ELECTRONIC SUPPLEMENTARY INFORMATION

Feb. 9, 2018

Atmospheric Chemistry of CH_3CHO: The Hydrolysis of CH_3CHO Catalyzed by H_2SO_4

Xing-Feng Tan[a] Bo Long*[b] Da-Sen Ren[b] Wei-Jun Zhang[c,d] Zheng-Wen Long[f] Ellen Mitchell*[e]

[a]School of Mechatronics Engineering, Guizhou Minzu University, Guiyang, 550025, China

[b]School of Materials Science and Engineering, Guizhou Minzu University, Guiyang, 550025, China

[c]Laboratory of Atmospheric Physico-Chemistry, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei, 230031, China

[d]Key Laboratory of Atmospheric Composition and Optical Radiation, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei, 230031, China

[e]Department of Chemistry, Bridgewater College, Bridgewater, VA, 22812, United States

[f]Department of Physics, Guizhou University, Guiyang, 550025, China

*corresponding author, E-mail: longbo@gzmu.edu.cn or wwwltcommon@sina.com (Bo Long), emitchel@bridgewater.edu (Ellen Mitchell)

Table S1. The scale factors for vibrational frequencies.[a]

Methods	Scale Factor
QCISD/VTZ	0.975
M06-2X/MG3S	0.970
MPWB1K/MG3S	0.954

[a] I. M. Alecu, J. Zheng, Y. Zhao and D. G. Truhlar, *J. Chem. Theory Comput.*, 2010, 6, 2872-2887.

Table S2. The relative energies, enthalpies, and Gibbs free energies. (in kcal/mol)

	M06-2X			CCSD(T)-F12a//M06-2X		
	ΔE^a	ΔH^a	ΔG^a	ΔE^b	ΔH^b	ΔG^b
$H_2SO_4(C2) \longrightarrow H_2SO_4(Cs)$						
$H_2SO_4(C2)$	0.00	0.00	0.00	0.00	0.00	0.00
$H_2SO_4(Cs)$	1.08	1.26	0.31	1.04	1.21	0.26
$H_2SO_4 + H_2O \longrightarrow H_2SO_4\cdots H_2O$						
M1A	−11.90	−12.52	−3.88	−10.65	−11.28	−2.63
M1B	−11.79	−12.39	−3.86	−10.56	−11.16	−2.63
M1C	−10.76	−11.35	−3.00	−9.50	−10.09	−1.74
M1D	−10.20	−10.75	−2.41	−8.94	−9.49	−1.14
$CH_3CHO + H_2O \longrightarrow CH_3CHO\cdots H_2O$						
C1A	−5.01	−5.19	1.84	−4.55	−4.73	2.30
C1B	−4.52	−4.79	2.90	−4.00	−4.27	3.42

*[a]ΔE, ΔH, and ΔG are obtained at the M06-2X/MG3S level. [b]ΔE, ΔH, and ΔG are calculated at the CCSD(T)-F12a/VTZ-F12//M06-2X/MG3S level.

Table S3. Cartesian coordinates (Å) of optimized structures at the M06-2X/MG3S level.

Species	Cartesian coordinates			
CH_3CHO	O	1.19612000	0.38145500	0.00000000
	C	0.00000000	0.46189000	0.00000000
	H	-0.48912800	1.45527100	0.00000000
	C	-0.92749300	-0.71644600	0.00000000
	H	-1.57525000	-0.66711800	0.87691100
	H	-1.57525000	-0.66711800	-0.87691100
	H	-0.36437100	-1.64534000	0.00000000
H_2O	O	0.00000000	0.00000000	0.11637100
	H	0.00000000	0.76143900	-0.46548400
	H	0.00000000	-0.76143900	-0.46548400
C1A	O	2.12333300	0.28300100	0.00290400
	H	2.96932900	-0.16494100	-0.01707000
	O	-0.32586100	-1.19590000	-0.00040600
	H	1.45073100	-0.41113300	0.00049200
	C	-1.21915800	-0.38842400	0.00051500
	H	-2.26571400	-0.74341500	0.00260300
	C	-1.03036000	1.09443100	-0.00092900
	H	-1.53252700	1.51240800	-0.87557700
	H	-1.52775900	1.51344900	0.87594900
	H	0.02326900	1.36078200	-0.00389800
TS1	O	1.06960200	-0.84880900	-0.16562500
	H	1.68489700	-1.10404900	0.53153800
	O	0.40222700	1.23485000	-0.14789000
	H	1.22458000	0.26091100	-0.46963300
	C	-0.14189300	0.19491100	0.41708300
	H	-0.03164500	0.08327100	1.50540300
	C	-1.42631300	-0.35183500	-0.12919700
	H	-1.65556800	-1.33319000	0.28024300
	H	-2.21963500	0.34379200	0.14757200
	H	-1.36802200	-0.39751800	-1.21431800
P	O	0.70295600	1.17249300	-0.03041400
	O	0.67429600	-1.13703100	-0.17538800
	C	0.04590000	-0.00283900	0.36311500
	H	0.11944800	-0.00433300	1.45352900
	C	-1.39706300	-0.03949200	-0.08333300
	H	-1.87999200	-0.94785700	0.27048400
	H	-1.92757300	0.82780400	0.30288800
	H	-1.43898900	-0.03137000	-1.17375000
	H	1.59468400	-1.12978500	0.10012400
	H	0.62137700	1.25582800	-0.98555400
M1A	S	0.57588300	-0.07268700	0.12377800
	O	1.73247300	-0.87356900	0.27427900
	O	-0.21668600	0.32606100	1.23708300
	O	0.99465400	1.27348000	-0.58300800
	O	-0.33748400	-0.74790900	-0.92809700
	H	-1.28783000	-0.48338200	-0.76548600

	H	1.75606700	1.11518800	-1.15585800
	O	-2.67165600	0.10179900	-0.11062200
	H	-2.28547500	0.37235600	0.73311800
	H	-3.40729300	-0.48006900	0.09068600
C2A	O	-1.58493300	-1.19057800	-0.57216900
	O	-1.08341300	1.95610500	-0.16695200
	H	-1.14545700	2.91219800	-0.22292400
	H	0.15207100	1.22397200	0.88778200
	O	0.85169600	0.61195900	1.20536000
	O	1.07985500	0.60475300	-1.20034100
	H	-0.54484400	1.66870900	-0.92232900
	S	1.54529100	-0.07607800	-0.02609300
	O	2.92335800	-0.18466900	0.24809200
	O	0.95018500	-1.50213400	0.00213800
	C	-2.18886200	-0.62595900	0.31187400
	H	-1.68283300	-0.41871900	1.26912000
	H	-0.00785700	-1.47954100	-0.28225500
	C	-3.60342700	-0.18441600	0.19068800
	H	-4.19327400	-0.63706300	0.98931500
	H	-3.63425800	0.89632000	0.33556800
	H	-4.00845200	-0.44986000	-0.78118900
TS2A	O	-1.52947400	-1.19435800	-0.66619700
	O	-1.64253400	1.99687000	-0.15981800
	H	-1.94610800	2.71040600	-0.72294300
	H	1.74418300	0.81065500	1.88265700
	O	1.15676400	0.16799300	1.46500200
	O	0.91972600	1.00272000	-0.81131100
	H	-0.74130000	1.79799200	-0.45272100
	S	1.57953100	-0.02025800	-0.05913700
	O	2.98937900	-0.12299000	-0.12166500
	O	0.93478800	-1.37045100	-0.32521100
	C	-2.07448600	-0.60824200	0.24981000
	H	-1.46928600	-0.22198900	1.08200500
	H	-0.08486500	-1.30055800	-0.52165100
	C	-3.54393300	-0.42243100	0.33337800
	H	-3.91690300	-1.00522900	1.17877700
	H	-3.75046400	0.62632800	0.53797900
	H	-4.02643600	-0.74771200	-0.58343000
C2B	C	-2.07872700	-0.64059600	0.20055700
	O	-1.97502700	2.03477900	-0.07032000
	O	-1.51032500	-1.08581300	-0.77765800
	H	-1.49128200	-0.21078300	1.02216500
	H	-0.04897000	-0.92249200	-0.93745800
	O	0.62383800	1.01834100	0.49515400
	H	-1.02057800	1.94985700	0.04972500
	O	0.96648100	-0.79154800	-1.07764900
	S	1.59019800	0.08918500	0.00647700
	O	1.79829700	-0.91167200	1.21499300

	O	2.86174900	0.52140400	-0.44084500
	H	-2.09797500	2.73037700	-0.71772800
	H	2.61236100	-1.41351600	1.07971800
	C	-3.55347600	-0.66854400	0.36232700
	H	-3.80197900	-1.25193200	1.25094900
	H	-3.88853100	0.35369700	0.53763600
	H	-4.03309200	-1.09124500	-0.51534300
TS2B	C	-1.96949500	-0.37765500	0.20771500
	O	-1.75070100	1.55773200	-0.15090000
	O	-1.55916400	-0.96504600	-0.82841500
	H	-1.27257800	-0.25757300	1.03992900
	H	-0.45564300	-1.05082800	-0.81384600
	O	0.83218000	1.26147700	-0.24643400
	H	-0.75817400	1.58489300	-0.19946300
	O	0.84269700	-1.11234500	-0.69713700
	S	1.54992600	0.02008300	-0.05519700
	O	1.36490100	-0.24403800	1.51483000
	O	2.94496000	0.01724800	-0.32242500
	H	-2.06524400	1.72082200	-1.04623500
	H	2.07426600	-0.82534600	1.81423300
	C	-3.42652500	-0.36386500	0.49606600
	H	-3.67707800	-1.33671600	0.92419100
	H	-3.67554100	0.41369600	1.21048800
	H	-3.99169100	-0.24138300	-0.42498100
C2P	C	2.04932000	0.04879800	0.20802400
	O	1.53555600	-0.97929300	-0.66592700
	O	2.04803700	1.26633600	-0.43916100
	H	1.35834800	0.03469700	1.05503800
	O	-0.99770500	-1.16512600	-0.66510200
	H	0.02119700	-1.10686400	-0.69578500
	O	-0.78664900	1.22025500	-0.29326300
	S	-1.61296600	0.09026900	-0.02793700
	O	-1.42819500	-0.17053500	1.52293900
	O	-2.99676100	0.10210200	-0.31938200
	H	1.97410200	-0.88509500	-1.51924600
	H	-2.14222800	-0.73709700	1.84294600
	H	1.13226500	1.56675200	-0.51726400
	C	3.45879800	-0.28597700	0.62467400
	H	3.81809700	0.45905100	1.33089700
	H	3.49374000	-1.27073300	1.08410400
	H	4.10896300	-0.27184200	-0.25072000
$H_2SO_4(C_2)$	O	1.20642300	0.84272200	0.00000000
	O	-0.03408200	-0.84365200	1.22343600
	S	-0.03408200	0.14709700	0.00000000
	O	-0.03408200	-0.84365200	-1.22343600
	O	-1.28622300	0.78697300	0.00000000
	H	0.86451000	-0.94633700	-1.56112700
	H	0.86451000	-0.94633700	1.56112700

$H_2SO_4(C_S)$	O	0.00000000	1.24636600	0.81980200
	O	1.22367900	0.03921200	-0.83652400
	S	0.00000000	0.00000000	0.15404000
	O	-1.22367900	-0.03921200	-0.83652400
	O	0.00000000	-1.24636600	0.81980200
	H	-1.46056300	0.86028700	-1.09854800
	H	1.46056300	-0.86028700	-1.09854800
M1A	S	0.57588300	-0.07268700	0.12377800
	O	1.73247300	-0.87356900	0.27427900
	O	-0.21668600	0.32606100	1.23708300
	O	0.99465400	1.27348000	-0.58300800
	O	-0.33748400	-0.74790900	-0.92809700
	H	-1.28783000	-0.48338200	-0.76548600
	H	1.75606700	1.11518800	-1.15585800
	O	-2.67165600	0.10179900	-0.11062200
	H	-2.28547500	0.37235600	0.73311800
	H	-3.40729300	-0.48006900	0.09068600
M1B	S	0.57935800	-0.09033900	0.10751300
	O	1.78506100	-0.82918500	0.08287700
	O	-0.20312000	0.04376600	1.28872300
	O	0.89843000	1.39120500	-0.33902200
	O	-0.32043300	-0.60908300	-1.04013800
	H	-1.27579600	-0.40215000	-0.83499700
	H	1.65857700	1.39116400	-0.93498000
	O	-2.67903100	-0.04501100	-0.05396400
	H	-2.28497900	0.12224600	0.81248400
	H	-3.21477100	0.72062400	-0.27053000
M1C	S	0.58136000	-0.08680300	0.10461500
	O	1.56045800	-1.07151700	0.33800600
	O	-0.23327500	0.42682500	1.16495900
	O	1.34304600	1.12384700	-0.55127200
	O	-0.35542500	-0.55397500	-1.03861500
	H	-1.30604100	-0.36295200	-0.80035600
	H	0.79564600	1.91864800	-0.52369700
	O	-2.69932400	0.08626600	-0.06628500
	H	-2.30355600	0.28053400	0.79364700
	H	-3.41164400	-0.53895600	0.08223000
M1D	S	0.56736200	-0.09890700	0.09114600
	O	1.39046100	-1.23579500	0.20912400
	O	-0.23078900	0.35720300	1.18920700
	O	1.52187400	1.07052500	-0.34846800
	O	-0.35523200	-0.22884000	-1.15015100
	H	-1.31053900	-0.16926000	-0.86896300
	H	1.07123500	1.92024800	-0.26637300
	O	-2.71095800	-0.07219600	-0.01964600
	H	-2.32247100	0.17696100	0.82882700
	H	-3.43887100	0.52739200	-0.19234300
C1A	O	2.12333300	0.28300100	0.00290400

	H	2.96932900	-0.16494100	-0.01707000
	O	-0.32586100	-1.19590000	-0.00040600
	H	1.45073100	-0.41113300	0.00049200
	C	-1.21915800	-0.38842400	0.00051500
	H	-2.26571400	-0.74341500	0.00260300
	C	-1.03036000	1.09443100	-0.00092900
	H	-1.53252700	1.51240800	-0.87557700
	H	-1.52775900	1.51344900	0.87594900
	H	0.02326900	1.36078200	-0.00389800
C1B	O	2.40155200	-0.37823500	0.00000300
	H	3.28286100	-0.00460000	-0.00000300
	O	-0.08114600	0.95113700	-0.00000100
	H	1.79289500	0.37192500	0.00000300
	C	-0.61455400	-0.12924100	-0.00000600
	H	0.00598300	-1.04241000	-0.00002200
	C	-2.09700200	-0.32443100	0.00000500
	H	-2.38203500	-0.90901300	-0.87633800
	H	-2.38201900	-0.90911000	0.87628700
	H	-2.61159300	0.63202900	0.00005900

Table S4. The calculated frequencies (cm^{-1}) and the symmetry symmetry of the vibrational modes for symmetrical molecules of optimized structures at the M06-2X/MG3S level.

Species	Frequencies		
CH_3CHO (C_s)	160.8165 (A")	513.9921 (A')	775.8427 (A")
	900.6858 (A')	1137.6910 (A')	1144.9077 (A")
	382.2017 (A')	1431.7623 (A')	1468.2156 (A')
	476.3690 (A")	1870.1767 (A')	2943.6569 (A')
	064.1192 (A')	3126.8167 (A")	3180.6627 (A')
H_2O (C_{2v})	1630.0122 (A1)	3888.2980 (A1)	3992.6254 (B2)
C1A (C_1)	37.2733	78.4163	118.8929
	157.7477	189.0648	366.3864
	523.3394	535.8080	784.9110
	906.5700	1150.6014	1156.9736
	1391.6238	1435.2025	1471.3478
	1478.2841	1641.0310	1851.8228
	2966.4349	3060.9998	3122.4918
	3180.5787	3774.4940	3960.9114
TS1 (C_1)	-1576.5879	225.2971	306.2090
	417.0992	508.7878	559.5249
	728.0958	856.1060	924.7098
	1004.0869	1159.5687	1229.1959
	1333.6803	1355.9879	1398.7767
	1467.9585	1482.3467	1527.9913
	2026.6922	3004.4715	3074.7045
	3150.0973	3174.0166	3857.6787
P (C_1)	245.5811	323.7837	381.1580
	402.4897	497.0049	585.7846
	883.8218	971.2879	1052.7480
	1115.3847	1170.1851	1281.7953
	1310.5362	1398.7440	1424.9484
	1471.7926	1489.0261	1499.3473
	3065.8650	3073.2378	3148.5853
	3169.8917	3862.3097	3885.3588
M1A (C_1)	45.6573	162.5782	208.3185
	229.7025	264.6293	354.4626
	392.0098	436.4139	510.1326
	550.4985	572.1240	582.5705
	842.6368	888.6065	969.9040
	1168.5339	1246.1830	1378.1954
	1497.0995	1627.0420	3104.9724
	3803.9430	3837.9388	3948.5310
C2A (C_1)	45.9864	50.6586	76.1195
	83.2208	117.8600	137.8968
	159.1569	194.3579	204.1352
	209.7238	299.3540	352.3158
	382.9884	428.6884	531.6309
	548.4590	567.8137	580.2881
	616.0411	720.6388	805.3825

	871.7579	900.1600	925.1931
	977.9714	1155.8921	1158.9176
	1220.9978	1327.6433	1350.4334
	1384.5172	1444.4234	1464.6569
	1474.5097	1489.3064	1637.0040
	1825.8751	3002.8836	3070.5364
	3100.1375	3135.8327	3187.7374
	3463.2968	3727.6433	3934.2257
TS2A (C_1)	-61.9939	29.3479	50.3019
	68.1971	85.3558	102.4925
	146.9514	153.4047	173.7450
	195.8452	227.8080	251.1066
	358.8868	412.7942	428.4594
	534.8177	553.4415	557.4158
	573.3053	582.9092	817.5657
	855.7496	928.2315	1012.8764
	1093.8353	1152.0099	1162.2192
	1178.0374	1255.4203	1385.3980
	1404.9264	1452.2293	1462.3827
	1478.7670	1487.8590	1651.1657
	1791.9086	2462.4328	3053.2995
	3070.2387	3145.0453	3191.4567
	3755.1431	3842.9469	3949.7281
C2B (C_1)	4.3919	33.6276	82.4413
	93.3591	117.3965	128.5505
	130.8729	165.1591	171.0606
	218.5203	247.0005	256.3023
	340.4740	397.4457	442.9509
	475.6022	541.0998	563.0903
	571.1317	578.7382	816.0519
	877.4131	925.2942	1007.8963
	1056.5601	1159.5794	1163.5399
	1167.3064	1244.2215	1382.7455
	1412.2828	1447.8899	1465.3230
	1476.0886	1500.3285	1640.2895
	1796.6244	2559.2023	3063.6449
	3072.0959	3139.8445	3187.6461
	3803.6878	3841.1512	3956.4920
TS2B (C_1)	-269.1385	30.7675	42.0015
	104.6539	125.8851	200.3697
	203.0359	216.0331	307.3026
	323.2396	364.2019	410.5324
	437.4355	449.5245	520.2932
	577.7525	596.3788	647.0521
	670.0708	843.3951	917.4917
	943.9734	1007.1627	1018.7243
	1127.4078	1162.0246	1176.9105
	1196.2954	1317.4143	1384.5481

	1404.6278	1413.5576	1467.8194
	1483.8106	1566.1342	1616.8640
	1660.9606	1796.3060	3076.3519
	3113.9658	3151.4693	3197.7502
	3208.1782	3853.9161	3881.7887
C2P (C_1)	34.2764	44.6776	87.8640
	124.5502	154.9094	208.6100
	252.3623	278.3750	357.1216
	399.9291	426.7415	442.6264
	508.3221	539.8263	549.7906
	572.6161	574.0903	641.4439
	862.4021	875.3758	964.8674
	987.6444	995.7097	1085.6909
	1099.6695	1166.4761	1190.2370
	1251.1580	1279.4709	1343.2769
	1408.7325	1411.4806	1435.4472
	1477.7228	1490.0513	1499.6442
	1508.7418	2744.4081	3074.7001
	3081.1346	3154.5773	3174.2338
	3790.8252	3837.1245	3847.1874
H_2SO_4(C_2)	106.0341 (A)	341.9778 (B)	375.4408 (A)
	428.4444 (A)	512.5290 (B)	558.6587 (A)
	571.0632 (B)	875.5576 (A)	925.7638 (B)
	1142.9383 (A)	1176.9116 (B)	1257.8997 (A)
	1508.6686 (B)	3843.0280 (B)	3849.6881 (A)
H_2SO_4(C_S)	262.9653 (A")	342.4874 (A')	384.1660 (A')
	446.2914 (A")	509.0269 (A')	560.2784 (A')
	571.4957 (A")	876.3187 (A')	923.9760 (A")
	1153.0383 (A")	1174.1590 (A')	1264.2641 (A')
	1509.1565 (A')	3830.8542 (A")	3835.4809 (A')
M1A (C_1)	45.6573	162.5782	208.3185
	229.7025	264.6293	354.4626
	392.0098	436.4139	510.1326
	550.4985	572.1240	582.5705
	842.6368	888.6065	969.9040
	1168.5339	1246.1830	1378.1954
	1497.0995	1627.0420	3104.9724
	3803.9430	3837.9388	3948.5310
M1B (C_1)	40.8976	162.2257	205.3741
	221.0918	269.1443	326.6744
	388.1923	441.3332	524.3022
	548.1442	567.6933	580.8457
	872.0775	892.8630	971.1231
	1170.3929	1246.6703	1358.8636
	1495.0768	1629.2403	3129.2472
	3804.2196	3837.2611	3949.2666
M1C (C_1)	29.1819	171.3100	205.8226
	223.2297	252.7147	345.4107

	394.8608	433.5082	516.8940
	563.0642	566.9038	587.0454
	836.1486	892.8092	968.1179
	1165.7967	1229.8345	1380.8870
	1494.5816	1620.6860	3119.2952
	3803.9048	3844.4120	3947.4426
M1D (C_1)	34.4603	166.1883	201.8510
	221.4828	241.4956	328.8422
	398.1920	433.2494	507.6904
	541.0963	564.4124	585.4899
	806.2389	892.1822	962.5655
	1164.1775	1230.4193	1380.7495
	1486.5600	1620.0602	3142.5979
	3812.1824	3844.9212	3956.4567
C1B (C_1)	69.4909	96.1155	136.4121
	161.3785	190.4557	385.3304
	512.4107	527.7448	791.9928
	909.9346	1144.8033	1155.3876
	1386.9203	1446.5955	1467.6876
	1475.6150	1645.1821	1847.2921
	2991.5836	3066.1630	3128.2122
	3182.8292	3780.7930	3967.0464

Table S5. The total energies (a.u.) of optimized structures at the CCSD(T)-F12A/VTZ-F12//M06-2X/MG3S level.

Species	total energies
CH_3CHO	-153.6586886
H_2O	-76.3740934
C1A	-230.04280126
TS1	-229.97498782

P	-230.0505701
C2A	-929.7176385
TS2A	-929.7114241
C2B	-929.7138982
TS2B	-929.7010967
C2P	-929.7236891
$H_2SO_4(C_2)$	-699.64722423
$H_2SO_4(C_S)$	-699.64519504
M1A	-776.04141233
M1B	-776.03858349
M1C	-776.04153683
M1D	-776.03963066
C1B	-230.04220520

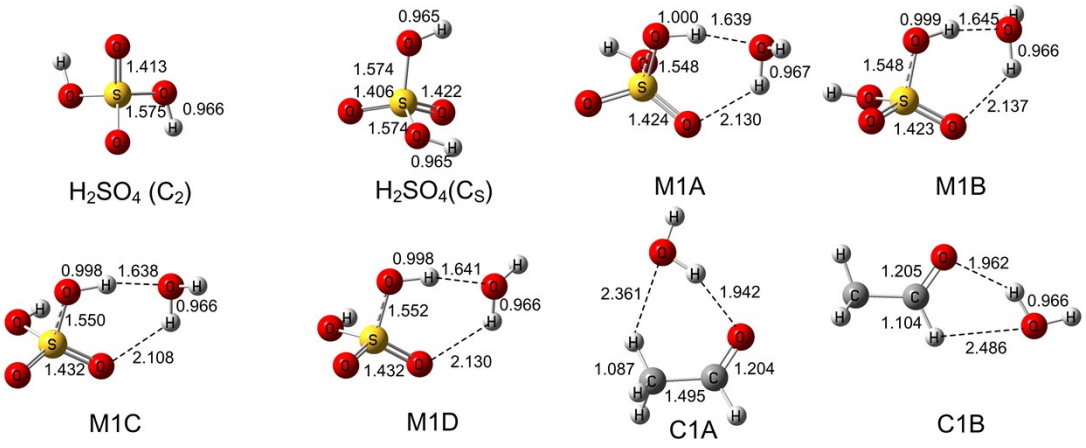

Figure S1. The optimized geometries of sulfuric acid, $CH_3CHO\cdots H_2O$ complexes and $H_2SO_4\cdots H_2O$ complexes.

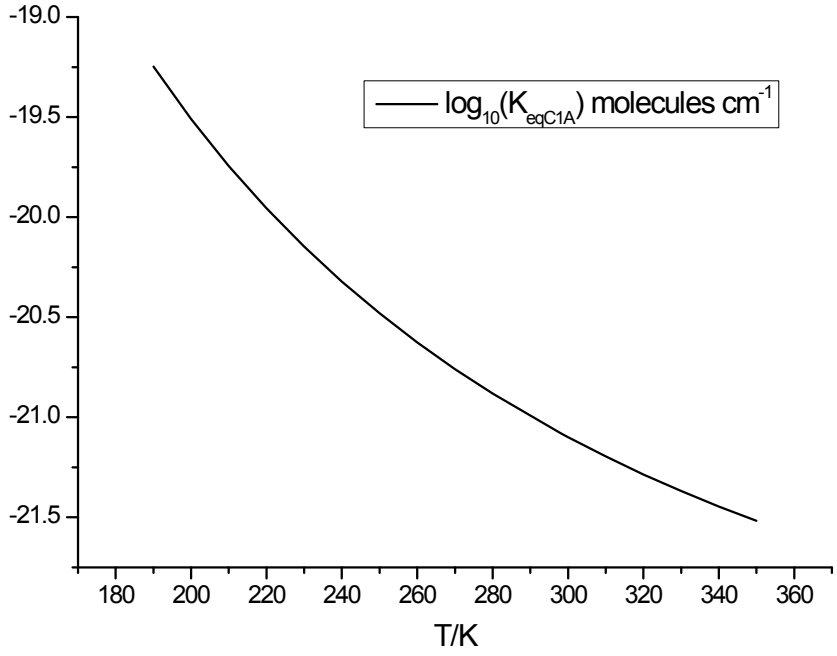

Figure S2. The temperature-dependent equilibrium constant (K_{eqC1A}) between 190 and 350 K.

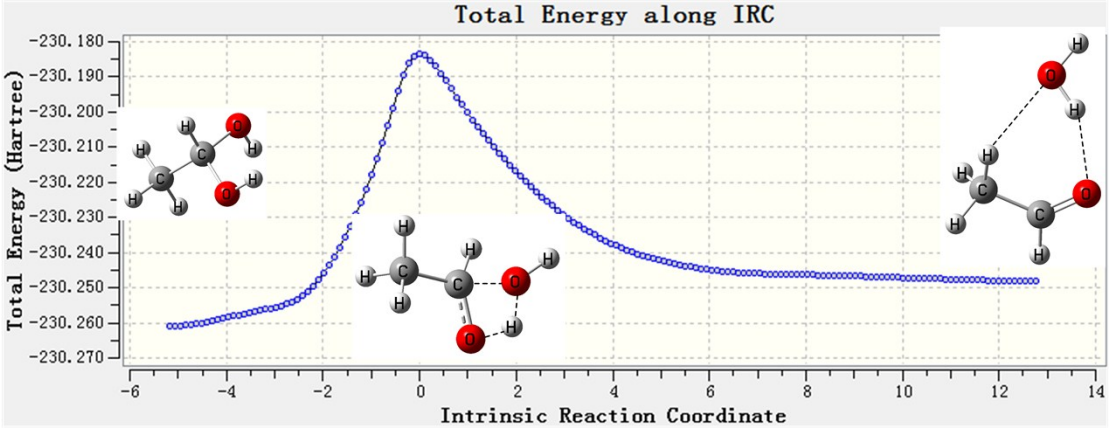

Figure S3. Intrinsic reaction coordinate results of TS1. Note that the reaction starts from the right side to the left side.

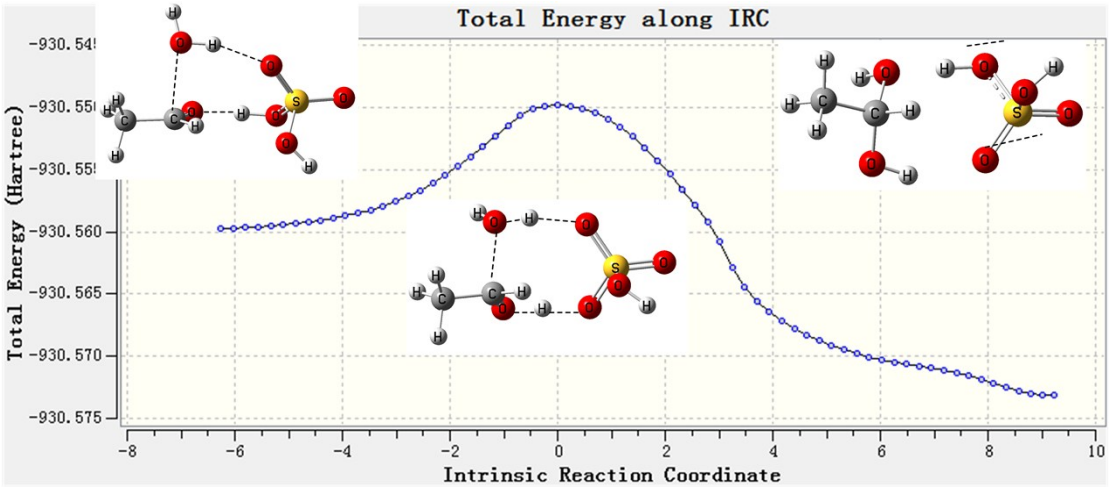

Figure S4. Intrinsic reaction coordinate results of TS2B.