Supplementary Material

Acid-Catalyzed Carboxylic Acid Esterification and Ester Hydrolysis Mechanism: Acylium Ion as a Sharing Active Intermediate via a Spontaneous Trimolecular Reaction Based on Density Functional Theory Calculation and Supported by Electrospray Ionization- Mass Spectrometry

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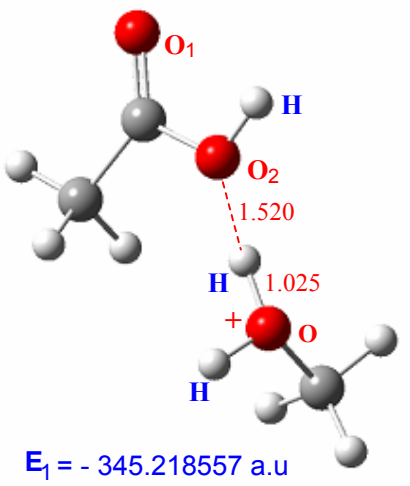
10. The atom coordinate tables of structure 1, 2 in Figure 15

1. The atom coordinate tables of system 1, 2 in Figure 1

Initial bimolecular system 1

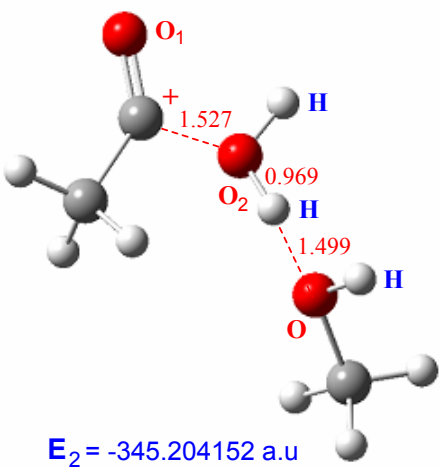


1

Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=ch3oh,pcm)
Zero-point correction= 0.127746 Hartree
Sum of electronic and zero-point Energies= -345.218557 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.197285	1.479976	0.079073
2	1	0	0.735312	1.614943	1.059032
3	1	0	0.478027	1.800635	-0.678243
4	1	0	2.099026	2.082406	0.006997
5	6	0	1.547215	0.041335	-0.131441
6	8	0	2.613549	-0.429616	-0.397508
7	6	0	-2.832950	0.095829	-0.508891
8	1	0	-3.865064	0.004073	-0.188269
9	1	0	-2.626067	-0.542004	-1.361385
10	1	0	-2.545961	1.127777	-0.689214
11	8	0	-2.009055	-0.452057	0.598524
12	1	0	-2.131780	0.024590	1.436254
13	8	0	0.442321	-0.789982	0.014230
14	1	0	0.717901	-1.710270	-0.131542
15	1	0	-1.011781	-0.539571	0.377175

The protonated system 2



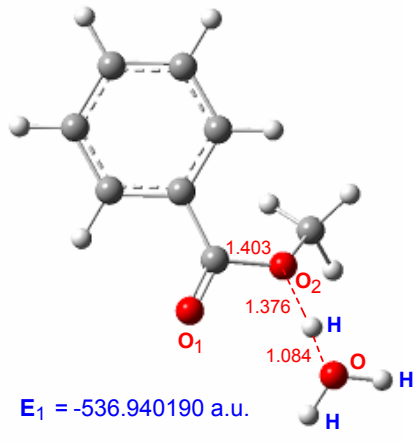
2

Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=ch3oh,pcm)
Zero-point correction= 0.125201 Hartree
Sum of electronic and zero-point Energies= -345.204152 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.190312	1.419823	-0.062799
2	6	0	1.593952	-0.001997	-0.022876
3	8	0	2.605585	-0.574636	0.098683
4	1	0	2.034564	2.029022	0.250197
5	1	0	0.322887	1.590942	0.576050
6	1	0	0.908398	1.671320	-1.088984
7	8	0	0.367132	-0.882335	-0.250575
8	1	0	-0.501671	-0.589585	0.066252
9	1	0	0.550214	-1.831022	-0.127107
10	6	0	-2.950579	0.048047	-0.333374
11	8	0	-1.795454	0.003046	0.535990
12	1	0	-3.649650	0.805442	0.022007
13	1	0	-2.586411	0.324188	-1.320693
14	1	0	-3.438987	-0.926760	-0.379147
15	1	0	-2.068812	-0.229235	1.431177

2. The atom coordinate tables of system 1, 2 in Figure 2

Initial bimolecular system 1



1

Basis set: rb3lyp/6-311g(d,p)

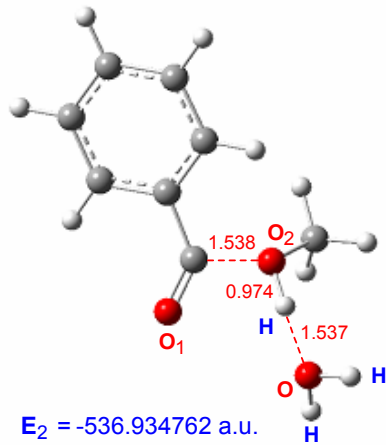
scrf=(solvent=h2o,pcm)

Zero-point correction= 0.178025 Hartree

Sum of electronic and zero-point Energies= -536.940190 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.944320	0.850220	0.404576
2	6	0	-1.579824	1.106363	0.363419
3	6	0	-0.712250	0.177838	-0.229075
4	6	0	-1.224936	-0.990527	-0.808359
5	6	0	-2.594749	-1.229307	-0.782085
6	6	0	-3.452264	-0.316588	-0.168594
7	1	0	-3.612148	1.560264	0.876873
8	1	0	-1.174279	2.014409	0.791472
9	1	0	-0.567666	-1.693896	-1.302608
10	1	0	-2.992109	-2.125693	-1.242194
11	1	0	-4.517891	-0.511599	-0.142002
12	6	0	0.718659	0.536444	-0.306747
13	8	0	3.873918	0.327125	-0.967066
14	1	0	4.201614	1.005004	-0.352845
15	1	0	4.542779	-0.371909	-1.056330
16	1	0	2.909079	-0.057308	-0.657793
17	8	0	1.162868	1.646221	-0.408087
18	8	0	1.654190	-0.508948	-0.318437
19	6	0	1.518241	-1.740618	0.469323
20	1	0	2.429669	-1.831388	1.055785
21	1	0	0.656329	-1.659966	1.124489
22	1	0	1.413997	-2.576269	-0.217767

The protonated system 2



2

Basis set: rb3lyp/6-311g(d,p)

scrf=(solvent=h2o,pcm)

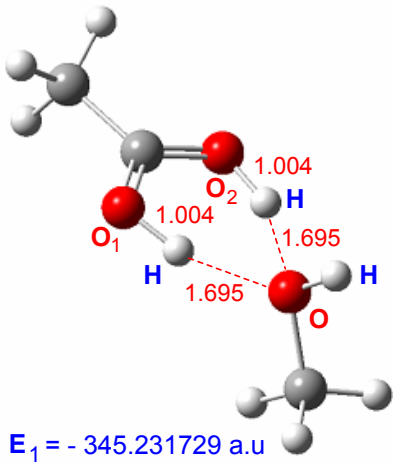
Zero-point correction= 0.178652 Hartree

Sum of electronic and zero-point Energies= -536.934762 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.017291	0.922162	0.415226
2	6	0	-1.661888	1.150236	0.594201
3	6	0	-0.729897	0.237272	0.068084
4	6	0	-1.162520	-0.888621	-0.651209
5	6	0	-2.522932	-1.098640	-0.831631
6	6	0	-3.447097	-0.200415	-0.296406
7	1	0	-3.739704	1.615818	0.826539
8	1	0	-1.312145	2.016706	1.140583
9	1	0	-0.445065	-1.573655	-1.081452
10	1	0	-2.863265	-1.960008	-1.392259
11	1	0	-4.507399	-0.373641	-0.436849
12	6	0	0.673593	0.550035	0.265889
13	8	0	1.567421	-0.664757	-0.033072
14	8	0	3.832018	0.081312	-0.817990
15	1	0	4.453173	0.382408	-0.143674
16	1	0	4.317078	-0.548095	-1.365612
17	1	0	2.447059	-0.360674	-0.320206
18	6	0	1.695241	-1.709931	1.015233
19	1	0	2.329568	-2.476345	0.581293
20	1	0	2.141655	-1.263962	1.900356
21	1	0	0.697863	-2.089042	1.208616
22	8	0	1.241536	1.532011	0.585345

3. The atom coordinate tables of system 1 in Figure 3

The optimized initial bimolecular system 1



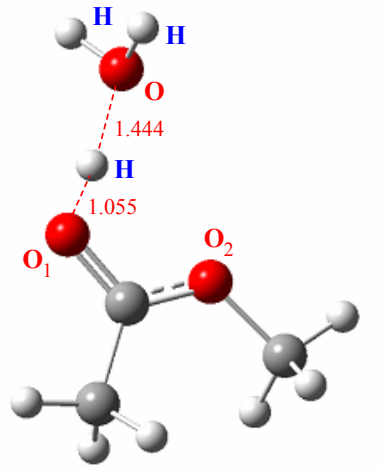
1

Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=ch3oh,pcm)
Zero-point correction= 0.128492 Hartree
Sum of electronic and zero-point Energies= -345.231729 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.799846	0.112487	-0.124340
2	1	0	2.030987	-0.920925	0.124869
3	1	0	2.492982	0.805292	0.347919
4	1	0	1.873674	0.232989	-1.210554
5	6	0	0.413359	0.432921	0.267375
6	8	0	0.117618	1.644205	0.561824
7	8	0	-0.458410	-0.505848	0.281577
8	8	0	-2.416155	1.099143	0.972473
9	6	0	-3.505131	1.505402	0.093852
10	1	0	-4.314225	0.778620	0.153687
11	1	0	-3.853938	2.497415	0.377858
12	1	0	-3.095466	1.527021	-0.913098
13	1	0	-2.728129	1.064034	1.886823
14	1	0	-1.363803	-0.156386	0.536807
15	1	0	-0.856889	1.736120	0.782981

4. The atom coordinate tables of system 1, 2 in Figure 4

The optimized initial bimolecular system 1



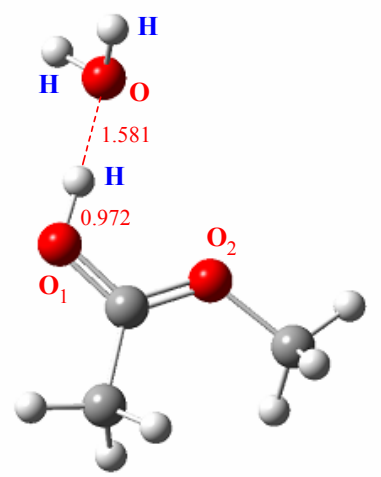
E_1 = -345.233742 a.u.

1

Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=h2o,pcm)
Zero-point correction= 0.125698 Hartree
Sum of electronic and zero-point Energies= -345.233742 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.448035	1.716843	-0.057921
2	6	0	0.280219	0.429558	-0.198346
3	8	0	-0.294908	-0.700864	-0.184729
4	1	0	-0.315577	2.307377	-0.968483
5	1	0	-0.029085	2.290635	0.771527
6	1	0	-1.506373	1.539668	0.110750
7	8	0	1.556171	0.360114	-0.350829
8	8	0	-2.777419	-0.573990	0.130756
9	1	0	-3.117890	-1.013582	0.920396
10	1	0	-3.310595	-0.887109	-0.611063
11	1	0	-1.326704	-0.659588	-0.057678
12	6	0	2.394149	1.557653	-0.388870
13	1	0	3.397024	1.177162	-0.548212
14	1	0	2.089625	2.194323	-1.216840
15	1	0	2.329170	2.079318	0.563794

The protonated system 2



E_2 = -345.231154 a.u.

2

Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=h2o,pcm)
Zero-point correction= 0.126280 Hartree
Sum of electronic and zero-point Energies= -345.231154 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.040438	1.311494	-0.001863
2	6	0	-0.264188	-0.155199	-0.000761
3	8	0	0.687741	-1.002535	0.000572
4	1	0	-0.491809	1.747578	0.893232
5	1	0	-0.532309	1.755970	-0.870522
6	1	0	1.022954	1.533041	-0.023658
7	8	0	-1.427234	-0.694673	0.000715
8	8	0	2.985576	0.107589	-0.001557
9	1	0	3.554426	-0.059974	-0.762727
10	1	0	3.535688	-0.026115	0.779794
11	1	0	1.572774	-0.600663	-0.000346
12	6	0	-2.651643	0.107958	0.000384
13	1	0	-3.450117	-0.625422	0.009797
14	1	0	-2.684076	0.724320	0.896098
15	1	0	-2.692237	0.709736	-0.904910

5. The potential energy surface scan (PES) curve of the carbonyl-oxygen protonated methyl acetate (III) or methyl benzoate (IV) and H_2O

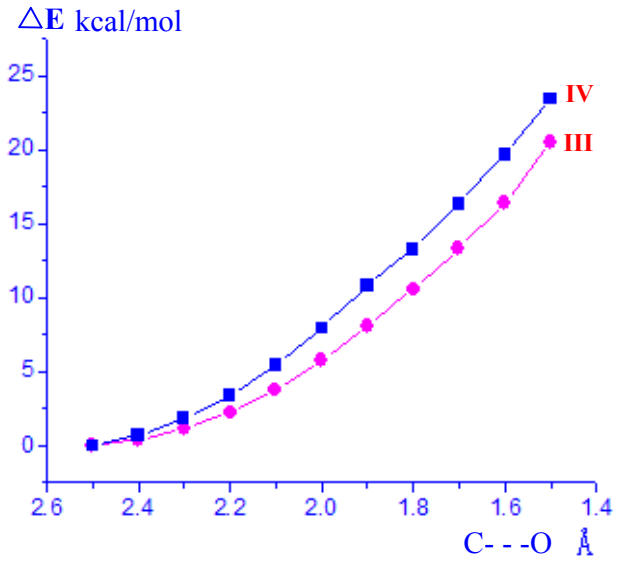
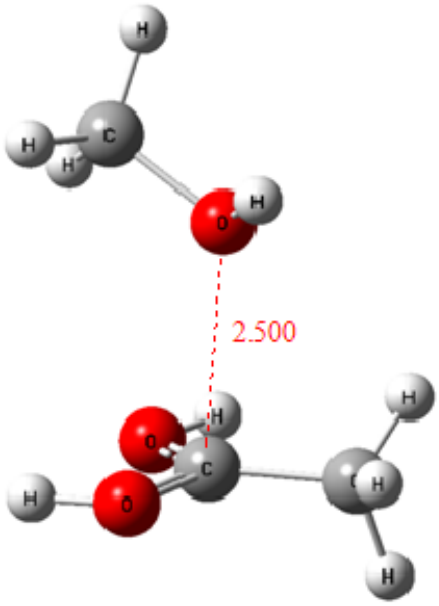


Figure 1. The potential energy surface scan (PES) curves of the carbonyl oxygen protonated methyl acetate (**III**) or methyl benzoate (**IV**) and water. The energies of the two systems are obtained by DFT calculation at the B3LYP/6-311G(d,p) level using PCM model to estimate the solvent effect of water. This figure set that C^+---OH_2 distance is 2.5 Å when the energy of the system is zero.

6. The atom coordinate table of the structure in Figure 7

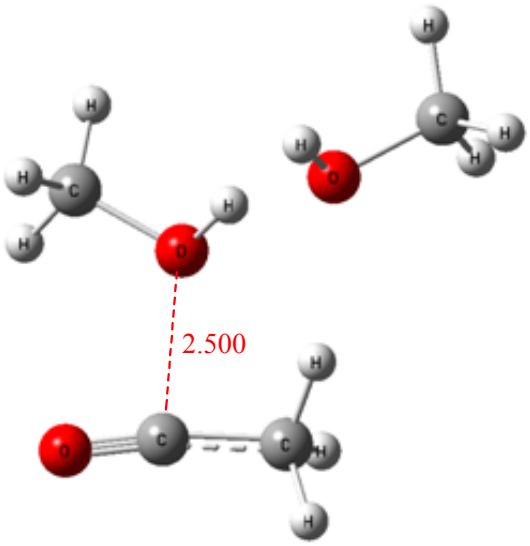


Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=ch3oh,pcm)
Zero-point correction= 0.127333 Hartree
Sum of electronic and zero-point Energies= -345.209829 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.500290	1.209914	0.111259
2	1	0	-1.498821	1.673606	-0.871806
3	1	0	-0.893668	1.783696	0.809131
4	1	0	-2.528149	1.163384	0.487504
5	6	0	-0.999849	-0.175614	0.016910
6	8	0	-0.683640	-0.900409	1.032367
7	8	0	-1.032943	-0.762501	-1.121325
8	8	0	1.335508	0.706120	-0.119840
9	1	0	-0.742082	-1.692000	-1.067111
10	1	0	-0.685658	-0.406113	1.869059
11	6	0	2.448392	-0.184008	0.039545
12	1	0	1.523535	1.297476	-0.857052
13	1	0	3.352055	0.363136	0.323558
14	1	0	2.190149	-0.873629	0.843112
15	1	0	2.641744	-0.757004	-0.872301

7. The atom coordinate tables of structure 1-8 in Figure 13.

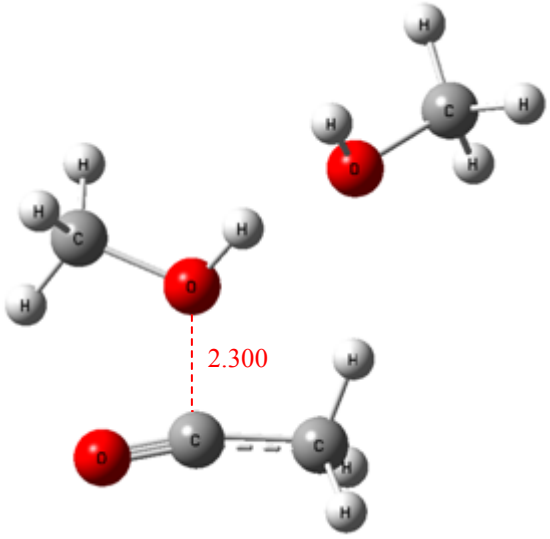
Structure 1



Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=ch3oh,pcm)
Zero-point correction= 0.151107 Hartree
Sum of electronic and zero-point Energies= -384.472552 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.658534	-1.798811	0.498735
2	6	0	1.678156	-0.984898	-0.069609
3	1	0	0.931784	-2.844468	0.326222
4	1	0	-0.296932	-1.532460	0.020247
5	1	0	0.603358	-1.571983	1.566930
6	8	0	-1.849590	-0.199901	-0.551256
7	8	0	0.342522	1.035199	0.551111
8	1	0	-1.973643	-0.135727	-1.505191
9	8	0	2.570167	-0.520337	-0.564287
10	6	0	0.835592	2.280311	0.049262
11	1	0	1.787215	2.479172	0.542355
12	1	0	0.995349	2.250708	-1.033827
13	1	0	0.143418	3.094630	0.284934
14	1	0	-0.514109	0.827758	0.128747
15	6	0	-3.140090	-0.226876	0.086674
16	1	0	-2.957921	-0.295573	1.157909
17	1	0	-3.700751	0.686681	-0.125349
18	1	0	-3.715708	-1.096793	-0.237887

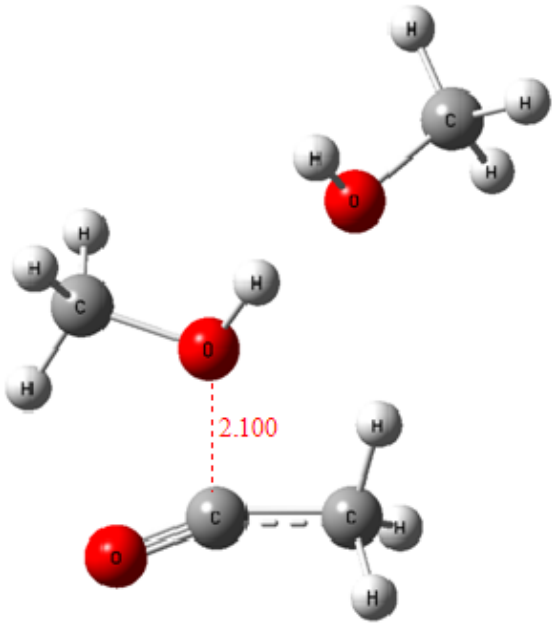
Structure 2



Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=ch3oh,pcm)
Zero-point correction= 0.151382 Hartree
Sum of electronic and zero-point Energies= -384.475041 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.714243	-1.821992	0.434224
2	6	0	1.658160	-0.868232	-0.065963
3	1	0	1.096675	-2.819599	0.201043
4	1	0	-0.257061	-1.627546	-0.037662
5	1	0	0.624309	-1.672472	1.513037
6	8	0	-1.873168	-0.189949	-0.556132
7	8	0	0.337840	0.918312	0.529869
8	1	0	-2.019229	-0.094081	-1.504246
9	8	0	2.566307	-0.393210	-0.529681
10	6	0	0.827894	2.185002	0.072423
11	1	0	1.784566	2.363428	0.562361
12	1	0	0.968223	2.198484	-1.012500
13	1	0	0.132829	2.979324	0.356907
14	1	0	-0.526414	0.716834	0.106801
15	6	0	-3.146176	-0.187429	0.117579
16	1	0	-2.937077	-0.291096	1.180996
17	1	0	-3.679965	0.750020	-0.055703
18	1	0	-3.759416	-1.028617	-0.213056

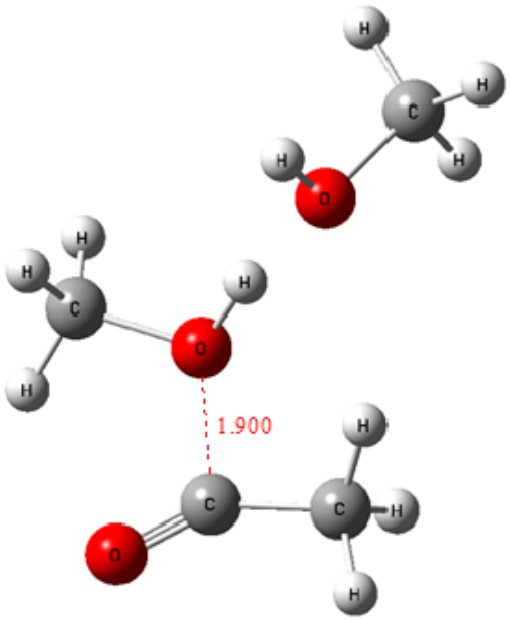
Structure 3



Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=ch3oh,pcm)
Zero-point correction= 0.151707 Hartree
Sum of electronic and zero-point Energies= -384.478567 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.819134	-1.844008	-0.328597
2	6	0	-1.653318	-0.728756	0.052595
3	1	0	-1.339302	-2.762050	-0.047468
4	1	0	0.148895	-1.749175	0.171090
5	1	0	-0.664422	-1.792756	-1.408975
6	8	0	1.892163	-0.193125	0.550422
7	8	0	-0.321228	0.800045	-0.493578
8	1	0	2.058392	-0.036281	1.487111
9	8	0	-2.591950	-0.230366	0.441432
10	6	0	-0.738883	2.110684	-0.075403
11	1	0	-1.776604	2.239001	-0.380218
12	1	0	-0.655388	2.230344	1.006880
13	1	0	-0.124586	2.857549	-0.581966
14	1	0	0.558746	0.567278	-0.095527
15	6	0	3.145862	-0.197265	-0.160738
16	1	0	2.908731	-0.363490	-1.210022
17	1	0	3.661334	0.759650	-0.052182
18	1	0	3.785161	-1.006431	0.197923

Structure 4



Basis set: rb3lyp/6-311g(d,p)
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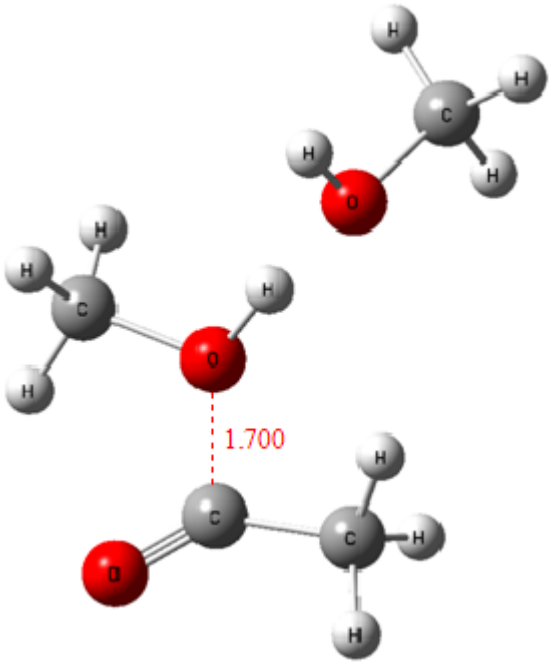
Zero-point correction= 0.151976 Hartree
Sum of electronic and zero-point Energies= -384.483621

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.917320	-1.848073	-0.254188
2	6	0	-1.616270	-0.602677	0.032536
3	1	0	-1.556760	-2.675696	0.053068
4	1	0	0.038509	-1.856893	0.272805
5	1	0	-0.721878	-1.884961	-1.328486
6	8	0	1.890279	-0.213482	0.558216
7	8	0	-0.305008	0.691961	-0.430609
8	1	0	2.084858	0.000812	1.478149
9	8	0	-2.583783	-0.095246	0.363942
10	6	0	-0.651634	2.050602	-0.082678
11	1	0	-1.700524	2.196484	-0.332598
12	1	0	-0.490108	2.232220	0.980212
13	1	0	-0.037284	2.718203	-0.686245
14	1	0	0.585538	0.421347	-0.035459
15	6	0	3.112503	-0.200427	-0.210324
16	1	0	2.837937	-0.439976	-1.235713
17	1	0	3.583362	0.784062	-0.177744
18	1	0	3.800771	-0.958011	0.167545

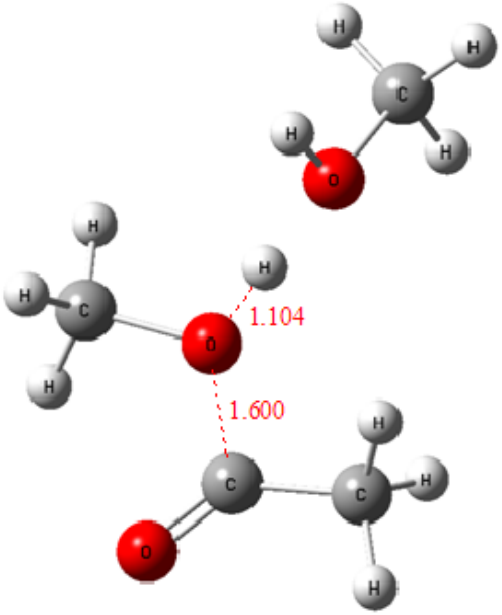
Structure 5



Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=ch3oh,pcm)
Zero-point correction= 0.151776 Hartree
Sum of electronic and zero-point Energies= -384.490730 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.980079	-1.839847	-0.163330
2	6	0	-1.556597	-0.497666	0.000253
3	1	0	-1.734207	-2.576698	0.106598
4	1	0	-0.089636	-1.941030	0.458466
5	1	0	-0.683024	-1.962283	-1.207610
6	8	0	1.879013	-0.242938	0.560329
7	8	0	-0.294436	0.597632	-0.311629
8	1	0	2.108637	0.020571	1.459771
9	8	0	-2.573627	0.005370	0.222548
10	6	0	-0.578299	2.002479	-0.062915
11	1	0	-1.593812	2.194515	-0.397653
12	1	0	-0.474940	2.222859	0.998539
13	1	0	0.128720	2.575766	-0.658271
14	1	0	0.632298	0.286938	0.066083
15	6	0	3.052846	-0.188985	-0.287236
16	1	0	2.731774	-0.498445	-1.279336
17	1	0	3.454765	0.824404	-0.325245
18	1	0	3.804602	-0.882994	0.088034

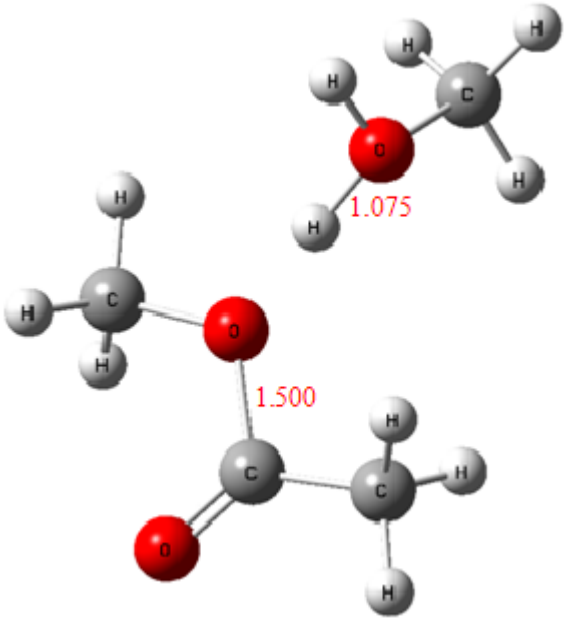
Structure 6



Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=ch3oh,pcm)
Zero-point correction= 0.150937 Hartree
Sum of electronic and zero-point Energies= -384.495664 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.028689	-1.830233	-0.099179
2	6	0	-1.522021	-0.439266	-0.023319
3	1	0	-1.863100	-2.506223	0.073929
4	1	0	-0.242942	-1.991291	0.640384
5	1	0	-0.601823	-2.002061	-1.089758
6	8	0	1.875260	-0.276580	0.559704
7	8	0	-0.274433	0.546463	-0.201826
8	1	0	2.136881	-0.000236	1.447552
9	8	0	-2.562572	0.074730	0.095211
10	6	0	-0.527930	1.972298	-0.032281
11	1	0	-1.435808	2.215104	-0.576104
12	1	0	-0.633721	2.205007	1.025893
13	1	0	0.325322	2.485941	-0.467824
14	1	0	0.706309	0.196057	0.163117
15	6	0	2.999479	-0.179098	-0.358726
16	1	0	2.630318	-0.500709	-1.329095
17	1	0	3.359468	0.848100	-0.411417
18	1	0	3.788019	-0.848799	-0.020357

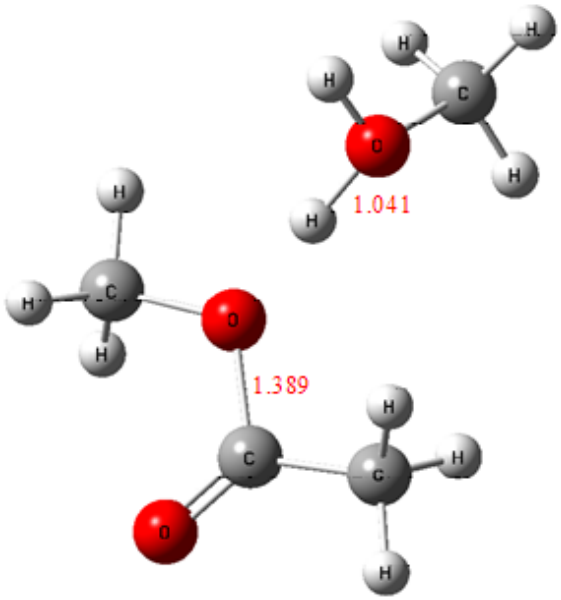
Structure 7



Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=ch3oh,pcm)
Zero-point correction= 0.153781 Hartree
Sum of electronic and zero-point Energies= -384.498976 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.995805	-1.830629	-0.000568
2	6	0	-1.466226	-0.418394	-0.033078
3	1	0	-1.859184	-2.491050	0.030702
4	1	0	-0.361695	-2.001188	0.870789
5	1	0	-0.404581	-2.037354	-0.895890
6	8	0	1.970934	-0.213950	0.601433
7	8	0	-0.296711	0.518969	0.026801
8	1	0	2.310756	0.229198	1.395101
9	8	0	-2.554538	0.037978	-0.111459
10	6	0	-0.622211	1.933529	-0.020335
11	1	0	-1.206487	2.141132	-0.914303
12	1	0	-1.178306	2.216009	0.872242
13	1	0	0.329517	2.457802	-0.060459
14	1	0	0.978928	0.126438	0.362644
15	6	0	2.924976	-0.164259	-0.525039
16	1	0	2.458460	-0.726967	-1.326990
17	1	0	3.096655	0.871332	-0.807259
18	1	0	3.834054	-0.650805	-0.186654

Structure 8



Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=ch3oh,pcm)
Zero-point correction= 0.155332 Hartree
Sum of electronic and zero-point Energies= -384.501340 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.975621	-1.818260	-0.002174
2	6	0	-1.424327	-0.388722	-0.037461
3	1	0	-1.850162	-2.463774	0.010152
4	1	0	-0.360954	-2.010115	0.879018
5	1	0	-0.373271	-2.035800	-0.887844
6	8	0	1.986513	-0.259588	0.580187
7	8	0	-0.353478	0.490737	0.060754
8	1	0	2.303716	0.122125	1.415196
9	8	0	-2.541721	0.023835	-0.149023
10	6	0	-0.670832	1.915756	0.007273
11	1	0	-1.194070	2.130401	-0.921308
12	1	0	-1.286085	2.180989	0.864245
13	1	0	0.285008	2.430303	0.040265
14	1	0	1.021201	0.069548	0.370664
15	6	0	2.948929	-0.085737	-0.534977
16	1	0	2.502095	-0.595357	-1.381976
17	1	0	3.088635	0.975137	-0.722986
18	1	0	3.866212	-0.573137	-0.222467

8. The microscopic process of Acid-Catalyzed Ester hydrolysis: a spontaneous trimolecular reaction

Figure 4 shows nine intermediate structures and one final optimized structure with HOMO graphs of the reaction system ($CH_3C^+=O + 2\ H_2O$).

Structure **1** and **2** in Figure **4**: the C^+---O distance is 2.500 and 2.300Å; at this point the HOMO of the system basically is that of H_2O **1**. Because the oxygen of H_2O **1** is far from the acylium ion, only a small amount of HOMO electrons are on the acylium ion, indicating the presence of only a small interaction between the acylium ion and H_2O **1**. At this time, the H_2O **2** has not yet entered in the reaction.

Structure **3**: the C^+---O distance is 2.100 Å, the HOMO of the reaction system ($CH_3C^+=O + 2\ H_2O$) is become into the HOMO of H_2O **2**, this reflects the H_2O **2** has participated in this reaction system.

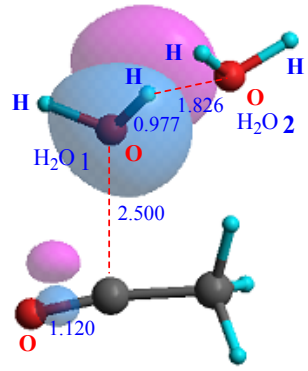
Structure **4** - **8**: as shortening of the C^+---OH_2 1 distance, the HOMO electrons of the reaction system continuously transferred to the region of acylium ion and H_2O **1**.

In the same time, the –O-H bond length of H_2O 1 continuously was stretched. From the structure **1** to **8**, the oxygen hydrogen bond length is 0.977, 0.982, 0.992, 0.999, 1.010, 1.026, 1.051 and 1.142 Å, to the structure **8**, the bond has been disconnected. But the distance between the H of H_2O **1** and the hydroxyl oxygen of H_2O **2** is getting closer; the distances are 1.826, 1.770, 1.691, 1.642, 1.582, 1.518, 1.441 and 1.263 Å. These data suggest that the H proton of H_2O **1** constantly close to the oxygen of H_2O **2**.

Structure **9**: the C^+---O distance is 1.50 Å, the carbon-oxygen bond formed, i.e. a neutral acetic acid generated. The HOMO electrons have occurred mainly in the acetic acid molecule. Another important phenomenon is that the H proton of H_2O **1** has been completely transferred to the H_2O **2**, i.e., a protonated water molecule H_3O^+ formed. This process can be considered as an electrophilic transfer of the positive charge of acylium ion toward H_2O **2**, because the H_2O **2** ultimately get a proton (H^+).

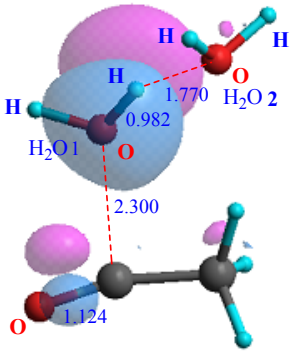
Structure **10** is the final optimized Structure. The system energy **E** of structure **1**-**10** is continuously reducing (from -305.916878 to -305.938446 a.u.); this indicates that the trimolecular reaction of the acetic acid acylium ion and two water molecules is a spontaneous process. The process reduces the energy of 13.5 kcal/mol, and the carbon oxygen bond (C-OH) length is 1.397 Å, which shows that the trimolecular

reaction generated a real stable bond (the C-OH bond distance of neutral carboxylic acids is 1.35-1.40 Å). It must be noted, the nine structures (**1-9**) in front of **10**, regardless of which one are optimized, and you will get the final structure **10**. The illustrations clearly display that it also is a trimolecular reaction.



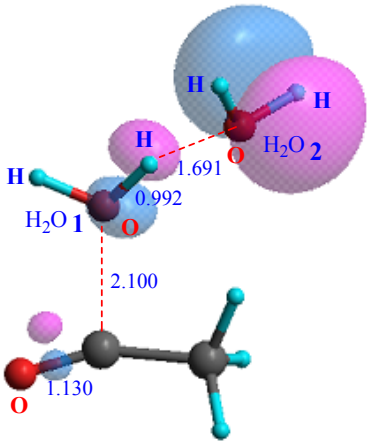
HOMO E = -305.916878 a.u.

1



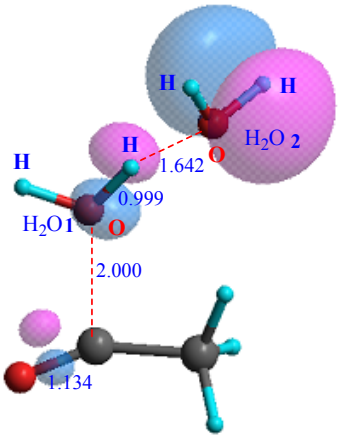
HOMO E = -305.918425 a.u.

2



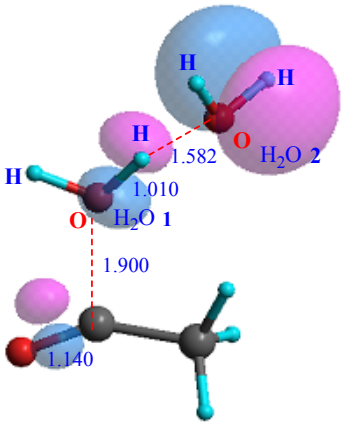
HOMO E = -305.920536 a.u.

3



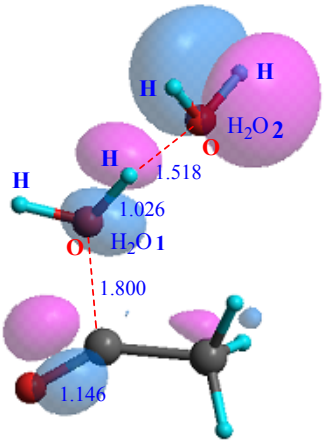
HOMO E = -305.921929 a.u.

4



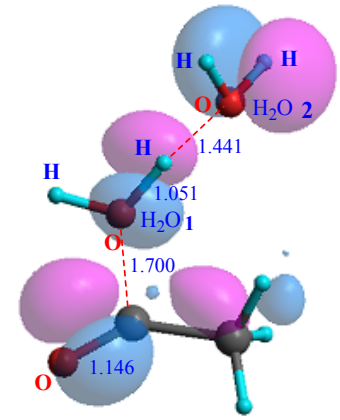
HOMO E = -305.923897 a.u.

5



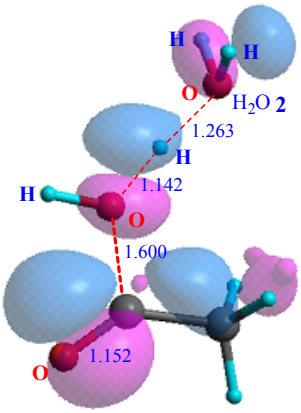
HOMO E = -305.926199 a.u.

6



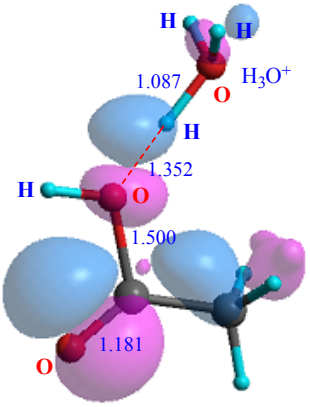
HOMO E = -305.929180 a.u.

7



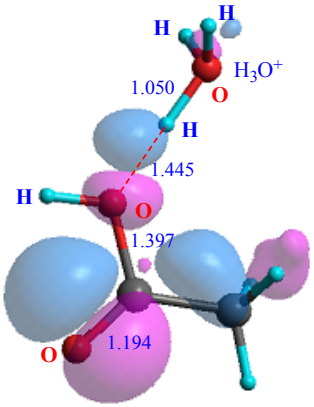
HOMO E = -305.934100 a.u.

8



HOMO E = -305.929180 a.u.

9



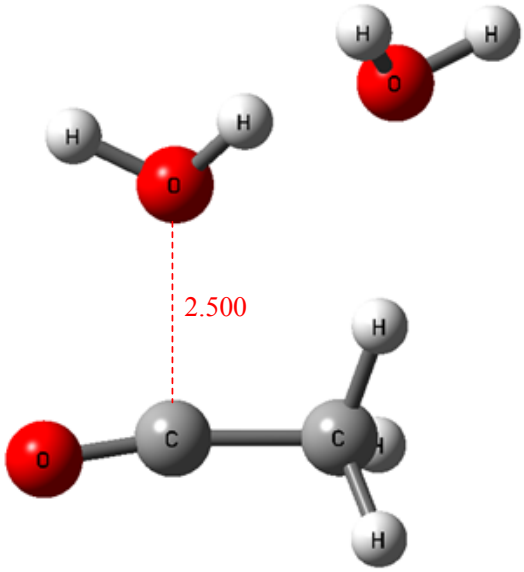
HOMO E = -305.938446 a.u.

10

Figure . HOMO graphs and system energies **E** of the typical intermediates of $CH_3C^+=O$ + $2H_2O$ system obtained by scan **(1-9**) and optimization (**10)** calculations at the B3LYP/6-311G(d,p) level, using PCM model to estimate the solvent effect of H_2O and including zero point energy corrections. The distance is in angstroms, The **E** is in a.u., orbital contour value = 0.05.

The atom coordinate tables of **structure 1-10** in above Figure

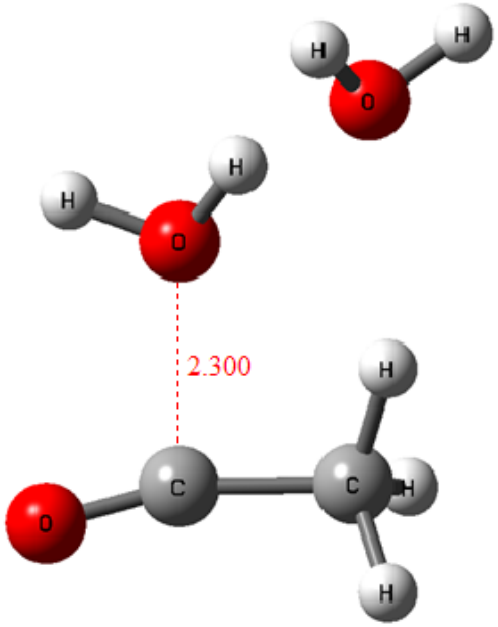
Structure 1



Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=H_2O, pcm)
Zero-point correction= 0.093698 Hartree
Sum of electronic and zero-point Energies= -305.916878 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.533070	-1.286797	0.519619
2	6	0	1.320008	-0.273219	-0.093361
3	8	0	2.065330	0.372044	-0.625046
4	1	0	1.027182	-2.245168	0.331586
5	1	0	-0.478834	-1.245903	0.087389
6	1	0	0.479461	-1.070581	1.590055
7	8	0	-0.401539	1.411908	0.574936
8	1	0	-1.218932	1.003403	0.228493
9	1	0	-0.275699	2.216203	0.058562
10	8	0	-2.290419	-0.334415	-0.401571
11	1	0	-2.558235	-0.300675	-1.327396
12	1	0	-3.080382	-0.593482	0.087208

Structure 2



Basis set: rb3lyp/6-311g(d,p)

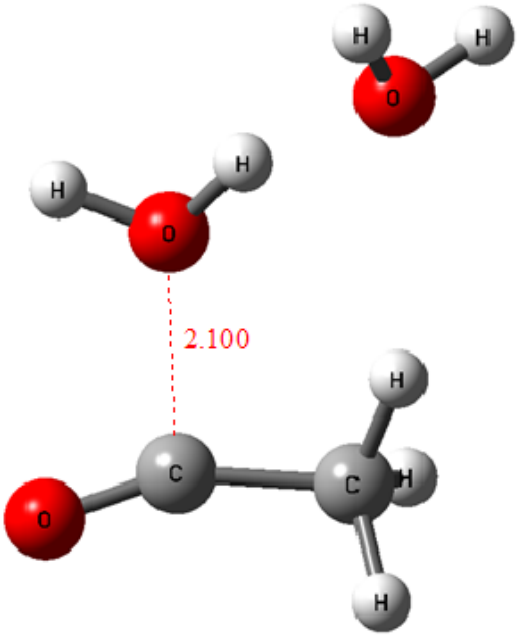
scrf=(solvent=H_2O, pcm)

Zero-point correction = 0.094224 Hartree

Sum of electronic and zero-point Energies = -305.918425Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.556076	1.325541	0.464127
2	6	0	-1.258720	0.215528	-0.103030
3	8	0	-2.017684	-0.421604	-0.632632
4	1	0	-1.116850	2.229983	0.211834
5	1	0	0.460808	1.336513	0.051760
6	1	0	-0.504936	1.177065	1.545422
7	8	0	0.329864	-1.278723	0.627458
8	1	0	1.170366	-0.923085	0.264064
9	1	0	0.189812	-2.131813	0.198657
10	8	0	2.310884	0.257995	-0.397497
11	1	0	2.590626	0.144887	-1.313454
12	1	0	3.114439	0.458698	0.096505

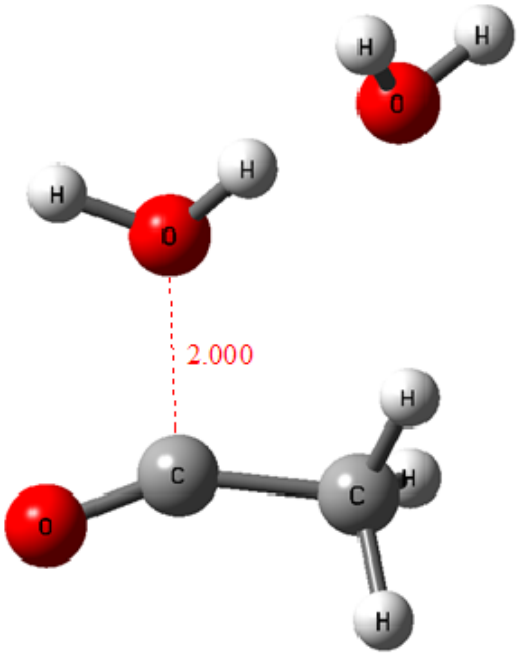
Structure 3



Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=H_2O, pcm)
Zero-point correction = 0.094709 Hartree
Sum of electronic and zero-point Energies = -305.920536 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.548363	1.374491	0.309605
2	6	0	-1.224379	0.160731	-0.078485
3	8	0	-2.071795	-0.460205	-0.494200
4	1	0	-1.165903	2.213165	-0.018954
5	1	0	0.446861	1.389078	-0.143569
6	1	0	-0.441607	1.366510	1.397068
7	8	0	0.269121	-1.171857	0.556862
8	1	0	1.140512	-0.826501	0.232778
9	1	0	0.123292	-2.024558	0.125549
10	8	0	2.381347	0.177060	-0.325473
11	1	0	2.800370	-0.051131	-1.163732
12	1	0	3.103539	0.362122	0.286632

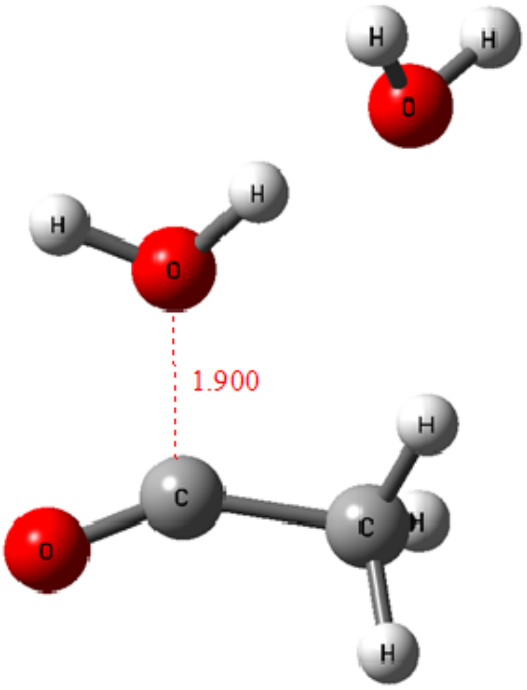
Structure 4



Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=H_2O, pcm)
Zero-point correction = 0.095004 Hartree
Sum of electronic and zero-point Energies = -305.921929 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.581606	1.389058	0.270696
2	6	0	-1.191898	0.120632	-0.072208
3	8	0	-2.048872	-0.501875	-0.477736
4	1	0	-1.242711	2.182243	-0.081437
5	1	0	0.408277	1.444597	-0.188403
6	1	0	-0.467561	1.426266	1.356667
7	8	0	0.258532	-1.102195	0.560994
8	1	0	1.138139	-0.757743	0.235018
9	1	0	0.118995	-1.973893	0.164690
10	8	0	2.386811	0.156103	-0.314386
11	1	0	2.809551	-0.119374	-1.136589
12	1	0	3.104565	0.323503	0.308156

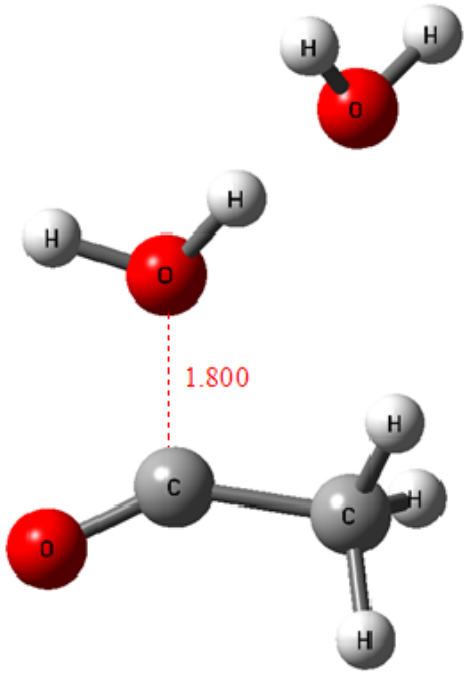
Structure 5



Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=H_2O, pcm)
Zero-point correction = 0.095060 Hartree
Sum of electronic and zero-point Energies = -305.923897 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.637447	1.403515	0.224267
2	6	0	-1.159625	0.075790	-0.062811
3	8	0	-2.021569	-0.560860	-0.450842
4	1	0	-1.356104	2.134846	-0.145971
5	1	0	0.338648	1.516414	-0.251518
6	1	0	-0.510711	1.493292	1.305639
7	8	0	0.260470	-1.024604	0.555625
8	1	0	1.149211	-0.673848	0.226800
9	1	0	0.132871	-1.917120	0.200849
10	8	0	2.398339	0.144024	-0.297552
11	1	0	2.820905	-0.180985	-1.101879
12	1	0	3.109682	0.283090	0.339497

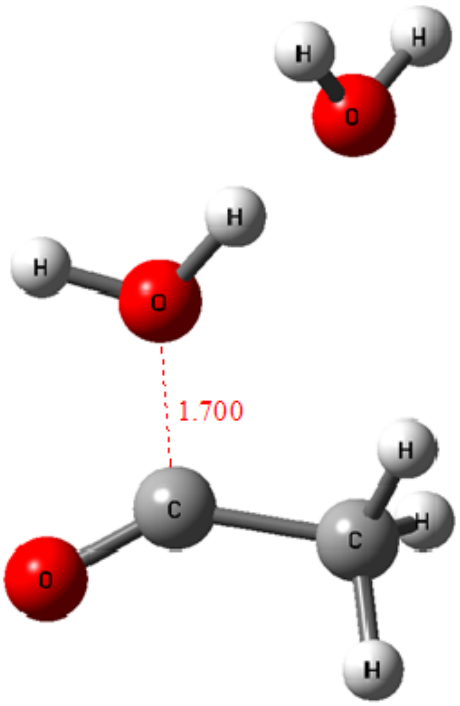
Structure 6



Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=H_2O, pcm)
Zero-point correction = 0.095231 Hartree
Sum of electronic and zero-point Energies = -305.926199 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.679390	1.411151	0.179007
2	6	0	-1.126171	0.038410	-0.050580
3	8	0	-2.001909	-0.607153	-0.411505
4	1	0	-1.445624	2.087504	-0.197125
5	1	0	0.276714	1.569978	-0.322468
6	1	0	-0.533392	1.549095	1.252864
7	8	0	0.258279	-0.955343	0.528861
8	1	0	1.164144	-0.599477	0.204228
9	1	0	0.138575	-1.867633	0.222237
10	8	0	2.405659	0.131054	-0.274830
11	1	0	2.838019	-0.232680	-1.057484
12	1	0	3.098697	0.247384	0.386980

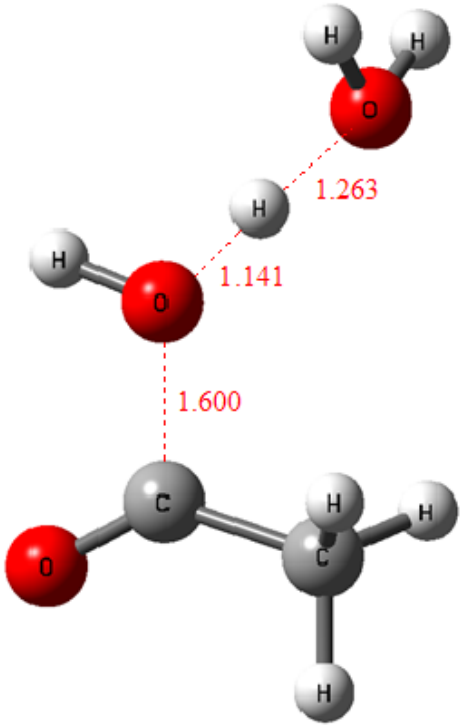
Structure 7



Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=H_2O, pcm)
Zero-point correction = 0.095149 Hartree
Sum of electronic and zero-point Energies = -305.929180 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.715578	1.414320	0.139590
2	6	0	-1.087738	0.004908	-0.036360
3	8	0	-1.981852	-0.645987	-0.367686
4	1	0	-1.527767	2.036549	-0.230951
5	1	0	0.213480	1.617831	-0.395249
6	1	0	-0.544970	1.597284	1.203119
7	8	0	0.256119	-0.894580	0.488016
8	1	0	1.189977	-0.530256	0.173478
9	1	0	0.139630	-1.824489	0.234693
10	8	0	2.404463	0.121472	-0.247790
11	1	0	2.837726	-0.263677	-1.020337
12	1	0	3.081981	0.204150	0.435550

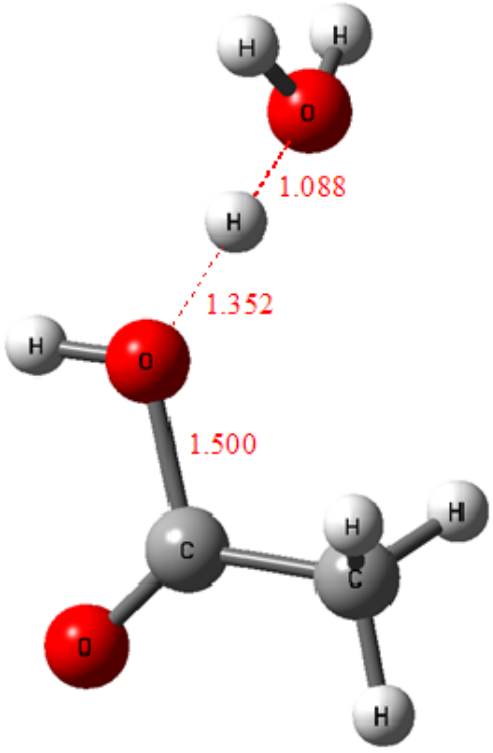
Structure 8



Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=H_2O, pcm)
Zero-point correction = 0.092346 Hartree
Sum of electronic and zero-point Energies = -305.934100 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.849676	1.408856	0.000964
2	6	0	-1.102011	-0.044536	-0.001040
3	8	0	-2.027257	-0.731136	-0.006178
4	1	0	-1.804589	1.929223	-0.020314
5	1	0	-0.250484	1.676660	-0.870951
6	1	0	-0.290733	1.678046	0.899117
7	8	0	0.307402	-0.801776	0.010800
8	1	0	1.365409	-0.373350	0.002805
9	1	0	0.200742	-1.764823	0.002170
10	8	0	2.519770	0.138334	-0.006068
11	1	0	3.046262	-0.104792	-0.780870
12	1	0	3.044192	-0.070263	0.780063

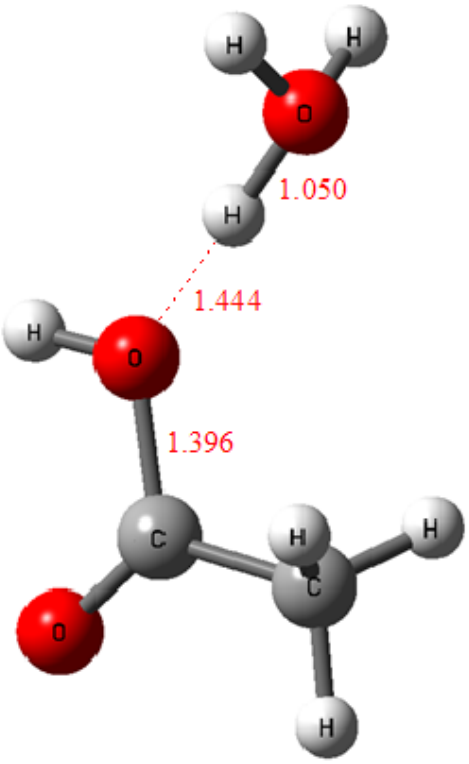
Structure 9



Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=H_2O, pcm)
Zero-point correction = 0.095861 Hartree
Sum of electronic and zero-point Energies = -305.936950 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.868229	1.404868	-0.000801
2	6	0	-1.058029	-0.068552	0.000005
3	8	0	-2.030880	-0.738372	0.002731
4	1	0	-1.841967	1.888606	0.001118
5	1	0	-0.302695	1.702993	-0.885792
6	1	0	-0.299125	1.703528	0.881719
7	8	0	0.270597	-0.764784	-0.003739
8	1	0	1.534742	-0.285177	-0.000676
9	1	0	0.124152	-1.723555	-0.002235
10	8	0	2.542400	0.123839	0.001653
11	1	0	3.044656	-0.134510	-0.788889
12	1	0	3.040857	-0.135244	0.794376

Structure 10

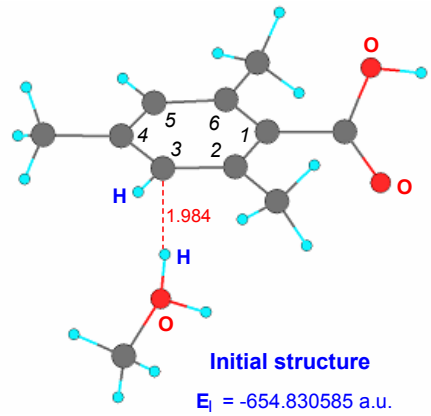


Basis set: rb3lyp/6-311g(d,p)
scrf=(solvent=H_2O, pcm)
Zero-point correction = 0.097759 Hartree
Sum of electronic and zero-point Energies = -305.938446 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.843142	1.401238	-0.000086
2	6	0	-1.016865	-0.082977	0.000206
3	8	0	-2.030343	-0.714411	0.000125
4	1	0	-1.821498	1.874582	-0.000569
5	1	0	-0.280189	1.710953	-0.883184
6	1	0	-0.280894	1.711355	0.883319
7	8	0	0.208870	-0.751986	0.000478
8	1	0	1.568511	-0.264437	0.000303
9	1	0	0.056280	-1.711688	0.000317
10	8	0	2.551491	0.104907	0.000080
11	1	0	3.040488	-0.169413	-0.795252
12	1	0	3.040814	-0.169840	0.795077

9. The atom coordinate tables of structure 1-4 in Figure 14

The initial structure 1 of benzene ring C_3 protonation by $CH_3OH_2^+$



1

Basis set: rb3lyp/6-311g(d,p)

scrf=(solvent=ch3oh, pcm)

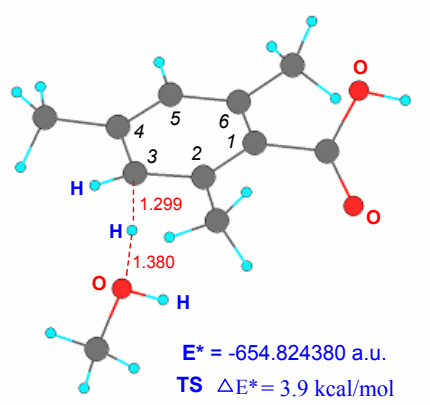
Zero-point correction = 0.263141 Hartree

Sum of electronic and zero-point Energies = -654.830585 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.703987	-1.410283	-0.534043
2	6	0	-1.087067	-0.310747	0.263807
3	6	0	0.637308	-1.802883	-0.537208
4	6	0	-0.134581	0.380932	1.039689
5	6	0	1.601526	-1.159376	0.236685
6	6	0	1.199086	-0.056404	1.007675
7	6	0	3.025231	-1.650309	0.271196
8	6	0	-1.678101	-2.168663	-1.405318
9	6	0	-0.498106	1.551838	1.922805
10	1	0	-2.328091	-1.498336	-1.971440
11	1	0	-1.138682	-2.799575	-2.112237
12	1	0	-2.326444	-2.806598	-0.800745
13	1	0	3.131139	-2.442036	1.020220
14	1	0	3.325144	-2.068107	-0.691609
15	1	0	3.719822	-0.852021	0.538434
16	1	0	-1.314286	1.295147	2.602857

17	1	0	0.359786	1.856114	2.522941
18	1	0	-0.834641	2.404800	1.331694
19	6	0	-2.503294	0.176531	0.274278
20	1	0	0.932493	-2.641106	-1.159068
21	8	0	-3.395766	-0.811323	0.475902
22	8	0	-2.836258	1.331439	0.133528
23	1	0	-4.282507	-0.417369	0.441164
24	1	0	1.922916	0.430682	1.654595
25	8	0	1.743384	1.728452	-1.322008
26	1	0	1.493765	1.145977	-0.542064
27	6	0	2.862395	2.675098	-1.035007
28	1	0	3.680528	2.050118	-0.694953
29	1	0	0.947825	2.170729	-1.667622
30	1	0	2.536993	3.383469	-0.279384
31	1	0	3.089113	3.148666	-1.983653

The transition structure 2 of benzene ring C_3 protonation by $CH_3OH_2^+$



2

Basis set: rb3lyp/6-311g(d,p)

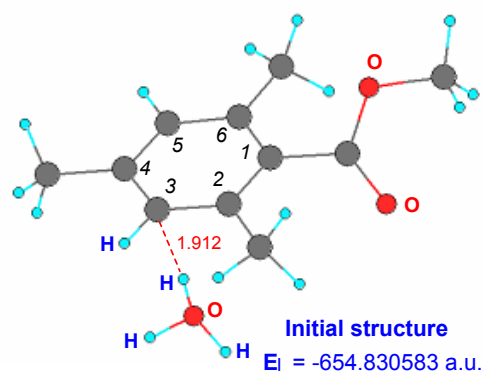
scrf=(solvent=ch3oh, pcm)

Zero-point correction = 0.257068 Hartree

Sum of electronic and zero-point Energies = -654.824380 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.034398	1.290282	-0.343989
2	6	0	1.103377	-0.046954	0.121613
3	6	0	-0.130351	2.045481	-0.131736
4	6	0	0.012310	-0.625521	0.768658
5	6	0	-1.228931	1.524640	0.522594
6	6	0	-1.199946	0.135530	0.891286
7	6	0	-2.454482	2.338638	0.796568
8	6	0	2.176266	1.940744	-1.074110
9	6	0	0.025573	-2.029643	1.301154
10	1	0	2.593290	1.281050	-1.837758
11	1	0	1.851355	2.865807	-1.548179
12	1	0	2.986193	2.169887	-0.377200
13	1	0	-2.593686	2.453241	1.876184
14	1	0	-2.388068	3.328424	0.346244
15	1	0	-3.345504	1.834617	0.411860
16	1	0	0.897494	-2.192950	1.939350
17	1	0	-0.872029	-2.233621	1.883317
18	1	0	0.093560	-2.750163	0.483846
19	6	0	2.338883	-0.876715	-0.089406
20	1	0	-0.151500	3.071886	-0.477838
21	8	0	3.455246	-0.252933	0.319962
22	8	0	2.337666	-1.989589	-0.558346
23	1	0	4.209803	-0.835448	0.133581
24	1	0	-1.899485	-0.186586	1.662622
25	8	0	-2.668495	-0.748036	-1.162555
26	1	0	-1.857249	-0.339580	-0.124021
27	6	0	-3.547364	-1.880195	-0.918443
28	1	0	-4.118374	-1.637912	-0.025674
29	1	0	-2.130237	-0.909650	-1.950157
30	1	0	-2.969384	-2.791488	-0.765032
31	1	0	-4.219626	-1.988663	-1.768383

The initial structure 3 of benzene ring C_3 protonation by H_3O^+



3

Basis set: rb3lyp/6-311g(d,p)

scrf=(solvent=h2o, pcm)

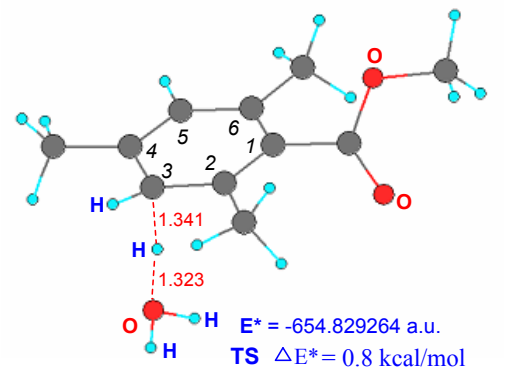
Zero-point correction = 0.261545 Hartree

Sum of electronic and zero-point Energies = -654.830583 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.440848	-0.968629	-0.632416
2	6	0	-0.422283	0.019964	-0.120279
3	6	0	1.794516	-0.642181	-0.824013
4	6	0	0.061512	1.307542	0.188057
5	6	0	2.296571	0.640509	-0.541159
6	1	0	2.448820	-1.378985	-1.279647
7	6	0	1.414373	1.588599	-0.026789
8	1	0	1.784325	2.580222	0.210439
9	6	0	3.749984	0.970958	-0.767115
10	6	0	-0.045961	-2.347090	-1.013589
11	6	0	-0.824098	2.389764	0.759099
12	1	0	-0.854180	-2.284199	-1.747535
13	1	0	0.763129	-2.931555	-1.451937
14	1	0	-0.440541	-2.884060	-0.149900
15	1	0	3.870873	2.013089	-1.068409
16	1	0	4.328309	0.828240	0.151969
17	1	0	4.188031	0.332478	-1.536004
18	1	0	-1.431756	2.019178	1.588026

19	1	0	-0.220331	3.220303	1.125583
20	1	0	-1.512089	2.771459	0.001818
21	6	0	-1.859409	-0.338427	0.125313
22	8	0	-2.224265	-1.288429	0.781781
23	8	0	-2.702901	0.511323	-0.477360
24	6	0	-4.113955	0.273433	-0.265268
25	1	0	-4.352513	0.342027	0.796234
26	1	0	-4.624208	1.053302	-0.823830
27	1	0	-4.390374	-0.711806	-0.640401
28	8	0	2.231931	-1.408314	1.967963
29	1	0	3.192857	-1.418817	2.137220
30	1	0	2.039284	-1.171948	0.996472
31	1	0	1.846411	-2.274241	2.201213

The transition structure 4 of the benzene ring C_3 protonation by H_3O^+



4

Basis set: rb3lyp/6-311g(d,p)

scrf=(solvent=h2o, pcm)

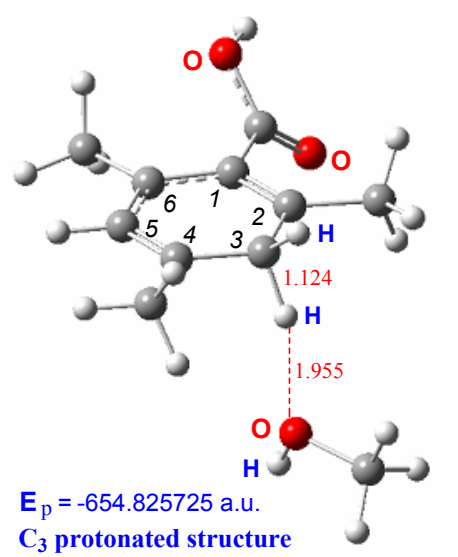
Zero-point correction = 0.255644 Hartree

Sum of electronic and zero-point Energies = -654.829264 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.426767	-0.925721	-0.542734
2	6	0	-0.474051	0.018535	-0.049785
3	6	0	1.803381	-0.555976	-0.678474
4	6	0	-0.041366	1.330984	0.255455
5	6	0	2.222706	0.796861	-0.466015
6	1	0	2.420755	-1.179097	-1.324616
7	6	0	1.298843	1.690231	0.043996
8	1	0	1.606138	2.704091	0.271511
9	6	0	3.640420	1.190516	-0.748122
10	6	0	0.024908	-2.332377	-0.887084
11	6	0	-0.979687	2.364736	0.815751
12	1	0	-0.812391	-2.332575	-1.589923
13	1	0	0.853725	-2.875645	-1.339518
14	1	0	-0.307847	-2.866269	0.004934
15	1	0	3.860977	2.189540	-0.373379
16	1	0	4.338622	0.480921	-0.296238
17	1	0	3.823432	1.175315	-1.827329
18	1	0	-1.577876	1.959367	1.634998
19	1	0	-0.426590	3.228456	1.182508
20	1	0	-1.678610	2.698011	0.044999
21	6	0	-1.905359	-0.391300	0.169650
22	8	0	-2.243215	-1.345592	0.831440
23	8	0	-2.758374	0.415922	-0.469996
24	6	0	-4.167672	0.125448	-0.304764
25	1	0	-4.445983	0.203390	0.746086
26	1	0	-4.685670	0.875032	-0.896175
27	1	0	-4.388791	-0.876285	-0.672101
28	8	0	2.854570	-1.573193	1.541361
29	1	0	2.976224	-2.530783	1.452504
30	1	0	2.259227	-1.068155	0.473433
31	1	0	2.321834	-1.429004	2.338206

10. The atom coordinate tables of two product structures in Figure 15

The optmizated product structure of C_3 protonated 2, 4, 6-trimethyl -benzoic acid



Basis set: rb3lyp/6-311g(d,p)

scrf=(solvent=ch3oh, pcm)

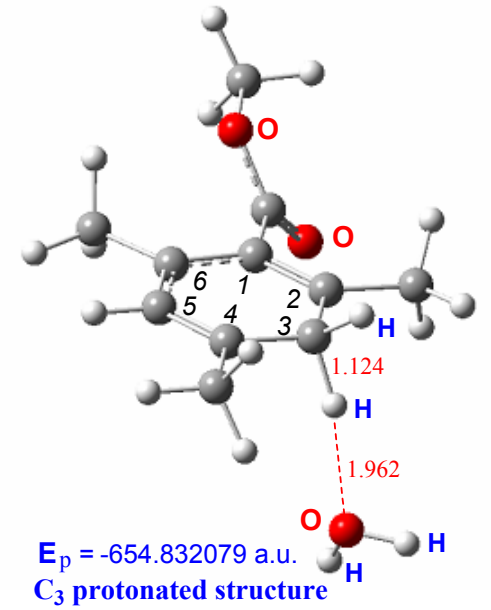
Zero-point correction = 0.259119 Hartree

Sum of electronic and zero-point Energies = -654.825725 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.211553	1.349167	-0.320802
2	6	0	1.329871	-0.005686	0.112583
3	6	0	-0.018538	2.032355	-0.224255
4	6	0	0.229427	-0.673072	0.611398
5	6	0	-1.138017	1.435540	0.293559
6	6	0	-1.065078	0.022949	0.693968
7	6	0	-2.444680	2.139848	0.414651
8	6	0	2.374433	2.088254	-0.900844
9	6	0	0.254204	-2.101607	1.054061
10	1	0	2.906013	1.481400	-1.637349
11	1	0	2.054303	3.019722	-1.363503
12	1	0	3.094488	2.315002	-0.108843
13	1	0	-2.754321	2.181564	1.464240
14	1	0	-2.398508	3.153043	0.018353
15	1	0	-3.212666	1.569509	-0.117799

16	1	0	1.135468	-2.321420	1.659083
17	1	0	-0.641629	-2.352365	1.620468
18	1	0	0.306524	-2.752816	0.176608
19	6	0	2.637331	-0.745041	-0.000140
20	1	0	-0.062627	3.059160	-0.565537
21	8	0	3.656613	-0.063790	0.542792
22	8	0	2.752857	-1.836409	-0.500334
23	1	0	4.468432	-0.583621	0.422446
24	1	0	-1.532430	-0.143232	1.673964
25	8	0	-3.373420	-0.878364	-1.059310
26	1	0	-1.786995	-0.521475	0.026701
27	6	0	-4.318717	-1.897167	-0.706704
28	1	0	-4.523491	-1.784229	0.357502
29	1	0	-3.160214	-0.968685	-1.994666
30	1	0	-3.919650	-2.899746	-0.887888
31	1	0	-5.254489	-1.774534	-1.260130

The product structure of C_3 protonated methyl 2, 4, 6-trimethyl -benzoate



Basis set: rb3lyp/6-311g(d,p)

scrf=(solvent=h2o, pcm)

Zero-point correction = 0.257928 Hartree

Sum of electronic and zero-point Energies = -654.82079 Hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.360513	-0.894933	-0.474973
2	6	0	-0.589835	-0.006837	-0.016230
3	6	0	1.745899	-0.438944	-0.670655
4	6	0	-0.231569	1.344655	0.263237
5	6	0	2.068511	0.974434	-0.426287
6	1	0	2.133136	-0.780704	-1.640200
7	6	0	1.087695	1.800048	0.057354
8	1	0	1.314379	2.834166	0.285555
9	6	0	3.466270	1.432445	-0.661702
10	6	0	0.074000	-2.335126	-0.761205
11	6	0	-1.235529	2.318036	0.791774
12	1	0	-0.835511	-2.449584	-1.354922
13	1	0	0.904083	-2.804991	-1.286683
14	1	0	-0.094843	-2.868558	0.178419
15	1	0	3.612101	2.466602	-0.353089
16	1	0	4.157921	0.782906	-0.116056
17	1	0	3.717505	1.340516	-1.723748
18	1	0	-1.818770	1.883627	1.607246
19	1	0	-0.753769	3.229915	1.139096
20	1	0	-1.947788	2.571735	0.000954
21	6	0	-1.996541	-0.499001	0.215790
22	8	0	-2.267138	-1.463028	0.891622
23	8	0	-2.893427	0.243719	-0.436331
24	6	0	-4.284250	-0.133232	-0.274451
25	1	0	-4.571810	-0.057149	0.773776
26	1	0	-4.843598	0.573658	-0.880121
27	1	0	-4.436923	-1.152143	-0.628479
28	8	0	3.947560	-1.531516	1.124136
29	1	0	4.272168	-2.390454	0.829240
30	1	0	2.399590	-1.024080	0.031235
31	1	0	3.667456	-1.677610	2.035377