Electronic Supplemental Information

Reaction Pathways and Kinetics Study of Syngas Combustion System: CO + HO_2 in H_2O Environment

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Table S1 The energies (kcal mol^{-1}) of reaction CO + HO_2 calculated by different CBS extrapolation schemes

products/TS	this work[a]	CCSD(T)/CBS(TZ,QZ)[b]	CCSD(T)/CBS(DZ,TZ,QZ)[c]	USTE[d]
CO_2+OH	-62.26988799	-62.2880341	-62.21557628	-62.35870688
trans-HOOCO	3.686663671	3.675957898	3.796241488	3.839727571
TS1	16.39687853	16.39963396	16.42142785	16.49721161
TS2	11.50071796	11.49758792	11.58028842	11.67103989
cis-TS3	17.58119668	17.58397918	17.59721115	17.65935828
TS5	13.54835227	13.5416544	13.6381106	13.700404
HCO+O_2	35.5402456	35.55675786	35.49933118	35.64313871
trans-TS4	23.73974992	23.74482523	23.74684917	23.82337918
TS7	35.19543515	35.21385556	35.15877712	35.33503179
trans-HCOOO	-3.203471028	-3.20415932	-3.116763293	-2.983177786
tor-TS	5.764414502	5.766817886	5.841735044	5.999613549
cis-HCOOO	-0.937934981	-0.938819607	-0.851425371	-0.720380332
RC-1	-1.707906211	-1.701375327	-1.71703207	-1.648466143
RC-2	-3.583251548	-3.575434348	-3.583787771	-3.484557477
PC	-63.86786568	-63.88379796	-63.81727047	-63.93751952

[a] Two-point exponential scheme:[30] $E(x) = E_{\mathrm{CBS}} + \frac{B}{(x+1)^4}$, where x is 2, 3, and 4 for the aug-cc-pVXZ (X = D, T, and Q) basis set.

[b] Power function extrapolation scheme:[31] $E(x) = E_{\mathrm{cbs}} + \mathrm{B}x^{-\alpha}$

[c] Mixed Gaussian/ exponential extrapolation scheme:[32] $E(x) = E_{\mathrm{cbs}} + \mathrm{A}e^{-(x-1)} + \mathrm{B}e^{-(x-1)^2}$

[d] USTE scheme:[33, 34] $E(x) = E_{\mathrm{cbs}} + \frac{\mathrm{A}_3}{(x+\alpha)^3} + \frac{\mathrm{A}_5}{(x+\alpha)^5}$

Table S2 Optimized geometries of reactants, complexes, transition states and products obtainedusing M06-2X/aug-cc-pVTZ level

CO	(T1 value: 0.01786836)			C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	-0.64079400	O	0.00000000	0.00000000	1.15532100
O	0.00000000	0.00000000	0.48059500	O	0.00000000	0.00000000	-1.15532100
HO_2	(T1 value: 0.02878968)			OH	(T1 value: 0.01003236)		
O	0.05504600	-0.60001600	0.00000000	O	0.00000000	0.00000000	0.10799900
H	-0.88074300	-0.86540800	0.00000000	H	0.00000000	0.00000000	-0.86399400
O	0.05504600	0.70819200	0.00000000	CHO	(T1 value: 0.02137496)		
H_2O	(T1 value: 0.01001375)			C	0.06172800	0.58084200	0.00000000
H	0.00000000	0.76274700	-0.46544900	H	-0.86418700	1.21158700	0.00000000
O	0.00000000	0.00000000	0.11636200	O	0.06172800	-0.58708000	0.00000000
H	0.00000000	-0.76274700	-0.46544900	O_2	(T1 value: 0.01711721)		
CO_2	(T1 value: 0.01757480)			O	0.00000000	0.00000000	0.59492200

O	0.00000000	0.00000000	-0.59492200

RC1 (T1 value: 0.02562272)

C	1.76519200	0.58544400	0.00000100
O	1.47257300	-0.50106100	-0.00000100
O	-1.47081000	-0.55191000	0.00000100
H	-0.58956300	-0.97108100	-0.00000300
O	-1.25196200	0.73527400	-0.00000100

RC2 (T1 value: 0.02588428)

H	-0.80602900	-0.96917700	0.00000200
O	-1.41282800	0.74667200	0.00000100
O	-1.68112100	-0.53106000	-0.00000200
C	1.27783800	-0.38358700	0.00000400
O	2.23632400	0.19322600	-0.00000200

RC-3a (T1 value: 0.01502960)

C	-0.98111000	0.08822700	-0.00026400
O	-2.09294400	-0.04256800	0.00016800
O	2.31070700	-0.12475500	0.00004800
H	1.37445900	0.09230700	-0.00055600
H	2.77010000	0.71691200	0.00041300

RC-3b (T1 value: 0.01503555)

C	2.11531700	-0.20132500	-0.00008200
O	1.06963300	0.20639400	0.00007500
O	-2.15433900	-0.15672100	0.00002700
H	-2.74570700	0.59826700	-0.00031000
H	-1.26854200	0.21229500	-0.00001200

RC4 (T1 value: 0.02496675)

O	-0.97378000	-0.64136100	0.00806900
H	-0.00098300	-0.80886300	-0.00217900
O	-1.07193100	0.66074500	0.01178400
O	1.61521900	-0.02034200	-0.08930200
H	2.28803500	-0.01126200	0.59459600
H	1.15687900	0.82779000	-0.03683200

WRC1 (T1 value: 0.02344670)

H	1.80626200	0.08765700	-0.04179400
O	0.59202400	-1.26614100	0.04658800
O	1.84439100	-0.90320800	-0.02394200
C	-1.78517800	0.45696300	0.00668200
O	-2.60670900	-0.30258700	-0.01202300
O	1.10269100	1.64787700	-0.08093800
H	0.15973200	1.44374500	-0.01546100
H	1.28590500	2.31929600	0.57969000

WRC3 (T1 value: 0.02342655)

C	-2.50894200	-0.69392800	0.01145100
O	-2.02980800	0.32207400	0.02443200
O	1.97165000	-0.74863100	0.07054100
H	1.87467000	0.23531000	0.06211800
O	0.74735500	-1.18303700	-0.06250500
O	0.86154100	1.65954400	-0.10087700
H	0.02727300	1.17687300	-0.13694500
H	0.74581100	2.35178300	0.55339300

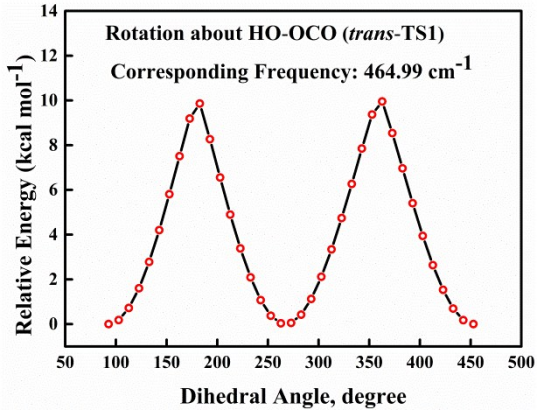
WRC4 (T1 value: 0.02352490)

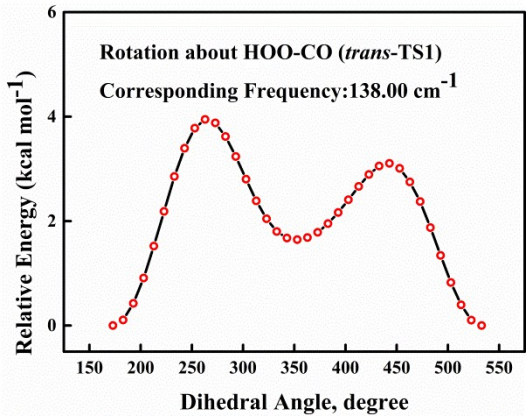
C	1.90117000	-0.47136200	0.10465500
O	2.95902400	-0.17422700	-0.11457100
O	-1.23716100	-1.03345200	0.13416500
H	-0.56640300	-0.31403000	0.20127500
O	-2.36058500	-0.43501800	-0.14986800
O	-0.48791800	1.57039600	-0.03058000
H	-1.43738300	1.46951100	-0.18063900
H	-0.39011600	2.25109900	0.63826500

trans-TS1 (T1 value: 0.02774918)

H	-1.98350900	-0.39807200	0.78162500
O	-0.56606200	0.52071300	0.02748000

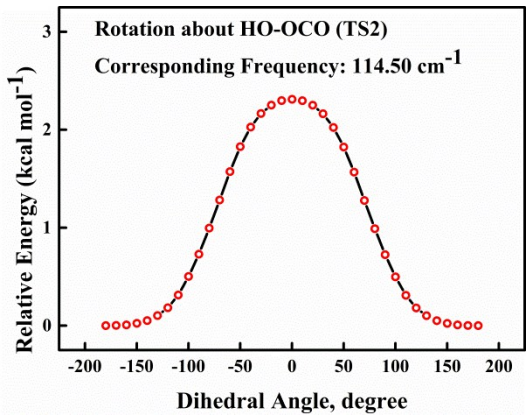
O	-1.70505800	-0.20421100	-0.12443100
C	0.86961700	-0.46239500	0.00188300
O	1.86684500	0.08005300	-0.00216400





TS2 (T1 value: 0.04739620)

O	1.64077300	-0.36252400	-0.00012200
H	2.30107200	0.34796700	0.00147400
O	0.36034100	0.56754400	-0.00016700
C	-0.63636900	-0.18149400	0.00002900
O	-1.81147200	-0.11239500	0.00008300



cis-TS3 (T1 value: 0.02826035)

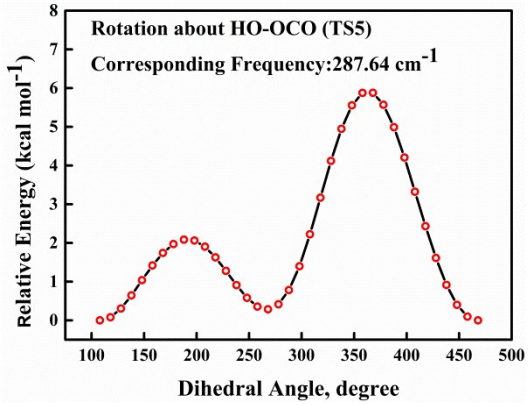
C	0.99401700	0.54434800	-0.00439300
O	1.47830100	-0.48265200	-0.00053100
O	-1.30476500	-0.52657300	-0.12335300
H	-1.38268700	-0.86828300	0.77907600
O	-0.74621300	0.70950000	0.02979500

trans-TS4 (T1 value: 0.02279456)

C	0.75995900	-0.31202400	0.00009600
O	1.82248400	0.07078200	-0.00005900
O	-1.50506400	-0.40186300	-0.00005300
H	-0.28112300	-1.04183100	0.00010400
O	-0.85225000	0.69532800	0.00002700

TS5 (T1 value: 0.02161000)

O	-1.38071300	-0.47552900	-0.04973000
H	-1.98293000	-0.15470700	0.63547900
O	-0.49890600	0.63574500	-0.18770600
C	0.70913800	0.23004300	0.38640200
O	1.59563200	-0.31341000	-0.13180100



tor-TS (T1 value: 0.02710485)

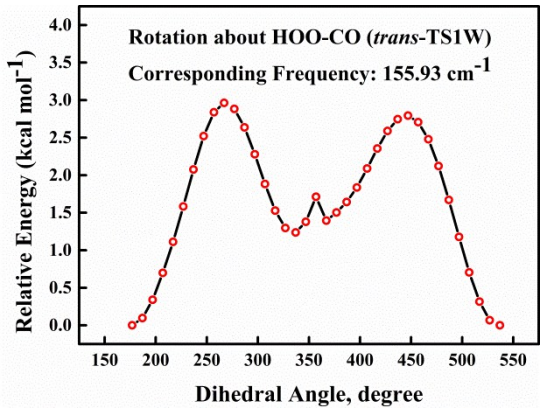
C	-0.66258800	0.36757300	0.22790700
O	-1.44609000	-0.43190900	-0.11795600
O	1.40712900	-0.43882900	0.19647400
H	-0.78057800	1.13932200	0.99438600
O	0.63347400	0.45264200	-0.37374600

TS7 (T1 value: 0.04275995)

C	1.15854000	0.51668400	-0.00009200
H	1.88006200	1.36198100	0.00216700
O	1.37785300	-0.62259200	-0.00021600
O	-1.09600100	0.61655500	-0.00039400
O	-1.38576500	-0.55172400	0.00040700

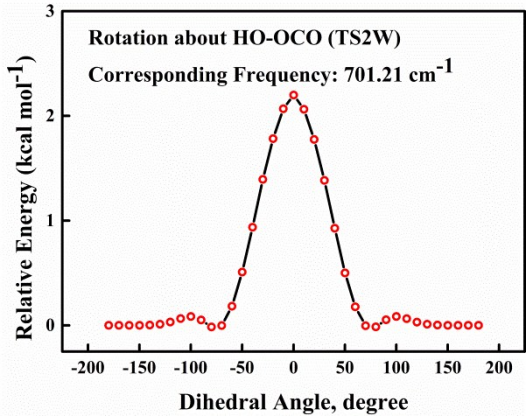
trans-TS1W (T1 value: 0.02521208)

H	-1.40388200	0.69770600	-0.30255800
O	0.25012300	0.70050700	0.49272600
O	-0.68660700	1.36114400	-0.22900100
C	1.36036200	-0.19143500	-0.47096000
O	2.20116700	-0.72223800	0.08289100
O	-2.14241900	-0.92485900	0.03505000
H	-2.21419800	-1.62082700	-0.62241400
H	-1.52220000	-1.24469700	0.69740200



TS2W (T1 value: 0.04128301)

O	-0.47148200	1.10667800	-0.00002000
H	-1.34865000	0.66587600	0.00013100
O	0.38567800	-0.23934100	-0.00146200
C	1.58478300	0.07790000	0.00040300
O	2.65776500	-0.41209400	0.00065800
O	-2.84918800	-0.36469900	0.00025400
H	-2.97204900	-0.92758700	0.76850600
H	-2.97018500	-0.93004300	-0.76649000



cis-TS3W (T1 value: 0.02580070)

C	1.32767700	0.77862400	-0.22878100
O	0.56909600	1.43447600	0.31859600
O	0.13929900	-1.31793200	0.50946700
H	-0.73206600	-0.95630100	0.23553200
O	0.99247500	-0.89494100	-0.45986700
O	-2.02566500	0.16935700	-0.23590400
H	-1.69464500	1.03319500	0.02955400
H	-2.94099100	0.12368500	0.04926600

trans-TS4W (T1 value: 0.02094704)

C	-0.99784900	0.06848700	-0.30972700
O	-1.90705200	0.62087100	0.06103200
O	0.84197300	-1.30082800	-0.43189300
H	-0.05828500	-0.38946200	-0.99203900
O	0.15030200	-1.21639600	0.64136700
O	1.24695600	1.50917700	-0.00409500
H	1.81421600	0.78423400	0.27468900
H	1.57372800	2.29171800	0.44442200

TS5W (T1 value: 0.01919628)

O	-0.07425200	1.45799800	-0.38834200
H	0.80550900	1.03350600	-0.27304200
O	-0.83806000	0.68975000	0.54427100
C	-1.24191600	-0.43335200	-0.13723000
O	-0.72177300	-1.48314100	-0.15352500

O	1.94754200	-0.27083000	0.14960300
H	2.74388400	-0.52406500	-0.32218300
H	1.39444700	-1.05954400	0.20254000

TS6W (T1 value:0.02977720)

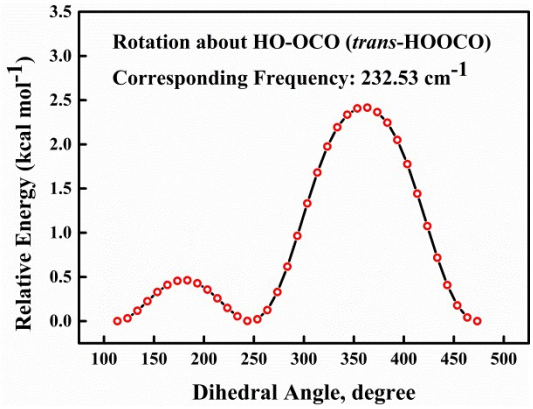
O	-0.24110900	-1.37958700	-0.48923100
H	0.65186500	-1.06154200	-0.23139700
O	-1.08548200	-0.59794000	0.49072400
C	-1.05814800	0.65779300	0.29952000
O	-0.50686200	1.43003000	-0.39733100
O	2.01714900	0.04883500	0.10894600
H	1.68180100	0.90907300	-0.16682300
H	2.54565500	0.19501700	0.89623700

tor-TSW (T1 value: 0.02443618)

C	-1.23043500	0.57786500	-0.01585000
O	-0.45531400	1.44852800	-0.15190100
O	-0.35954200	-1.41538100	-0.41679600
H	-2.29468200	0.57881000	-0.26568200
O	-0.83672400	-0.67394600	0.55279300
O	2.39802500	0.13416800	0.08197400
H	1.64749600	0.73074800	0.01416800
H	2.05823600	-0.72370500	-0.18194100

trans-HOOCO (T1 value: 0.02047995)

H	-2.00045800	-0.01341400	0.76541700
O	-0.39680500	0.50393800	-0.03284700
O	-1.60680600	-0.23741500	-0.08874500
C	0.64450300	-0.33634000	0.01197200
O	1.77029100	-0.01259100	0.01693600



trans-HCO_3 (T1 value: 0.02649506)

C	-0.59495400	0.34701000	0.00004700
O	-1.67885900	-0.10412600	-0.00000300
O	1.63470900	0.17967800	0.00000600
H	-0.26766200	1.39269300	0.00017500
O	0.52382400	-0.50989600	-0.00006000

cis-HCO_3 (T1 value: 0.02659692)

C	0.73077800	0.44666800	0.00000100
O	1.29060800	-0.58516600	-0.00000100
O	-1.31522200	-0.53416900	0.00000100
H	1.15771500	1.45435300	0.00000400
O	-0.66818400	0.60254000	-0.00000100

trans-W (T1 value: 0.01849110)

O	0.52731700	1.41406700	-0.24011000
H	1.24993400	0.75859200	-0.15071400
O	-0.51763200	0.74629500	0.45051000
C	-1.05078100	-0.20558900	-0.30964800
O	-1.93793900	-0.91414900	-0.00846700
O	2.07652100	-0.83961800	0.01833300
H	1.79933800	-1.49741500	-0.62538300
H	2.06927600	-1.28039700	0.87185700

cis-W (T1 value: 0.02599430)

O	-0.24703600	-1.34618400	-0.49162500
H	0.64874900	-1.03382200	-0.23362500

O	-1.08311700	-0.61121600	0.48211200
C	-1.07107500	0.66176200	0.30832700
O	-0.49868700	1.41540900	-0.39328400
O	2.02252200	0.04041600	0.10713700
H	1.68496500	0.90466700	-0.15336100
H	2.54328800	0.17118400	0.90230000

trans-$WHCO_3$ (T1 value: 0.02414143)

C	-0.77421800	-0.37010000	0.33920600
O	-1.42932500	-1.24617000	-0.08754200
O	0.16667200	1.65895500	0.17924600
H	-0.24852600	-0.27537200	1.29217500
O	-0.60671400	0.80624600	-0.43296200
O	1.90144000	-0.74505900	0.01801500
H	2.32005500	0.09548900	-0.18441300
H	2.31720000	-1.39129200	-0.55705600

cis-$WHCO_3$ (T1 value: 0.02411905)

C	-0.52451100	0.79104700	0.44353100
O	-0.37200400	1.33608200	-0.58684000
O	-0.83874800	-1.22287000	-0.54226500
H	-0.45249300	1.20567100	1.45193100
O	-0.88634100	-0.56278300	0.58226500
O	2.02771200	-0.16530300	0.11809800
H	1.73717000	0.00900700	-0.78237500
H	2.41744100	-1.04196500	0.09920100

PC (T1 value: 0.01604591)

C	-0.79408500	0.14823500	0.00000000
O	-1.34501000	-0.86456400	0.00000600
O	1.90026900	-0.46824500	-0.00001300
H	2.36203500	0.38726100	0.00010700
O	-0.25495000	1.17322500	-0.00000600

WPC (T1 value: 0.01482076)

O	-0.52777100	1.69092900	-0.14278200
H	-1.31413200	1.12562200	0.02081500
O	2.21904300	0.26502500	0.18751700
C	1.32094700	-0.42581800	-0.01144600
O	0.44650300	-1.16172600	-0.21132100
O	-2.35818600	-0.39980600	0.20416900
H	-1.68782800	-1.05891100	-0.00407800
H	-3.16043100	-0.66718800	-0.24872400

Vibrational frequencies (cm^{-1}) of reactants, complexes, transition states and products obtained using M062X/aug-cc-pVTZ level.

Reactants and Products:

CO	HO_2	CO_2	OH	CHO	O_2
2272.15	1252.7495	696.0518	3744.2123	1105.22	1757.9954
	1459.4265	696.0518		2001.06	
	3686.9375	1412.2075		2718.93	
		2449.5672			

Complexes:

RC1	RC2	RC-3a	RC-3b	RC4	WRC1	WRC3	WRC4
61.9809	69.8369	46.4727	32.6607	160.8653	32.9476	23.1141	22.3923
77.4145	123.4533	59.0288	71.1538	196.8752	62.0795	41.5893	33.1105
146.1768	180.5227	102.7244	108.5061	246.3696	88.48	50.8642	77.7467
170.7083	220.4963	207.5038	133.1186	282.0422	108.4455	73.2247	84.9065
268.9084	455.8957	306.4322	207.8484	484.2033	163.6875	99.702	139.1186
1264.7382	1269.1671	1621.8486	1619.6591	637.5818	188.1999	149.0848	192.0264
1477.9598	1492.7615	2290.2823	2264.1491	1284.9572	209.1269	198.6696	227.2242
2239.19	2293.7063	3853.5291	3868.2352	1561.1954	268.2388	251.8953	229.5564
3641.6491	3570.7354	3959.3573	3969.2438	1611.9377	340.2598	301.8715	305.691
				3418.5241	522.034	471.4904	515.2174
				3808.8355	684.436	647.1546	596.2185
				3941.6083	1290.2474	1287.7412	1289.8836
					1585.5742	1569.6098	1514.549
					1621.0056	1618.763	1617.948
					2294.6656	2255.1806	2280.6789
					3302.8856	3378.0848	3486.2751
					3773.3895	3829.5766	3789.3935
					3932.6419	3942.7859	3936.9974

trans-HOOCO	*cis*-HOOCO	*trans*-HCO_3	*cis*-HCO_3	*trans*-W	*cis*-W	*trans*-WHCO3	*cis*-$WHCO_3$
232.5329	139.5624	178.6635	247.7583	54.9609	92.0643	71.8835	58.1247
261.1467	298.8188	431.672	349.9343	121.5911	144.8239	123.9189	98.5434
370.9699	407.3846	626.0762	825.1712	154.6318	207.3592	151.2725	146.0178
624.1023	792.4319	1033.6588	943.4018	208.425	221.0665	179.1949	176.9894
1039.9432	954.8773	1039.3306	1005.5449	276.0988	242.5522	207.6182	234.4698
1087.355	1411.1009	1243.9948	1189.7203	282.3008	322.872	280.3329	262.091
1446.3178	1537.1727	1346.8193	1393.4877	293.7917	346.8534	293.1296	354.3249
1941.3031	1874.819	1948.5556	1938.3701	373.4447	478.2969	432.6292	417.9918
3792.9382	3763.1281	3124.4902	3142.4987	628.9904	591.0864	620.0847	820.7554
				704.2998	688.2918	1022.8346	942.3163
				1039.5139	813.389	1033.4466	1009.0346
				1117.032	1099.3406	1264.2235	1202.3744
				1530.5859	1486.4715	1366.2478	1390.0281
				1620.0689	1606.4704	1619.8406	1620.0012
				1931.2187	1939.4771	1945.7468	1921.3127
				3537.6301	3474.4523	3162.492	3151.24
				3851.7269	3828.0898	3861.4244	3847.283
				3951.5453	3953.5643	3964.9796	3957.2944

Transition states:

trans-TS1	TS2	*cis*-TS3	*trans*-TS4	TS5	*tor*-TS	TS7
596.9286*i*	1528.4147*i*	656.2992*i*	1407.4581*i*	290.5738*i*	214.3915*i*	322.2521*i*
137.9959	114.4981	107.561	192.6024	287.6355	332.562	138.1872

283.0911	336.0972	244.7343	272.07	346.2847	633.2067	150.6044
431.4183	379.2324	483.6773	626.9979	640.3919	932.9712	316.2506
464.9914	808.2947	490.8097	860.1627	881.506	1072.7256	385.513
1068.9438	1000.9623	1035.9126	1156.0678	1001.6809	1241.0499	1064.4638
1453.7366	1259.4098	1428.4941	1323.8508	1418.9682	1365.3011	1590.2908
2118.1501	2015.9506	2109.5626	1854.6565	1970.8661	1941.6462	2003.2013
3771.116	3762.3706	3768.6266	2232.1947	3798.2958	3122.8865	2851.364
trans-TS1W	TS2W	*cis*-TS3W	TS4W	TS5W	TS6W	*tor*-TSW
641.021*i*	1571.9775*i*	704.2813*i*	1194.3625*i*	259.495*i*	366.4725*i*	212.3233*i*
48.711	50.5958	90.3483	85.1151	119.0983	98.5813	63.2226
129.9028	60.0126	110.4831	115.5982	131.5258	133.6468	74.0913
137.4896	117.8545	159.8071	154.3993	165.1146	163.6084	113.8452
155.9327	182.3999	182.8722	187.31	224.609	209.6537	187.3889
236.7403	243.9404	234.5222	226.8	315.166	247.2542	240.997
263.5539	270.1029	270.8264	266.8511	355.2832	374.5051	323.382
304.8777	357.4387	309.4385	292.9928	430.2888	396.529	339.3481
382.1118	385.5801	384.6423	349.0851	642.8065	505.8027	631.0417
447.4385	701.2082	505.965	602.0355	709.8844	706.4848	938.024
763.8083	804.5951	796.2116	873.8205	964.3903	801.3413	1066.0426
1083.8418	1014.2743	1050.0766	1172.2054	1006.6495	1107.4734	1244.5669
1549.8405	1355.6563	1550.2945	1322.0451	1549.8201	1426.4309	1355.9745
1617.003	1619.7127	1608.1222	1618.8763	1614.0703	1615.8926	1630.6853
2104.7044	2015.9386	2065.3621	1860.3844	1933.0879	1964.3301	1929.1869
3543.4511	3528.7463	3478.0973	2269.3489	3472.1916	3498.5237	3148.6002
3854.3036	3859.749	3846.0479	3855.983	3817.4891	3832.0772	3859.7104
3955.6813	3959.6048	3953.5409	3963.9249	3944.2343	3950.2785	3956.3624

Tabale S3 Dispersion corrected energies of two-body and three body complexes are computed at the M062X/aug-cc-pVTZ level.

Species	m062x/aug-cc-pvtz (Hartree)	D_3(Hartree)	ΔE_{D3}(kcal mol^{-1})
RC1	-264.210753	-264.210765	0.007530108
RC2	-264.21274	-264.212811	0.044553139
RC-3a	-189.72473	-189.724776	0.028865414
RC-3b	-189.723832	-189.723884	0.032630468
RC4	-227.314118	-227.31414	0.013805198
WRC-1	-340.632826	-340.632931	0.065888445

WRC-3	-340.630969	-340.631126	0.098518913
WRC-4	-340.630518	-340.630642	0.077811116

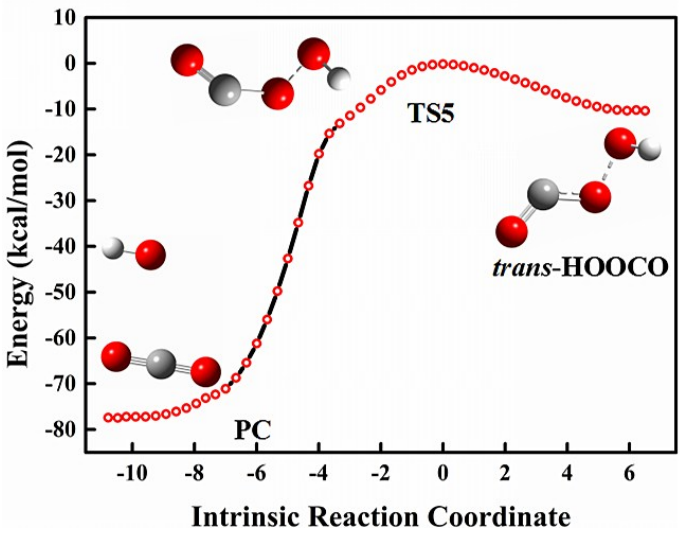


Fig. S1 IRC analysis of TS5 at the M062X/aug-cc-pVTZ level.

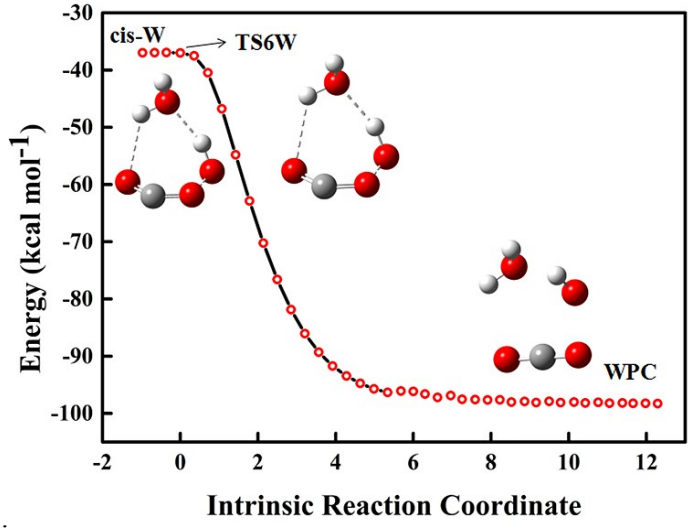


Fig. S2 IRC analysis of TS6W at the M062X/aug-cc-pVTZ level.

Table S4 Comparison of You et al.'s results with our calculations

T(K)	$k_{cis}^{\text{water-free}}$	$k_{trans}^{\text{water-free}}$	$k_{\text{overall}}^{\text{water-free}}$	k^*_{cis}	k^*_{trans}	k^*_{overall}	$^a\Delta k_{\text{overall}}/k^*_{\text{overall}}$
298	3.55E-27	2.79E-26	3.14E-26	9.57E-28	4.33E-27	4.47E-27	6.04

300	4.36E-27	3.40E-26	3.84E-26	1.20E-27	5.35E-27	5.55E-27	5.91
325	4.76E-26	3.25E-25	3.73E-25	1.56E-26	6.17E-26	6.69E-26	4.57
350	3.74E-25	2.29E-24	2.66E-24	1.42E-25	5.07E-25	5.72E-25	3.66
375	2.27E-24	1.25E-23	1.48E-23	9.79E-25	3.17E-24	3.71E-24	2.98
400	1.11E-23	5.63E-23	6.74E-23	5.34E-24	1.59E-23	1.93E-23	2.50
425	4.56E-23	2.14E-22	2.60E-22	2.41E-23	6.64E-23	8.29E-23	2.13
450	1.61E-22	7.05E-22	8.66E-22	9.27E-23	2.38E-22	3.06E-22	1.83
475	5.03E-22	2.07E-21	2.57E-21	3.12E-22	7.50E-22	9.89E-22	1.60
500	1.41E-21	5.48E-21	6.89E-21	9.34E-22	2.12E-21	2.86E-21	1.41

*Values are taken from Ref 8; $^{a}\Delta k_{\text{overall}} = k_{\text{overall}}^{\text{water-free}} - k_{\text{overall}}^{*}$

Table S5 Rate constants (cm^3 $molecule^{-1}$ s^{-1}) without $step_{0w}$ for the water-assisted reaction CO + HO_2 = Products

T(K)	$k_{cis}^{\text{water-assisted}}$	$k_{trans}^{\text{water-assisted}}$	$k_{\text{overall}}^{\text{water-assisted}}$	$k_{\text{overall}}^{\text{water-assisted}}/k_{\text{overall}}^{\text{water-free}}$
298	1.36E-25	2.24E-24	2.37E-24	75.61
300	1.55E-25	2.56E-24	2.71E-24	70.64
325	7.09E-25	1.19E-23	1.26E-23	33.89
350	2.67E-24	4.56E-23	4.83E-23	18.14
375	8.63E-24	1.49E-22	1.57E-22	10.64
400	2.48E-23	4.29E-22	4.54E-22	6.73
425	6.50E-23	1.12E-21	1.18E-21	4.55
450	1.59E-22	2.70E-21	2.86E-21	3.30
475	3.69E-22	6.10E-21	6.47E-21	2.52
500	8.18E-22	1.31E-20	1.39E-20	2.02
600	1.39E-20	1.87E-19	2.01E-19	1.21
700	1.41E-19	1.62E-18	1.76E-18	1.03
800	9.07E-19	9.36E-18	1.03E-17	0.99
900	4.14E-18	3.96E-17	4.37E-17	1.00
1000	1.45E-17	1.31E-16	1.46E-16	1.03
1100	4.17E-17	3.62E-16	4.04E-16	1.05
1200	1.03E-16	8.63E-16	9.65E-16	1.08
1300	2.24E-16	1.83E-15	2.06E-15	1.11
1400	4.45E-16	3.56E-15	4.00E-15	1.14
1500	8.17E-16	6.41E-15	7.22E-15	1.16

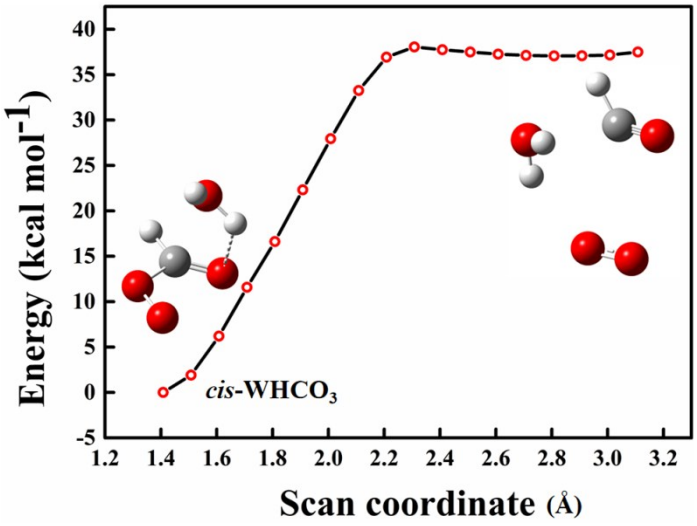


Fig. S3 The scan of C–O bond for cis-$WHCO_3$ at the M062X/aug-cc-pVTZ level.

About water concentration calculation formula:

$$[H_2O] = \frac{P(T)}{RT} * N_A * 10^{-6}\ cm^{-3}\ molecule$$

P(T) is the saturated vapor pressure at the specified temperature according to the IAPWS-95 formulation.