825106846
O	0.0000000000	-0.5569120684	-1.2894048393	-0.4189985272
O	0.0000000000	-1.7786250420	-1.4082990867	0.0085987305

TS1

C	0.0000000000	0.7778479870	0.5188872922	0.0000003791
H	0.0000000000	1.0974391974	1.0997494287	0.8912787504
H	0.0000000000	1.0974399344	1.0997495277	-0.8912776623
O	0.0000000000	-0.6713657221	0.7119820022	-0.0000002082
O	0.0000000000	-1.2599204979	-0.5172832328	-0.0000005099
H	0.0000000000	-0.4571142346	-1.1106495963	-0.0000002101
O	0.0000000000	1.1453363358	-0.7086694217	0.0000004609

TS2

C	0.0000000000	0.0047414116	-0.0017007418	-0.0011865644
H	0.0000000000	-0.0132250789	0.0071822004	1.0947835745
H	0.0000000000	1.0099326796	-0.0143783455	-0.4418680230
O	0.0000000000	-0.9487698935	0.5326773494	-0.6351675253
O	0.0000000000	-0.3736892734	-1.6335399664	-0.2936066603
O	0.0000000000	-1.3314041748	-2.0425278989	0.5686825960
H	0.0000000000	-2.0958574211	-2.1964377601	-0.0010911089

TS3

C	0.0000000000	-0.0099275292	0.0059433231	-0.0172578354
H	0.0000000000	-0.0073840023	-0.0277841762	1.2892156183
H	0.0000000000	1.0293033187	0.0170113908	-0.3406410977
O	0.0000000000	-0.7325117671	0.9887830095	-0.5928394227
H	0.0000000000	-1.6665664547	0.7867985606	-0.4781313436
O	0.0000000000	-0.6016630224	-1.2259565038	0.0400796887
O	0.0000000000	-0.5857771847	-1.1939626649	1.5037187988

TS4

C	0.0000000000	0.0003291152	0.0010278569	-0.0003268339
H	0.0000000000	-0.0073042260	0.0041305342	1.0881253939
H	0.0000000000	0.9893060938	-0.0053338116	-0.4571140674
O	0.0000000000	-0.8866118866	0.9118275251	-0.5681834241
O	0.0000000000	-0.9575135775	-0.7520362004	-0.6169405839
O	0.0000000000	-1.0283156900	2.3109249319	0.5591633793
H	0.0000000000	-1.9326981867	2.5202177459	0.2947108982

TS5

C	0.0000000000	-0.0007146861	-0.0106809231	-0.0004055310
H	0.0000000000	-0.0059266974	0.0001367935	1.0942198480
H	0.0000000000	0.9876709777	-0.0000235023	-0.4708626200
O	0.0000000000	-1.0085050946	0.3904295654	-0.6402456470
H	0.0000000000	-1.4944714787	-0.7624100500	-0.9486629816
O	0.0000000000	-0.2625494001	-1.8690617271	-0.1664435474
O	0.0000000000	-1.3386001398	-1.8816177801	-0.8496004581

QOOH

C	0.0000000000	-0.0062862376	0.0186256052	0.0008218907
H	0.0000000000	0.0137483455	-0.0140231205	1.1012833947
H	0.0000000000	1.0411519717	0.0057509420	-0.3553948002
O	0.0000000000	-0.5428681182	1.1556054700	-0.4323470769
O	0.0000000000	-0.6602936419	-1.1628422452	-0.3783339394
O	0.0000000000	-0.5129161675	-1.3032552654	-1.7823897497
H	0.0000000000	-1.2884538530	-0.8363152963	-2.1123304727

Int-2

C	0.0000000000	-0.0287546180	-0.0002033841	-0.0036855918
O	0.0000000000	-0.0003364020	0.0010529751	1.2002916338
H	0.0000000000	1.6138204441	-0.0014964658	1.9309540125
O	0.0000000000	3.0839494017	-0.0045618313	0.8530330042
O	0.0000000000	2.5900057502	-0.0033500393	2.0660352312
H	0.0000000000	0.8971512673	-0.0023072428	-0.5954299135
H	0.0000000000	-0.9894628124	0.0007558511	-0.5406506218

CH_2O

C	0.0000000000	0.0011696497	0.0000154956	0.0007329038
H	0.0000000000	-0.0039382613	-0.0000050482	1.1054408370
H	0.0000000000	0.9930491043	-0.0000050482	-0.4856628774
O	0.0000000000	-1.0124345993	0.0000760692	-0.6343926514

HO2

H	0.0000000000	0.0026120666	0.0000000000	0.0043162627
O	0.0000000000	0.0003509311	0.0000000000	1.8321080870
O	0.0000000000	0.6714299351	0.0000000000	0.7075246863

HCOOH

C	0.0000000000	-0.0509297624	-0.0342820638	-0.0717948298
H	0.0000000000	0.0337405165	0.1000808015	1.0114731087
O	0.0000000000	1.1644060204	-0.1780074025	-0.6085732287
H	0.0000000000	1.0520232822	-0.2912013299	-1.5603938821
O	0.0000000000	-1.0756139589	-0.0491383453	-0.6845336780

OCH_2O

C	0.0000000000	0.0280692408	0.0188627259	0.0184818093
H	0.0000000000	0.0106231197	-0.0110146553	1.1043374428
H	0.0000000000	1.0024792895	-0.0056175377	-0.4613206874
O	0.0000000000	-0.9260035340	0.8088099941	-0.5832495504
O	0.0000000000	-0.9832493641	-0.6594415501	-0.6245454968

OH

O	0.0000000000	0.0000000000	0.0000000000	-0.0048666837
H	0.0000000000	0.0000000000	0.0000000000	0.9648666837

$CH_2OH\ldots H_2O$

C	0.0000000000	0.0486527158	-0.0039557540	0.0087476161
H	0.0000000000	0.1966973397	0.0700866281	1.0730396851
H	0.0000000000	0.8748181314	-0.1266933499	-0.6768704164
O	0.0000000000	-1.0720260197	0.6309668457	-0.4354800810
H	0.0000000000	-1.1350102209	0.5674949200	-1.3888781115
H	0.0000000000	-2.8493507228	0.4534423643	0.3990043770
O	0.0000000000	-3.7640022895	0.3777901169	0.6916273820
H	0.0000000000	-3.9548407967	1.2071108009	1.1280697347

$CH_2OH\ldots O_2$

C	0.0000000000	-0.0031602723	-0.0027739050	0.0012481211
H	0.0000000000	-0.0045698086	0.0096388832	1.0787702020
H	0.0000000000	0.9197728232	-0.0317714411	-0.5620023361
O	0.0000000000	-1.0973846528	0.5708525973	-0.5596713209
H	0.0000000000	-0.9976803261	0.5965109460	-1.5117911702
O	0.0000000000	0.4319819071	0.4813485413	-3.4824921567
O	0.0000000000	1.5980409905	0.6618230202	-3.2920895155

O_2…H_2O

O	0.0000000000	0.0889537946	-0.0401543478	-0.1797437406
H	0.0000000000	-0.0643705223	0.0401971190	2.3837688508
O	0.0000000000	0.0342931576	0.0088738087	3.3355286875
H	0.0000000000	0.8852272954	-0.4031194468	3.4840379735
O	0.0000000000	1.0639792848	-0.4925894299	-0.7022260603

Int-1-H_2O

C	0.0000000000	-0.0596499412	0.0437634792	0.0328859719
H	0.0000000000	-0.0958686414	0.0504197882	1.1236030049
H	0.0000000000	0.9566380425	-0.0354723923	-0.3435909349
O	0.0000000000	-0.6925502682	1.0923828867	-0.5459563434
H	0.0000000000	-1.4796377048	1.3113277611	-0.0180694164
O	0.0000000000	-0.6422165625	-1.2531239052	-0.3683175166
O	0.0000000000	-1.8125343680	-1.4420885982	0.1563298189
H	0.0000000000	-2.7537641057	0.0816619857	1.0234339492
O	0.0000000000	-2.8185335462	1.0289937100	1.2080718344
H	0.0000000000	-3.7190916162	1.2814382700	1.0055236556

TS1h

C	0.0000000000	0.0276348145	0.0604791695	0.0163792893
H	0.0000000000	-0.0444368133	0.0269502184	1.1261660037
H	0.0000000000	1.1138185619	-0.0635786991	-0.2094142281
O	0.0000000000	-0.1867017470	1.4560703591	-0.2674320759
O	0.0000000000	-1.0943048119	1.6404929106	-1.2805183885
H	0.0000000000	-1.5199776257	0.7656748432	-1.4451184059
O	0.0000000000	-0.7084903963	-0.7911463258	-0.5874738858
H	0.0000000000	-2.3369515025	-1.0506405453	-1.9551294681
O	0.0000000000	-2.8337847700	-0.3310714059	-2.3547101722
H	0.0000000000	-2.7359396301	-0.4386459379	-3.3007355056

TS2h

C	0.0000000000	-0.0697073018	-0.0022004308	-0.0209157269
H	0.0000000000	-0.0990626032	0.0168410565	1.0725771024
H	0.0000000000	0.9388473085	-0.0057573008	-0.4489231290
O	0.0000000000	-1.0022053726	0.5823998318	-0.6703583990
O	0.0000000000	-0.4997372153	-1.5657874691	-0.3230305206
O	0.0000000000	-1.4264982398	-1.9642992177	0.5680036776
H	0.0000000000	-2.2669877478	-1.9018639522	0.0463198312
H	0.0000000000	-2.7526656711	-0.1729450294	-0.8433176081
O	0.0000000000	-3.3763175882	-0.9187096620	-0.8512023341
H	0.0000000000	-3.5094297505	-1.1274932551	-1.7760678037

TS3h

C	0.0000000000	-0.0292170026	0.0019155327	0.0246930141
H	0.0000000000	-0.0373241373	0.0352144721	1.3285282500
H	0.0000000000	1.0106373836	0.0172859166	-0.2969370709
O	0.0000000000	-0.7793065394	0.9390924098	-0.5534028386
H	0.0000000000	-1.7096952728	0.8184840119	-0.2546895566
O	0.0000000000	-0.5731185101	-1.2609879348	0.1437427629
O	0.0000000000	-0.6922276262	-1.1093232868	1.5957407622
O	0.0000000000	-3.0425440643	0.3229430877	0.8158805495
H	0.0000000000	-3.7137134913	-0.2187302399	0.3998941894
H	0.0000000000	-2.4888025995	-0.2917536805	1.3218637356

TS4h

C	0.0000000000	-0.0051511722	-0.0229882730	-0.0672782362
H	0.0000000000	0.0264734392	-0.0464262216	1.0205014985
H	0.0000000000	0.9624832813	-0.0173424573	-0.5674055455
O	0.0000000000	-0.9110712232	0.9109980460	-0.5933005949
O	0.0000000000	-0.9875670470	-0.7563296154	-0.6714151999
O	0.0000000000	-1.0937948424	2.2899502273	0.5118494916
H	0.0000000000	-2.0229659513	2.4266508570	0.2906692452
H	0.0000000000	-0.0903986253	1.5644129905	3.6377943767
O	0.0000000000	-0.5644307251	1.0123442735	3.0172827849
H	0.0000000000	-0.8090474999	1.5921857103	2.2836048939

TS5h

O	0.0000000000	1.5680154892	-0.4854884605	-0.5488111151
O	0.0000000000	1.3538655318	-1.0174927336	0.5905897678
H	0.0000000000	0.6029103828	-0.2973910825	0.9811933286
O	0.0000000000	-0.0690470978	0.8079265563	0.6665902309
C	0.0000000000	0.4484515027	0.9755952248	-0.4783090834
H	0.0000000000	1.2408604491	1.7181480286	-0.6076444431
H	0.0000000000	-0.1301417127	0.7297076898	-1.3730450996
O	0.0000000000	-2.4789560491	-0.3198365273	-0.3061485811
H	0.0000000000	-3.3203660486	-0.0327250247	0.0455508252
H	0.0000000000	-1.8076134473	0.0979213292	0.2493521697

TS6h

O	0.0000000000	-0.0247538013	-0.0053901477	-0.0267449109
O	0.0000000000	-0.0086062727	-0.0004718186	1.2480059737
H	0.0000000000	1.1268557341	0.0027481410	1.4011009036
O	0.0000000000	2.2562127412	0.0031217349	0.8151727266
C	0.0000000000	1.8514104651	-0.0023768722	-0.3786874802
H	0.0000000000	1.8450766616	-0.9284246448	-0.9593136990
H	0.0000000000	1.8407901391	0.9191649794	-0.9663745413
O	0.0000000000	0.0934473476	-0.0159715997	-2.9186204103
H	0.0000000000	-0.6767475338	-0.0156450482	-2.3481200179
H	0.0000000000	-0.2497876821	-0.0201603040	-3.8116708744

QOOH-H_2O

C	0.0000000000	-0.0108994851	0.0296477813	0.0015791604
H	0.0000000000	0.1887752359	-0.0025116235	1.0768754733
H	0.0000000000	0.9043532217	0.1104487785	-0.5867754311
O	0.0000000000	-0.9319961344	1.0168321272	-0.2770146851
O	0.0000000000	-0.6660628997	-1.1775974864	-0.3112247572
O	0.0000000000	-0.5040668857	-1.4394719493	-1.6913196728
H	0.0000000000	-1.3042217501	-1.0217377618	-2.0713208300
H	0.0000000000	-3.4063915988	-0.0308042802	-1.9865372344
O	0.0000000000	-2.5889914519	0.1930239525	-2.4337223983
H	0.0000000000	-2.2108648465	0.9114585936	-1.9144437522

Int-2-H_2O

C	0.0000000000	0.0526387377	-0.0047618798	0.0401452073
O	0.0000000000	0.0240226047	0.0203793586	1.2469110028
H	0.0000000000	1.3191492031	0.0076756416	2.3637629431
O	0.0000000000	3.1553421604	0.1925475644	2.5220905180
O	0.0000000000	1.9943324080	0.0133571109	3.0903231758
H	0.0000000000	1.0016728007	-0.0623764431	-0.5089547419
H	0.0000000000	-0.8893490702	0.0351462015	-0.5279298073
H	0.0000000000	3.2191037940	0.2307065606	0.6391156610
O	0.0000000000	3.1312368068	0.2129206731	-0.3260512855
H	0.0000000000	3.9673474489	-0.1130580725	-0.6558344845

H_2O

O	0.0000000000	-0.0152501390	0.0000000000	-0.0107777327
H	0.0000000000	0.0217368448	0.0000000000	0.9454211661
H	0.0000000000	0.8984491253	0.0000000000	-0.2950980192

Table S2: Calculated equilibrium constants (K_{eq} in cm^3 $molecule^{-1}$) for the formation of two-body complexes.

T(K)	$K_{eq(1)}$ (CH_2OH $+H_2O\rightarrow$ $CH_2OH—$ H_2O)	$K_{eq(2)}$ (CH_2OH $+O_2\rightarrow$ CH2OH--O_2	$K_{eq(3)}$ (O_2+ H_2O $\rightarrow$OH--H_2O)
200	6.47E-22	1.10E-24	1.58E-22
225	3.02E-22	1.00E-24	1.72E-22
250	1.68E-22	9.56E-25	1.88E-22
275	1.06E-22	9.40E-25	2.07E-22
300	7.32E-23	9.45E-25	2.28E-22
325	5.44E-23	9.63E-25	2.51E-22
350	4.27E-23	9.93E-25	2.77E-22
375	3.50E-23	1.03E-24	3.05E-22
400	2.98E-23	1.08E-24	3.35E-22

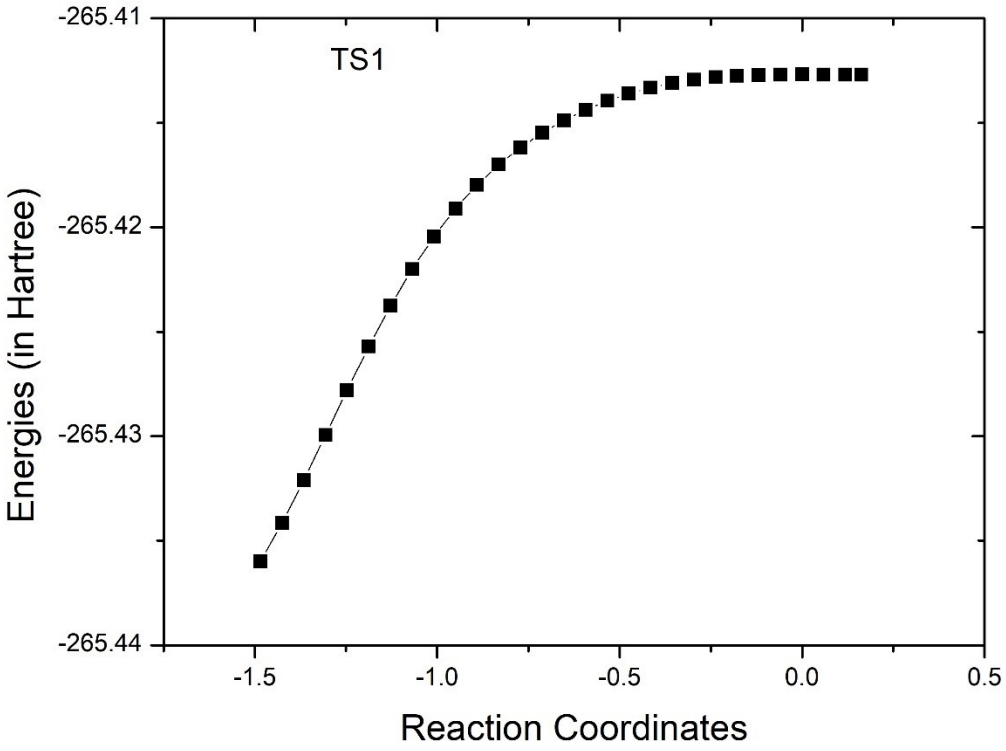
Table S3: Calculated equilibrium constants (K_{eq} in cm^3 $molecule^{-1}$) for the formation of three-body complex.

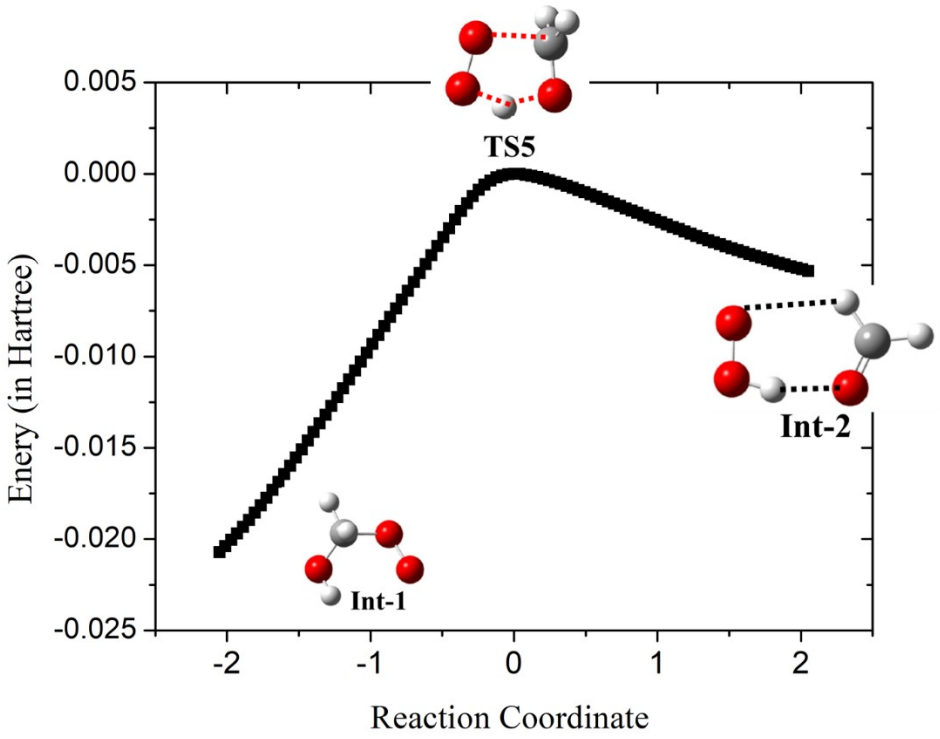
T (K)	$K_{eq(A)}$ (CH_2OH—H2O + O2 →Int-H2O)	$K_{eq(B)}$ (CH_2OH – O2 +H2O →Int-H2O)	$K_{eq(C)}$ (OH—H2O→ Int-H2O)
200	1.30E+12	7.78E+14	5.39E+12
225	3.74E+07	1.14E+10	6.67E+07
250	8.54E+03	1.52E+06	7.73E+03
275	8.86E+00	1.01E+03	4.59E+00
300	2.86E-02	2.24E+00	9.29E-03
325	2.22E-04	1.27E-02	4.85E-05
350	3.44E-06	1.49E-04	5.34E-07
375	9.24E-08	3.17E-06	1.07E-08
400	3.90E-09	1.09E-07	3.49E-10

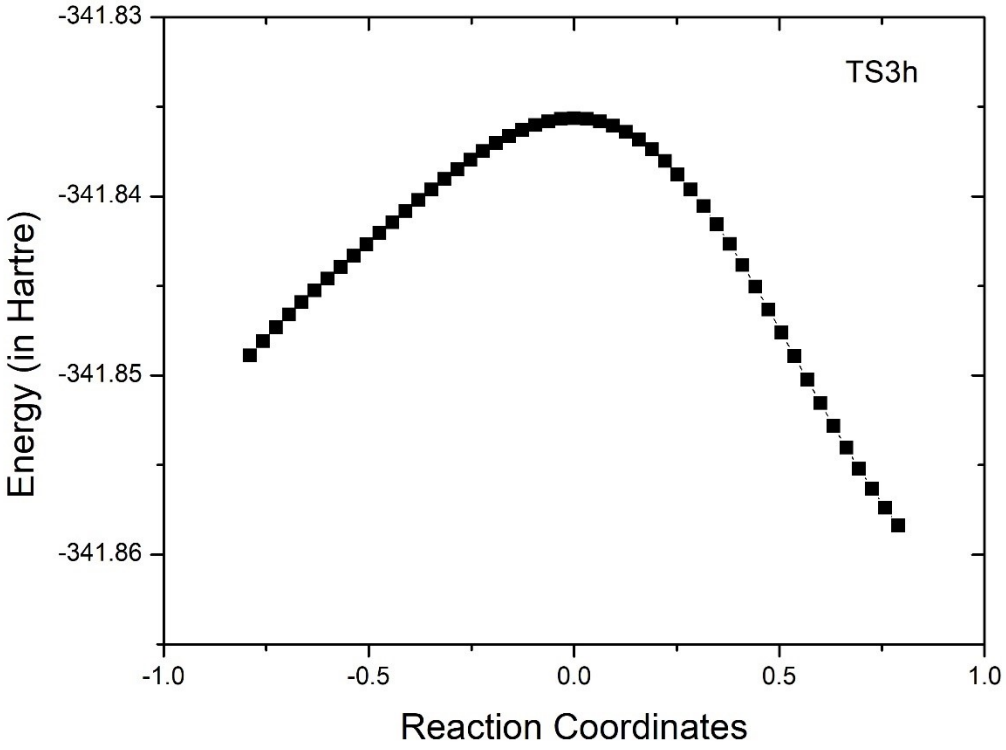
Table S4: Calculated rate coefficients for the $^{\bullet}CH_2OH + O_2$ and $^{\bullet}CH_2OH + O_2$ ($+H_2O$) in the temperature range of 500 to 1500K.

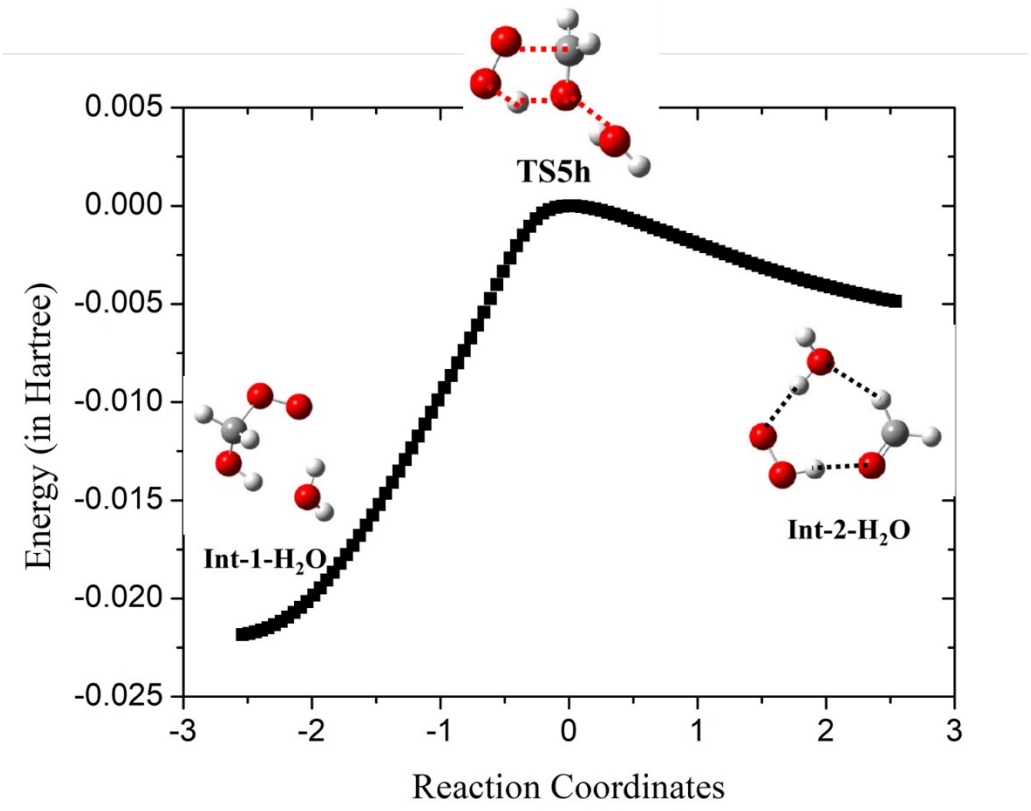
Temp	$k_{CH2OH+O2}$	*Literature Value*	k-TS5h	k-TS6h	$k_{total\text{-}cvt/sct}$	$k_{total\text{-}TST/Eckart}$
500	1.5×10^{-11}	3.1×10^{-11}	5.6×10^{-12}	4.8×10^{-13}	1.51×10^{-12}	6.1×10^{-12}
600	1.2×10^{-11}	6.4×10^{-11}	1.8×10^{-13}	1.6×10^{-14}	6.05×10^{-14}	1.9×10^{-13}
700	9.8×10^{-12}	1.12×10^{-11}	1.8×10^{-14}	1.5×10^{-15}	6.83×10^{-15}	1.9×10^{-14}
800	8.4×10^{-12}	-	3.4×10^{-15}	2.8×10^{-16}	1.46×10^{-15}	3.6×10^{-15}
900	7.2×10^{-12}	-	9.9×10^{-16}	8.3×10^{-17}	4.73×10^{-16}	1.1×10^{-15}
1000	6.2×10^{-12}	1.45×10^{-11}	3.9×10^{-16}	3.3×10^{-17}	2.04×10^{-16}	4.3×10^{-16}
1100	5.4×10^{-12}	1.82×10^{-11}	1.9×10^{-16}	1.6×10^{-17}	1.07×10^{-16}	2.1×10^{-16}
1200	4.7×10^{-12}	2.20×10^{-11}	1.2×10^{-16}	9.3×10^{-18}	6.59×10^{-17}	1.3×10^{-16}
1300	4.1×10^{-12}	2.59×10^{-11}	7.6×10^{-17}	6.1×10^{-18}	4.52×10^{-17}	8.2×10^{-17}
1400	3.7×10^{-12}	2.97×10^{-11}	5.5×10^{-17}	4.3×10^{-18}	3.37×10^{-17}	5.9×10^{-17}
1500	3.2×10^{-12}	-	4.4×10^{-17}	3.3×10^{-18}	2.70×10^{-17}	4.6×10^{-17}
$k = AT^n \exp(-B/T)$	$A=5.8\times10^{-06}$ n= -1.9 B= 456		$A=2.8\times10^{-38}$ n=5.5 B= -13342	$A=3.4\times10^{-38}$ n=5.1 B= -13133	$A=5.4\times10^{-38}$ n=5.4 B= -12633	$A=7.0\times10^{-38}$ n=5.3 B= -13271

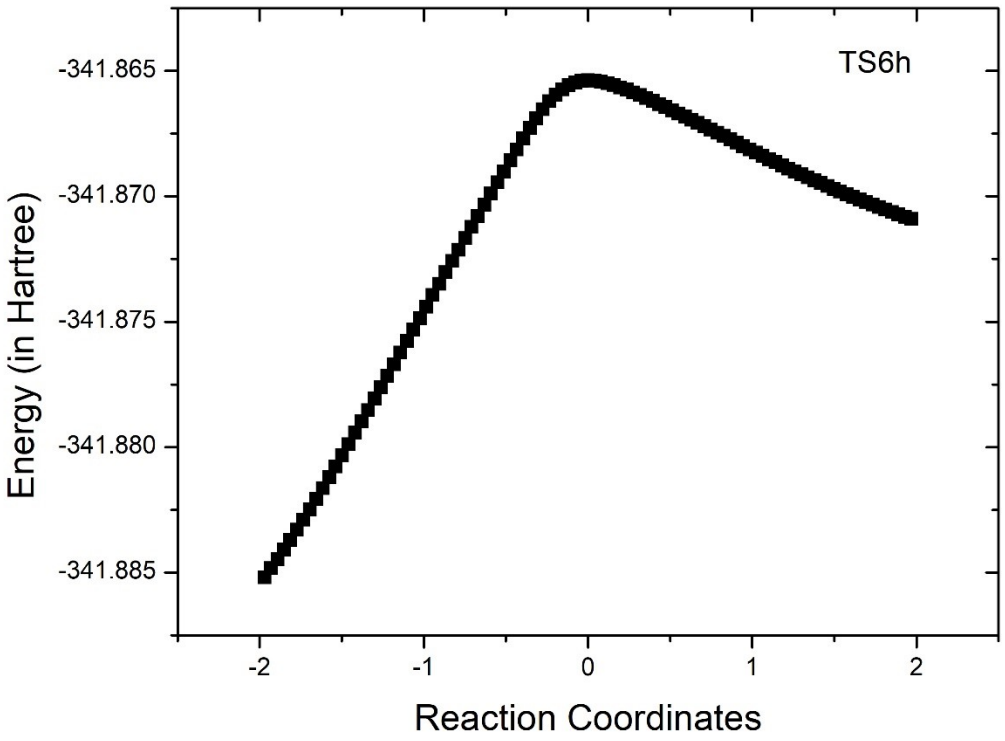
Figure S1: *IRC Calculations for the important transition states*






TS3h
-341.83
-341.84
-341.85
-341.86
Energy (in Hartre)
-1.0
-0.5
0.0
0.5
1.0
Reaction Coordinates


TS5h
0.005
0.000
-0.005
-0.010
-0.015
-0.020
-0.025
Energy (in Hartree)
Int-1-H2O
Int-2-H2O
-3
-2
-1
0
1
2
3
Reaction Coordinates


TS6h
-341.865
-341.870
-341.875
-341.880
-341.885
Energy (in Hartree)
-2
-1
0
1
2
Reaction Coordinates