

Electronic Supplementary Information (ESI) for

A W1 Computational Study on the Kinetics of Initial Pyrolysis of Biodiesel Model: Methyl Propanoate

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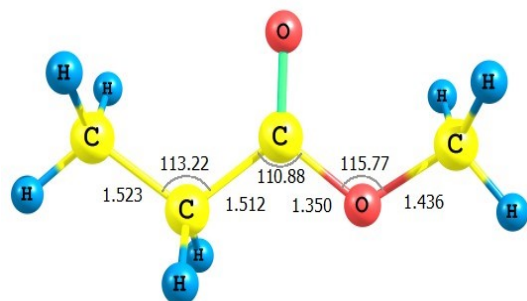
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Table 1S. Optimized structures of MePr and their transition states for unimolecular decomposition at W1 level.



MePr (A)

6	-1.213664000	-0.735594000	-0.000003000
1	-1.173016000	-1.396802000	0.868884000
1	-1.172928000	-1.396644000	-0.869009000
6	0.051184000	0.091857000	0.000139000
8	0.105304000	1.295638000	0.000020000
8	1.144609000	-0.700230000	0.000015000
6	2.409338000	-0.019529000	-0.000097000
1	2.507493000	0.606018000	-0.885670000
1	2.507768000	0.605785000	0.885612000
1	3.162986000	-0.801008000	-0.000313000
6	-2.482619000	0.105992000	-0.000002000
1	-2.526722000	0.749493000	-0.877500000
1	-3.363496000	-0.535800000	-0.000110000
1	-2.526825000	0.749339000	0.877604000

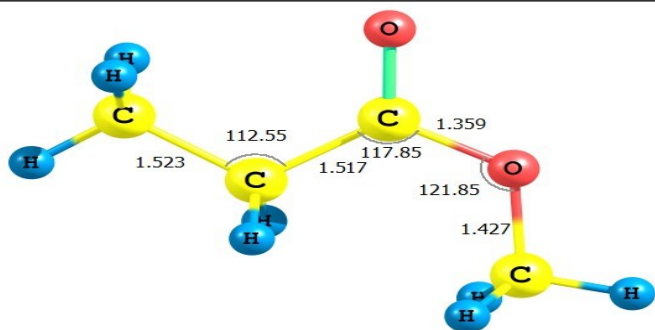
Rotational constants (GHZ): 9.5550804 2.1335621 1.8029798

Energies

W1U Electronic Energy	-307.839086		
W1U (0 K)=	-307.722947	W1U Energy=	-307.715466
W1U Enthalpy=	-307.714522	W1U Free Energy=	-307.754919

FREQUENCIES (in cm⁻¹)

38.9264	656.7671	1200.7614	1495.7512	3107.3757
126.6074	816.2987	1219.1439	1501.1827	3113.5436
154.4334	859.6700	1285.7509	1504.3725	3117.3517
207.5327	979.1429	1384.2165	1797.2100	3149.7440
215.2524	1031.5883	1423.5580	3037.4374	
329.5376	1106.2400	1464.8604	3045.0365	
444.8824	1112.4055	1473.4132	3049.1601	
583.7386	1175.8014	1485.5020	3061.0188	



MePr (B)

6	-2.241599000	-0.588682000	-0.000052000
1	-2.564088000	-0.030173000	0.876954000
1	-2.563922000	-0.030223000	-0.877151000
1	-2.744602000	-1.555871000	-0.000073000
6	-0.730011000	-0.778386000	0.000098000
1	-0.414123000	-1.360329000	0.870348000
1	-0.413954000	-1.360372000	-0.870062000
6	0.021895000	0.539728000	0.000153000
8	-0.514237000	1.613660000	-0.000100000
8	1.380317000	0.495838000	-0.000034000
6	2.094073000	-0.740333000	-0.000016000
1	1.879678000	-1.331659000	-0.891271000
1	3.146317000	-0.469828000	-0.000176000
1	1.879909000	-1.331497000	0.891402000

Rotational constants (GHZ): 6.23136 2.56590 1.88079

Energies

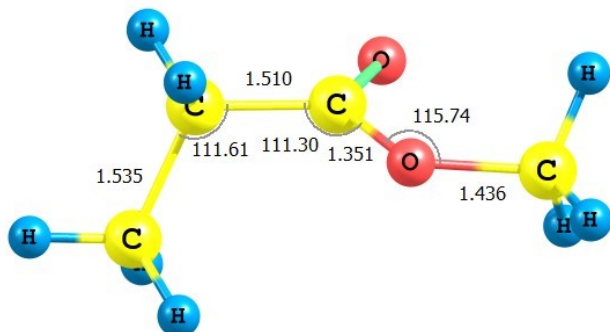
W1U Electronic Energy -307.827286

W1U (0 K)= -307.711194 W1UEnergy= -307.703869

W1U Enthalpy= -307.702925 W1U Free Energy= -307.742494

FREQUENCIES (in cm⁻¹)

82.5596	581.9490	1169.6602	1500.1209	3089.4926
119.1341	780.7698	1233.9364	1503.2279	3109.6515
190.5398	823.7355	1293.5582	1504.7252	3119.6845
216.8580	1002.4139	1381.4129	1818.6567	3132.5785
234.0881	1074.9155	1425.4807	3022.7192	
322.2675	1098.0346	1459.5652	3029.2134	
526.7418	1105.6630	1485.3816	3046.6401	
549.3061	1154.3022	1495.3529	3050.0737	



MePr(C)

6	2.160984000	-0.584703000	0.481649000
1	3.185601000	-0.747413000	0.148127000
1	2.195088000	-0.007809000	1.406039000
1	1.716458000	-1.555425000	0.698634000
6	1.361575000	0.157967000	-0.598388000
1	1.341306000	-0.432283000	-1.514931000
1	1.819454000	1.121516000	-0.813638000
6	-0.056124000	0.427039000	-0.154348000
8	-0.462073000	1.469866000	0.293264000
8	-0.830159000	-0.672286000	-0.290447000
6	-2.189997000	-0.536367000	0.151545000
1	-2.225095000	-0.280919000	1.209277000
1	-2.700012000	0.240570000	-0.415408000
1	-2.653573000	-1.502490000	-0.023377000

Rotational constants (GHZ): 6.6424425 2.4033480 2.0091126

Energies

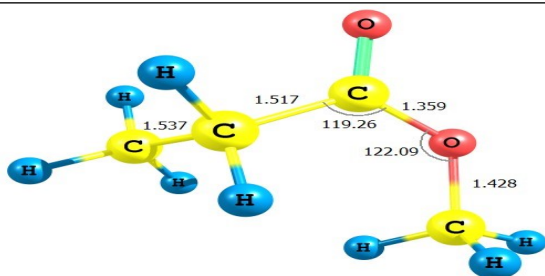
W1U Electronic Energy -307.837693

W1U (0 K)= -307.721244 W1U Energy= -307.713785

W1U Enthalpy= -307.712840 W1U Free Energy= -307.753946

FREQUENCIES (in cm⁻¹)

17.4976	757.2029	1208.1314	1500.6790	3103.9989
122.4340	799.6635	1237.7023	1502.3124	3117.7841
142.1431	854.1332	1308.6812	1511.6392	3119.6272
219.6495	959.6671	1351.8340	1797.5951	3149.3764
270.5053	1026.9714	1413.3965	3038.5651	
299.6486	1090.0132	1471.9554	3049.0611	
430.2170	1104.8868	1484.3951	3057.5620	
617.7427	1175.4934	1484.7161	3096.6332	



MePr(D)

6	-1.786411000	-0.958880000	-0.428175000
1	-1.178643000	-1.513073000	-1.144448000
1	-2.509201000	-1.650403000	0.003997000
1	-2.331530000	-0.190178000	-0.974340000
6	-0.930041000	-0.321020000	0.676951000
1	-0.408677000	-1.090796000	1.243502000
1	-1.574442000	0.220245000	1.367258000
6	0.019782000	0.710947000	0.097856000
8	-0.313605000	1.844947000	-0.114165000
8	1.281974000	0.336593000	-0.239716000
6	1.775492000	-0.980303000	0.010806000
1	2.768221000	-1.008400000	-0.430090000
1	1.857265000	-1.179186000	1.080246000
1	1.157125000	-1.744993000	-0.459705000

Rotational constants (GHZ): 4.45534 3.17887 2.10588

Energies

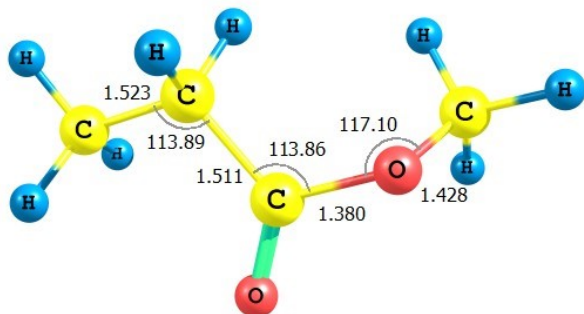
W1U Electronic Energy -307.824675

W1U (0 K)= -307.708223 W1U Energy= -307.700934

W1U Enthalpy= -307.699989 W1U Free Energy -307.739595

FREQUENCIES (in cm⁻¹)

68.4502	718.1711	1183.7042	1503.3192	3094.7885
128.8304	771.0595	1235.3869	1506.8020	3107.0795
186.4542	812.9397	1304.3408	1515.3741	3119.1627
215.8489	973.6815	1349.0842	1816.0427	3132.5510
244.7770	1056.5709	1415.4006	3028.9753	
324.6546	1088.0947	1481.7759	3037.6438	
484.4330	1098.2801	1489.5484	3068.7184	



TS(A---B)

6	-2.333898000	-0.380594000	0.227666000
1	-3.002506000	-1.231295000	0.095747000
1	-2.320755000	-0.116529000	1.284650000
1	-2.745261000	0.468907000	-0.314879000
6	-0.935100000	-0.718599000	-0.270820000
1	-0.523868000	-1.583993000	0.255263000
1	-0.946582000	-1.007115000	-1.326064000
6	0.047880000	0.423140000	-0.156431000
8	-0.232688000	1.542180000	0.160444000
8	1.329225000	0.098234000	-0.551876000
6	2.156408000	-0.565517000	0.404007000
1	3.106031000	-0.754322000	-0.089029000
1	2.323158000	0.069298000	1.276889000
1	1.725750000	-1.518843000	0.722339000

Rotational constants (GHZ): 6.7632949 2.3291463 1.9273154

Energies

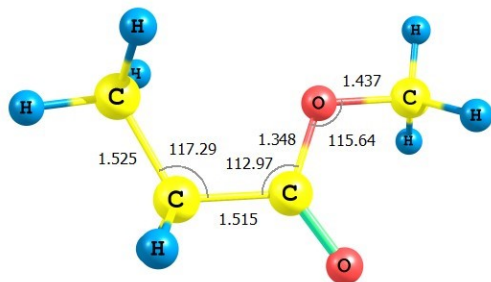
W1U Electronic Energy -307.818259

W1U (0 K)= -307.703083 W1U Energy= -307.696227

W1U Enthalpy= -307.695283 W1U Free Energy= -307.734110

FREQUENCIES (in cm⁻¹)

-122.0452	606.5239	1168.7028	1496.0237	3066.1527
64.5036	790.1592	1208.7399	1503.2303	3104.9653
139.0456	826.3218	1287.8652	1506.0635	3115.0885
196.3729	992.0120	1378.0755	1826.6697	3130.1922
242.8495	1046.8506	1423.1789	3007.4077	
268.9322	1086.8091	1455.6168	3028.9974	
460.9936	1111.8636	1480.2177	3043.8183	
575.2113	1139.9632	1495.0343	3051.5878	



TS(A---C)

6	-2.117294000	-0.803580000	-0.000158000
1	-3.197912000	-0.658135000	-0.000868000
1	-1.854944000	-1.391072000	-0.878860000
1	-1.856098000	-1.390976000	0.878959000
6	-1.409095000	0.547355000	0.000196000
1	-1.701991000	1.142712000	-0.867431000
1	-1.702104000	1.141921000	0.868425000
6	0.105693000	0.537456000	0.000011000
8	0.783785000	1.534262000	-0.000153000
8	0.623664000	-0.707464000	0.000064000

6	2.058327000	-0.783902000	0.000023000
1	2.466214000	-0.299338000	-0.885254000
1	2.466228000	-0.300013000	0.885669000
1	2.295227000	-1.843452000	-0.000363000

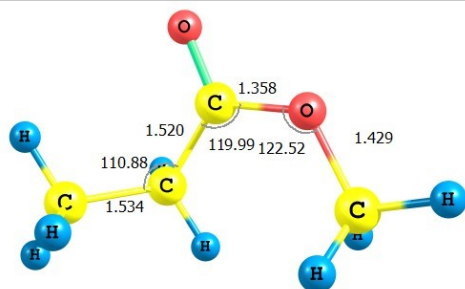
Rotational constants (GHZ): 6.0976530 2.6613900 1.9182221

Energies

W1U Electronic Energy -307.836991
W1U (0 K)= -307.720789 W1U Energy= -307.714252
W1U Enthalpy= -307.713308 W1U Free Energy= -307.751015

FREQUENCIES (in cm⁻¹)

-34.0638	615.4089	1209.0936	1499.3549	3101.9006
129.8940	810.9088	1263.0430	1500.4595	3112.5449
169.6439	845.3049	1294.9273	1506.4412	3119.5373
205.7113	967.0935	1358.5469	1790.8497	3150.2094
240.5060	1040.6531	1424.9033	3041.7506	
328.9290	1100.9094	1463.1648	3042.2824	
491.3143	1114.2147	1474.5680	3050.3073	
593.1308	1176.2923	1484.7065	3065.0690	



TS(B--D)

6	1.989574000	-0.796087000	-0.389703000
1	1.607713000	-1.164841000	-1.342677000
1	2.554348000	0.114292000	-0.580969000
1	2.666801000	-1.547888000	0.014801000
6	0.850027000	-0.515887000	0.598699000
1	0.287919000	-1.424896000	0.796693000
1	1.270805000	-0.181664000	1.548249000
6	-0.021944000	0.628846000	0.109606000
8	0.413237000	1.738654000	-0.036666000
8	-1.329201000	0.408560000	-0.185045000
6	-1.935862000	-0.879709000	-0.070257000
1	-1.952755000	-1.226356000	0.963678000
1	-2.957908000	-0.750410000	-0.415924000
1	-1.439975000	-1.618930000	-0.700233000

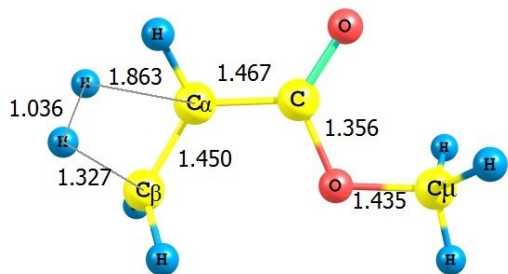
Rotational constants (GHZ): 5.0803887 2.8294163 2.0160031

Energies

W1U Electronic Energy -307.823940
W1U (0 K)= -307.707649 W1U Energy= -307.701175
W1U Enthalpy= -307.700231 W1U Free Energy= -307.737812

FREQUENCIES (in cm⁻¹)

-52.0781	689.9345	1174.5429	1502.3036	3096.2648
117.6591	781.3732	1233.7813	1508.0985	3106.8908
202.8253	807.7324	1296.1525	1513.5891	3125.0607
222.0165	981.7706	1366.3827	1812.9643	3131.9294
259.6395	1069.9622	1413.9127	3026.6939	
316.3607	1089.2619	1481.7909	3037.4176	
483.1799	1099.3517	1487.7500	3056.9804	
568.2495	1168.3810	1500.2695	3092.6978	



TS1

6	1.343861000	0.427066000	-0.051242000
1	1.797182000	1.335403000	-0.401243000
1	3.097802000	0.664902000	0.529837000
6	2.060895000	-0.833717000	-0.060071000
1	2.405715000	-1.272850000	0.866923000
1	1.656234000	-1.624464000	-0.704917000
1	3.211432000	-0.172004000	-0.069293000
6	-0.119277000	0.516980000	-0.001362000
8	-0.742420000	1.555880000	0.015900000
8	-0.703993000	-0.705593000	0.031116000
6	-2.139055000	-0.706673000	0.010049000
1	-2.531354000	-0.193123000	0.886200000
1	-2.511707000	-0.210125000	-0.884664000
1	-2.432542000	-1.751980000	0.016786000

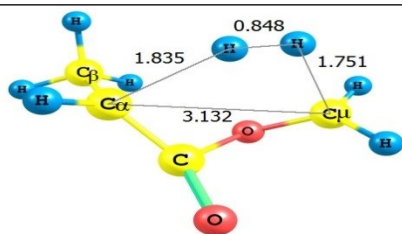
Rotational constants (GHZ): 6.3658688 2.5496878 1.8660241

Energies

W1U Electronic Energy	-307.638425		
W1U (0 K)=	-307.533507	W1U Energy=	-307.526040
W1U Enthalpy=	-307.525096	W1U Free Energy=	-307.564786

FREQUENCIES (in cm⁻¹)

-1775.7734	516.3818	1143.9549	1472.0111	3116.0579
101.9237	632.5859	1174.1539	1484.0409	3147.4076
132.4414	793.3747	1192.9544	1500.4727	3149.4460
150.9722	837.1148	1209.5937	1593.4993	3260.2212
190.9129	919.3557	1233.7702	1747.2100	
277.4807	975.1662	1310.9394	1872.3255	
324.3749	1027.9989	1376.8451	2983.6756	
400.2152	1040.1967	1418.0046	3047.9757	



TS2

6	1.116807000	0.465092000	0.373102000
1	1.494495000	1.262415000	1.002143000
1	0.050282000	-0.468252000	1.538575000
6	2.117533000	-0.523997000	-0.153875000
1	1.665447000	-1.240212000	-0.833953000
1	2.922851000	-0.011549000	-0.688419000
1	2.586476000	-1.082031000	0.659439000
6	-0.133886000	0.751856000	-0.156329000
8	-0.955031000	1.615051000	-0.113391000
8	-0.666557000	-0.686493000	-0.587596000
6	-1.593973000	-1.092045000	0.190331000
1	-0.644201000	-0.940501000	1.653983000
1	-2.343212000	-0.396229000	0.556578000
1	-1.798327000	-2.157541000	0.200176000

Rotational constants (GHZ): 4.9311389 3.0263199 2.1327463

Energies

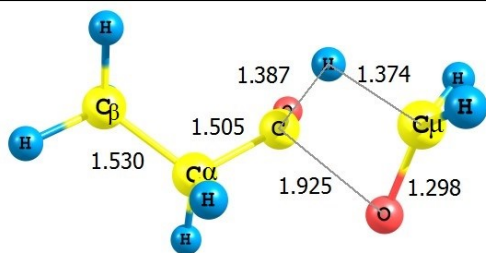
W1U Electronic Energy -307.670329

W1U (0 K)= -307.565124 W1U Energy= -307.557875

W1U Enthalpy= -307.556931 W1U Free Energy= -307.595922

FREQUENCIES (in cm⁻¹)

-772.889	544.6260	1074.9252	1420.6701	3087.4691
98.5625	613.9027	1090.4904	1490.4648	3130.8095
134.7277	695.7733	1116.9005	1506.4662	3159.8961
193.0642	726.3900	1156.8107	1541.2939	3201.7536
276.2677	776.6006	1196.4679	1878.6516	
319.1729	833.1710	1220.5440	2690.1813	
374.1863	911.2974	1383.2224	3012.6446	
516.4184	1050.1263	1407.7377	3051.2069	



TS3

6	-0.973996000	-0.569297000	-0.409565000
1	-0.579861000	-1.561145000	-0.217611000
1	-1.084022000	-0.461035000	-1.489188000
6	0.037312000	0.465805000	0.003977000
8	0.090158000	1.638066000	-0.076079000
8	1.569838000	-0.477662000	-0.677926000
6	1.806451000	-0.459426000	0.598296000

1	1.976467000	-1.409880000	1.130288000
1	2.352337000	0.390391000	1.036005000
1	0.602985000	-0.084592000	1.144096000
6	-2.305544000	-0.326523000	0.304834000
1	-2.689440000	0.671477000	0.098560000
1	-3.039833000	-1.054049000	-0.040287000
1	-2.203942000	-0.437752000	1.384933000

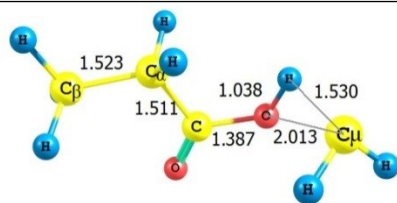
Rotational constants (GHZ): 5.8904406 2.4153940 2.0223197

Energies

W1U Electronic Energy -307.708918
W1U (0 K)= -307.599074 W1U Energy= -307.592044
W1U Enthalpy= -307.591100 W1U Free Energy= -307.629763

FREQUENCIES (in cm⁻¹)

-1143.322	553.9090	1204.0624	1497.3283	3067.3863
90.8648	693.9250	1260.1685	1507.0045	3102.1133
192.4502	726.3867	1280.2788	1527.6962	3111.2646
215.1803	808.3823	1308.4999	1611.8844	3149.6356
241.7373	918.5650	1339.9735	1922.3353	
314.0800	1009.6693	1417.5753	2913.0382	
358.1460	1089.1409	1472.1059	2972.8351	
407.8306	1149.3592	1476.5192	3039.0106	



TS4

6	0.883078000	-0.705095000	-0.351150000
1	0.916636000	-0.882053000	-1.430594000
6	2.286533000	-0.572516000	0.225457000
1	2.810682000	0.274445000	-0.213728000
1	2.253354000	-0.415118000	1.302648000
1	2.862640000	-1.476017000	0.028024000
6	0.029651000	0.521956000	-0.131738000
8	0.392002000	1.556525000	0.340777000
8	-1.278851000	0.407757000	-0.576194000
1	-3.296808000	-0.254285000	0.463289000
6	-2.420162000	-0.910469000	0.429613000
1	-1.543096000	-0.575858000	-0.779028000
1	-1.938398000	-0.822449000	1.411806000
1	0.355186000	-1.566175000	0.067823000

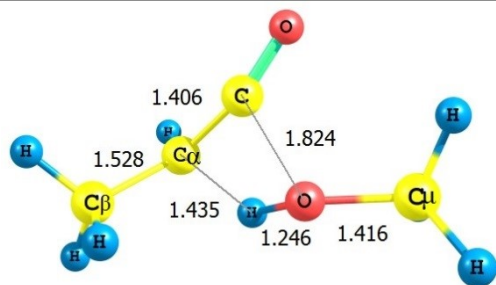
Rotational constants (GHZ): 5.6648519 2.2090544 1.7961745

Energies

W1U Electronic Energy -307.680047
W1U (0 K)= -307.572336 W1U Energy= -307.564302
W1U Enthalpy= -307.563358 W1U Free Energy= -307.604837

FREQUENCIES (in cm⁻¹)

-511.487	472.7260	1064.2876	1464.8049	3052.0715
63.8582	560.9218	1112.4425	1495.9331	3093.7110
73.3282	625.2989	1126.1463	1504.0248	3111.5826
141.7741	771.7190	1286.7498	1851.2106	3118.5558
208.3111	816.4705	1299.5188	2653.7512	
231.5569	830.0665	1383.3463	3012.4608	
281.4443	1007.0557	1405.8466	3025.7030	
346.5752	1032.9461	1425.2787	3048.3421	



TS5

6	1.226662000	0.197718000	0.564818000
1	1.722905000	0.887817000	1.242876000
1	0.132195000	-0.723308000	0.683457000
6	2.174260000	-0.688112000	-0.242848000
1	1.628766000	-1.343030000	-0.918540000
1	2.876407000	-0.096963000	-0.835120000
1	2.754510000	-1.312309000	0.435735000
6	0.117586000	0.800989000	-0.054704000
8	-0.564212000	1.728586000	-0.228884000
8	-0.721651000	-0.809657000	-0.220344000
6	-2.093125000	-0.742393000	0.125596000
1	-2.234998000	-0.634513000	1.206249000
1	-2.554241000	0.115670000	-0.370081000
1	-2.590933000	-1.654006000	-0.207930000

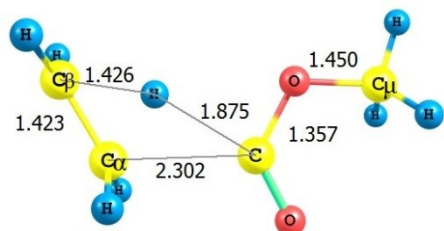
Rotational constants (GHZ): 5.1407488 2.6221948 1.8890457

Energies

W1U Electronic Energy -307.709609

FREQUENCIES (in cm⁻¹)

-1782.363	517.7495	1138.5500	1498.8473	3077.2172
104.3218	587.7793	1169.9318	1499.6682	3082.9439
145.8138	675.1543	1170.8944	1512.5632	3106.8371
165.2907	842.9645	1336.8122	1808.5573	3126.1328
177.5122	895.2202	1344.3404	2032.5197	
201.0224	1045.0942	1419.6311	2989.5598	
248.8661	1063.5873	1470.4064	3023.8279	
324.4099	1090.3213	1495.0021	3050.7751	



TS6

6	-0.309632000	0.449126000	-0.000856000
8	-0.864838000	1.513096000	-0.003706000
6	1.991969000	0.484906000	0.007231000
1	1.910348000	1.048649000	0.922864000
1	1.915213000	1.069980000	-0.895380000
6	2.695670000	-0.751803000	-0.004595000
1	2.926139000	-1.237254000	-0.939050000
1	2.921876000	-1.257399000	0.920159000
1	1.286715000	-0.534217000	-0.006422000
8	-0.953695000	-0.744944000	0.001866000
6	-2.403469000	-0.703320000	0.000320000
1	-2.764940000	-0.181525000	0.884536000
1	-2.763306000	-0.188517000	-0.888656000
1	-2.731004000	-1.738389000	0.004066000

Rotational constants (GHZ): 6.5518698 1.7675676 1.4314055

Energies

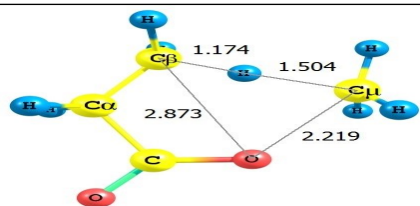
W1U Electronic Energy -307.649199

W1U (0 K)= -307.541713 W1U Energy= -307.534133

W1U Enthalpy= -307.533189 W1U Free Energy= -307.573908

FREQUENCIES (in cm⁻¹)

-1524.348	360.0865	1108.6752	1480.9945	3165.5384
21.655	532.8583	1152.7761	1492.6370	3168.9411
73.9279	725.7681	1183.2510	1495.9052	3249.0940
83.7728	739.2282	1206.1627	1760.6387	3278.5330
114.3356	767.1396	1236.5442	2281.5393	
247.3306	912.4403	1273.2231	3049.1068	
285.9162	949.9968	1447.6589	3120.6434	
325.9838	1021.5598	1456.6209	3150.4238	

**TS7**

1	1.921788000	-1.461282000	-0.882948000
6	2.113824000	-0.917944000	0.025227000
1	1.890385000	-1.432482000	0.942906000
8	-0.087499000	-1.193530000	-0.009447000
6	-0.991071000	-0.305796000	-0.002260000
8	-2.202381000	-0.456813000	-0.035289000
6	-0.506078000	1.212845000	0.088188000
1	-1.100963000	1.690631000	-0.688285000
6	0.943165000	1.487924000	-0.073143000
1	1.253425000	1.857240000	-1.048202000
1	1.430283000	0.420995000	-0.016027000
1	-0.876745000	1.536116000	1.059722000
1	3.009664000	-0.304313000	0.031804000
1	1.432163000	2.033666000	0.730843000

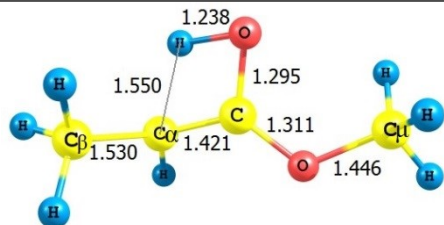
Rotational constants (GHZ): 4.8711853 2.7260983 1.8121315

Energies

W1U Electronic Energy -307.686448
W1U (0 K)= -307.578011 W1U Energy= -307.570578
W1U Enthalpy= -307.569634 W1U Free Energy= -307.610245

FREQUENCIES (in cm⁻¹)

-694.848	563.7570	1064.9917	1439.6759	3113.0123
34.5617	601.9122	1134.4869	1455.4640	3145.5746
77.3927	622.1959	1188.4265	1488.1254	3247.0807
157.5807	776.2775	1252.1482	1710.6028	3311.5418
281.7964	798.0341	1318.7294	2069.9948	
350.7028	859.1300	1321.4081	3063.1323	
419.6903	982.7512	1343.4620	3075.8847	
487.0043	1043.1289	1438.1521	3085.3346	



TS8

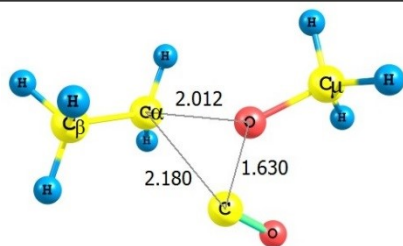
6	-1.257112000	-0.350147000	-0.567474000	
1	-1.304503000	-1.267156000	-1.148336000	
1	-0.888315000	1.150652000	-0.691808000	
6	0.042202000	0.033735000	-0.137864000	
8	0.155719000	1.321163000	-0.048911000	
8	1.075539000	-0.755775000	0.030699000	
6	2.376212000	-0.142267000	0.179673000	
1	2.472968000	0.279287000	1.177463000	
1	3.095109000	-0.942539000	0.034819000	
1	2.506903000	0.642250000	-0.562001000	
6	-2.418985000	-0.195540000	0.415833000	
1	-2.313816000	0.698166000	1.032182000	
1	-3.359998000	-0.104389000	-0.127320000	
1	-2.512322000	-1.054056000	1.089686000	
Rotational constants (GHZ):				8.7736379 2.1413086 1.8801627

Energies

W1U Electronic Energy -307.713520
W1U (0 K)= -307.602948 W1U Energy= -307.595816
W1U Enthalpy= -307.594872 W1U Free Energy= -307.633928

FREQUENCIES (in cm⁻¹)

-2052.434	707.7188	1151.1342	1497.5958	3086.8521
110.3332	741.7713	1173.0858	1503.4605	3112.9587
111.5664	842.4134	1207.7271	1516.5365	3136.1534
176.5870	878.4986	1295.3628	1530.6818	3157.5295
215.6844	965.1191	1406.2687	1969.8117	
284.8307	1044.8308	1425.7043	2989.5061	
308.0589	1079.4928	1482.1576	3056.6990	
459.2278	1100.1926	1490.8986	3058.0031	



TS9

6	-1.236160000	-0.129343000	0.678524000
1	-1.062303000	-1.107921000	1.107192000
1	-1.163843000	0.661891000	1.409525000
6	-2.342175000	-0.050239000	-0.309420000
1	-2.143732000	-0.683719000	-1.171251000
1	-2.514118000	0.966603000	-0.649305000
1	-3.252627000	-0.432260000	0.171191000
6	0.367970000	1.041228000	-0.220416000
8	1.382428000	1.546481000	0.076652000
8	0.413941000	-0.579970000	-0.380059000
6	1.571377000	-1.302538000	0.039909000
1	2.116564000	-1.662272000	-0.834427000
1	2.227486000	-0.662537000	0.634169000
1	1.255547000	-2.166521000	0.628574000

Rotational constants (GHZ): 4.8607811 2.5211937 1.8582214

Energies

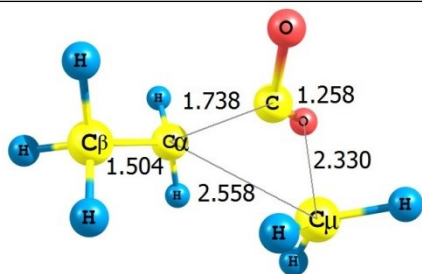
W1U Electronic Energy -307.666765

W1U (0 K)= -307.556886 W1U Energy= -307.548575

W1U Enthalpy= -307.547631 W1U Free Energy= -307.589400

FREQUENCIES (in cm⁻¹)

-759.44	335.9605	1144.8393	1491.8248	3098.0867
90.8529	440.4158	1162.2609	1501.2648	3131.0399
98.1769	660.2672	1183.0355	1507.9770	3145.8269
125.3916	791.0566	1228.8646	1878.5324	3218.1368
188.6509	895.4349	1400.6197	2988.3012	
216.1897	955.5750	1433.5743	3007.1410	
233.5799	972.8662	1455.6816	3074.6444	
262.1441	1094.8212	1473.6863	3079.1583	



TS10

6	0.897778000	-0.201827000	-0.779413000
6	2.077989000	0.073702000	0.110439000
6	-0.628066000	-0.388938000	0.030787000
8	-1.564554000	-0.407078000	-0.808306000
8	-0.484616000	-0.890196000	1.153729000

1	0.756624000	0.498486000	-1.594288000
1	0.918511000	-1.212135000	-1.180386000
1	2.994569000	-0.109674000	-0.458089000
1	2.124312000	1.106929000	0.456239000
1	2.073539000	-0.584777000	0.975871000
6	-0.719602000	1.460280000	0.300322000
1	0.136319000	1.618845000	0.937096000
1	-1.675078000	1.482181000	0.801735000
1	-0.704035000	1.919035000	-0.674368000

Rotational constants (GHZ): 4.9677209 2.7348070 2.6409773

Energies

W1U Electronic Energy -307.679552

W1U (0 K)= -307.569641 W1U Energy= -307.561807

W1U Enthalpy= -307.560863 W1U Free Energy= -307.601141

FREQUENCIES (in cm^{-1})

-470.15	395.6545	1071.1888	1485.0853	3125.2323
87.4778	458.8194	1151.0767	1487.3401	3164.3168
97.9780	660.2220	1220.7547	1502.1214	3266.8813
197.7572	759.9204	1259.8358	1620.6999	3282.0928
252.5467	806.3732	1288.0200	3022.4579	
273.5731	854.0782	1403.6793	3071.4205	
298.9909	959.3353	1430.2351	3097.1737	
339.9687	1022.3151	1448.2802	3117.1701	

Table 2SA. T1 diagnostic values at ROCCSD (T)/6-31+G (d) [1st single point level of ROCBS-QB3], before and after annihilation spin contamination $\langle S^2 \rangle$ for different structures at ROB3LYP/6-311G(d,p) level.

Structure	T1 diagnostic values	Before annihilation $\langle S^2 \rangle$	After annihilation $\langle S^2 \rangle$
MePr	0.014	-	-
TS1	0.017	-	-
TS2	0.019	-	-
TS3	0.015	-	-
TS4	0.018	-	-
TS5	0.017	-	-
TS6	0.022	-	-
TS7	0.016	-	-
TS8	0.017	-	-
TS9	0.028	-	-
TS10	0.026	-	-
$\bullet\text{CH}_3$	0.015	0.7536	0.7500
$\bullet\text{CH}_2\text{C}(\text{O})\text{OCH}_3$	0.019	0.7539	0.7500
$\text{CH}_3\bullet\text{CH}_2$	0.015	0.7540	0.7500
$\bullet\text{C}(\text{O})\text{OCH}_3$	0.025	0.7532	0.7500
$\text{CH}_3\text{CH}_2\bullet(\text{O})$	0.021	0.7529	0.7500
$\bullet\text{OCH}_3$	0.019	0.7535	0.7500
$\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{O}\bullet$	0.022	0.7560	0.7500
$\bullet\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3$	0.017	0.7539	0.7500
$\text{CH}_3\bullet\text{CHC}(\text{O})\text{OCH}_3$	0.018	0.7563	0.7500
$\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{O}\bullet\text{CH}_2$	0.018	0.7539	0.7500

Table 2SB. Reaction energy (ΔE_0), enthalpy change (ΔH_{298}), Gibbs free energy (ΔG_{298}) for MePr pyrolysis using W1 and ROCBS-QB3 (in parentheses) methods (kcal mol⁻¹, T = 298 K, P = 1 atm).

R	State	W1(ROCBS-QB3)		
		ΔE_0^\ddagger	ΔH_{298}^\ddagger	ΔG_{298}^\ddagger
	MePr [CH ₃ CH ₂ COOCH ₃]	0.00	0.00	0.00
R1	TS1[CH ₂ CHCOOCH ₃ --H ₂]	118.88(117.57)	118.87(117.55)	119.31(118.05)
	P1[CH ₂ CHCOOCH ₃ + H ₂]	29.59	31.16	23.35
R2	TS2[CH ₃ CHCOOCH ₂ --H ₂]	97.02(96.11)	98.89(96.20)	99.77(96.41)
	P2[CH ₃ CHCOOCH ₂ +H ₂]	28.05	29.07	22.52
R3	TS3[CH ₃ CH ₂ CH(O)--CH ₂ O]	77.73(78.12)	77.45(78.05)	78.54(77.12)
	P3[CH ₃ CH ₂ CH(O)+CH ₂ O]	31.41	32.27	20.75
R4	TS4[CH ₃ CH ₂ COOH--CH ₂]	94.51(95.25)	94.86(95.60)	94.18(94.94)
	P4[CH ₃ CH ₂ COOH+CH ₂]	87.25	88.59	77.43
R5	TS5[CH ₃ CHCO--CH ₃ OH]	77.62(77.44)	77.01(77.59)	76.58(77.71)
	P5[CH ₃ CHCO+CH ₃ OH]	39.11	40.10	28.07
R6	TS6[CH ₃ OHC(O)--CH ₂ CH ₂]	113.73(114.57)	113.79(114.57)	113.59(112.62)
	P6[CH ₃ OHC(O)+CH ₂ CH ₂]	29.41	30.11	19.08
R7	TS7[CH ₂ CH ₂ C(O)O--CH ₄]	90.95(91.22)	90.92(91.01)	90.78(90.8)
	P7[CH ₂ CH ₂ C(O)O+CH ₄]	17.77	18.19	9.95
R8	TS8[CH ₃ CH=C(OH)OCH ₃]	75.30(75.95)	75.08(75.71)	75.92(76.60)
	P8[CH ₃ CH=C(OH)OCH ₃]	28.77	28.75	28.57
R9	TS9[CH ₃ CH ₂ OCH ₃ --CO]	104.20(103.83)	104.73(104.32)	103.86(103.60)
	P9[CH ₃ CH ₂ OCH ₃ +CO]	23.80	24.71	14.38
R10	TS10[CH ₃ CH ₂ CH ₃ --CO ₂]	96.02(94.30)	96.42(94.42)	96.50(94.81)
	P10[CH ₃ CH ₂ CH ₃ +CO ₂]	-16.50	-16.07	-25.15
R11	P11 [\bullet CH ₃ + \bullet CH ₂ C(O)OCH ₃]	85.64(85.70)	87.13(87.20)	75.54(75.59)
R12	P12 [CH ₃ \bullet CH ₂ + \bullet C(O)OCH ₃]	93.72(93.59)	94.16(94.88)	81.55(81.15)
R13	P13[CH ₃ CH ₂ C \bullet (O) + \bullet OCH ₃]	100.61(100.67)	100.89(101.64)	88.94(88.77)
R14	P14 [CH ₃ CH ₂ C(O)O \bullet + \bullet CH ₃]	87.71(87.21)	89.30(88.65)	77.12(76.33)
R15	P15[\bullet CH ₂ CH ₂ C(O)OCH ₃ + \bullet H]	100.51(100.72)	102.12(102.33)	93.47(93.74)
R16	P16 [CH ₃ \bullet CHC(O)OCH ₃ + \bullet H]	92.70(92.59)	93.99(94.05)	85.79(85.84)
R17	P17[CH ₃ CH ₂ C(O)O \bullet CH ₂ + \bullet H]	97.91(98.10)	99.68(99.37)	90.59(91.45)

Table 3S. Unimolecular rate constants k_1 (s^{-1}) of R1 for the reported **MePr** reaction channels obtained by means of TST, TST/W, TST/Eck, W(T), Eck XT) and RRKM theories ($T = 400\text{--}2000$ K, $P = 1$ atm)

k_1 , R1, $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OCH}_3 \rightarrow \text{CH}_2=\text{CHC}(\text{O})\text{OCH}_3 + \text{H}_2$						
T K	TST	TST/ W	TST/Eck	W	Eck	RRKM
400	3.62E-53	1.06E-52	2.35E-51	2.93	64.95	3.75E-53
500	6.40E-40	1.43E-39	3.70E-39	2.24	5.78	6.60E-40
600	4.55E-31	8.46E-31	1.31E-30	1.86	2.88	4.67E-31
700	9.87E-25	1.61E-24	2.04E-24	1.63	2.07	1.01E-24
800	5.72E-20	8.47E-20	9.78E-20	1.48	1.71	5.84E-20
900	2.95E-16	4.07E-16	4.48E-16	1.38	1.52	3.00E-16
1000	2.78E-13	3.64E-13	3.86E-13	1.31	1.39	2.84E-13
1100	7.65E-11	9.64E-11	1.00E-10	1.26	1.31	7.78E-11
1200	8.31E-09	1.01E-08	1.05E-08	1.21	1.26	8.45E-09
1300	4.41E-07	5.20E-07	5.34E-07	1.18	1.21	4.48E-07
1400	1.33E-05	1.54E-05	1.57E-05	1.16	1.18	1.35E-05
1500	2.57E-04	2.93E-04	2.98E-04	1.14	1.16	2.61E-04
1600	3.44E-03	3.85E-03	3.89E-03	1.12	1.13	3.49E-03
1700	3.39E-03	3.76E-03	3.80E-03	1.11	1.12	3.44E-02
1800	2.60E-01	2.86E-01	2.89E-01	1.1	1.11	2.64E-01
1900	1.61E+00	1.75E+00	1.75E+00	1.09	1.09	1.63E+00
2000	8.34E+00	9.01E+00	9.01E+00	1.08	1.08	8.42E+00

Table 4S. Unimolecular rate constants k_2 (s^{-1}) of R2 for the reported **MePr** reaction channels obtained by means of TST, TST/W, TST/Eck, W(T), Eck(T) and RRKM theories ($T = 400\text{--}2000$ K, $P = 1$ atm)

$k_2, R2, CH_3CH_2C(O)OCH_3 \rightarrow CH_3CHC(O)OCH_2 \text{ Cyc} + H_2$						
T K	TST	TST/W	TST/Eck	W	Eck	RRKM
400	4.53E-41	5.80E-41	6.12E-41	1.28	1.35	2.19E-41
500	2.63E-30	3.10E-30	3.18E-30	1.18	1.21	1.32E-30
600	4.19E-23	4.69E-23	4.78E-23	1.12	1.14	2.18E-23
700	6.13E-18	6.68E-18	6.74E-18	1.09	1.1	3.24E-18
800	4.72E-14	5.05E-14	5.10E-14	1.07	1.08	2.52E-14
900	5.09E-11	5.34E-11	5.40E-11	1.05	1.06	2.74E-11
1000	1.38E-08	1.44E-08	1.45E-08	1.04	1.05	7.48E-09
1100	1.36E-06	1.41E-06	1.41E-06	1.04	1.04	7.44E-07
1200	6.32E-05	6.51E-05	6.51E-05	1.03	1.03	3.47E-05
1300	1.64E-03	1.69E-03	1.69E-03	1.03	1.03	9.00E-04
1400	2.67E-02	2.72E-02	2.72E-02	1.02	1.02	1.47E-02
1500	3.00E-01	3.06E-01	3.06E-01	1.02	1.02	1.67E-01
1600	2.53E+00	2.58E+00	2.58E+00	1.02	1.02	1.40E+00
1700	1.65E+01	1.68E+01	1.68E+01	1.02	1.02	9.14E+00
1800	8.78E+01	8.87E+01	8.96E+01	1.01	1.02	4.86E+01
1900	3.92E+02	3.96E+02	3.96E+02	1.01	1.01	2.16E+02
2000	1.51E+03	1.53E+03	1.53E+03	1.01	1.01	8.28E+02

Table 5S. Unimolecular rate constants k_3 (s^{-1}) of R3 for the reported **MePr** reaction channels obtained by means of TST, TST/W, TST/Eck, W(T), Eck(T) and RRKM theories ($T = 400\text{--}2000$ K, $P = 1$ atm)

$K_3, R3, CH_3CH_2C(O)OCH_3 \rightarrow CH_3CH_2CH(O) + CH_2(O)$						
T K	TST	TST/W	TST/Eck	W	Eck	RRKM
400	1.30E-30	1.96E-30	2.31E-30	1.51	1.78	1.34E-30
500	4.78E-22	6.36E-22	6.84E-22	1.33	1.43	4.89E-22
600	2.51E-16	3.09E-16	3.19E-16	1.23	1.27	2.56E-16
700	3.11E-12	3.64E-12	3.70E-12	1.17	1.19	3.16E-12
800	3.69E-09	4.17E-09	4.21E-09	1.13	1.14	3.74E-09
900	9.17E-07	1.01E-06	1.02E-06	1.1	1.11	9.28E-07
1000	7.61E-05	8.22E-05	8.29E-05	1.08	1.09	7.69E-05
1100	2.84E-03	3.04E-03	3.04E-03	1.07	1.07	2.87E-03
1200	5.83E-02	6.18E-02	6.18E-02	1.06	1.06	5.88E-02
1300	7.54E-01	7.92E-01	7.92E-01	1.05	1.05	7.60E-01
1400	6.78E+00	7.05E+00	7.12E+00	1.04	1.05	6.83E+00
1500	4.56E+01	4.74E+01	4.74E+01	1.04	1.04	4.59E+01
1600	2.42E+02	2.49E+02	2.49E+02	1.03	1.03	2.43E+02
1700	1.06E+03	1.09E+03	1.09E+03	1.03	1.03	1.06E+03
1800	3.92E+03	4.04E+03	4.04E+03	1.03	1.03	3.90E+03
1900	1.27E+04	1.30E+04	1.30E+04	1.02	1.02	1.25E+04
2000	3.65E+04	3.72E+04	3.72E+04	1.02	1.02	3.56E+04

Table 6S. Unimolecular rate constants k_4 (s^{-1}) of R4 for the reported **MePr** reaction channels obtained by means of TST, TST/W, TST/Eck, W(T), Eck (T) and RRKM theories ($T = 400$ – 2000 K, $P = 1$ atm)

$k_4, R4, CH_3CH_2C(O)OCH_3 \rightarrow CH_3CH_2C(O)OH + C\cdot H_2$						
T K	TST	TST/W	TST/Eck	W	Eck	RRKM
400	5.58E-39	5.97E-39	5.97E-39	1.07	1.07	5.71E-39
500	2.22E-28	2.31E-28	2.31E-28	1.04	1.04	2.26E-28
600	2.74E-21	2.82E-21	2.82E-21	1.03	1.03	2.78E-21
700	3.28E-16	3.35E-16	3.35E-16	1.02	1.02	3.33E-16
800	2.16E-12	2.20E-12	2.20E-12	1.02	1.02	2.19E-12
900	2.05E-09	2.07E-09	2.07E-09	1.01	1.01	2.07E-09
1000	4.98E-07	5.03E-07	5.03E-07	1.01	1.01	5.03E-07
1100	4.48E-05	4.52E-05	4.57E-05	1.01	1.02	4.53E-05
1200	1.92E-03	1.94E-03	1.92E-03	1.01	1	1.93E-03
1300	4.62E-02	4.67E-02	4.62E-02	1.01	1	4.65E-02
1400	7.08E-01	7.15E-01	7.15E-01	1.01	1.01	7.11E-01
1500	7.55E+00	7.55E+00	7.70E+00	1	1.02	7.56E+00
1600	6.00E+01	6.00E+01	6.00E+01	1	1	5.95E+01
1700	3.75E+02	3.75E+02	7.50E+02	1	1	3.66E+02
1800	1.91E+03	1.91E+03	1.97E+03	1	1.03	1.82E+03
1900	8.21E+03	8.21E+03	8.37E+03	1	1.02	7.51E+03
2000	3.05E+04	3.05E+04	3.05E+04	1	1	2.65E+04

Table 7S. Unimolecular rate constants k_5 (s^{-1}) of R5 for the reported **MePr** reaction channels obtained by means of TST, TST/W, TST/Eck, W(T), Eck(T) and RRKM theories ($T = 400\text{--}2000$ K, $P = 1$ atm)

k_5 , R5, $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OCH}_3 \rightarrow \text{CH}_3\text{CH}=\text{C}(\text{O}) + \text{CH}_3\text{OH}$						
T K	TST	TST/W	TST/Eck	W	Eck	RRKM
400	3.28E-30	8.13E-30	2.91E-29	2.48	8.87	3.39E-30
500	1.33E-21	2.59E-21	4.27E-21	1.95	3.21	1.37E-21
600	7.56E-16	1.21E-15	1.75E-15	1.66	2.31	7.76E-16
700	9.96E-12	1.39E-11	1.70E-11	1.48	1.71	1.02E-11
800	1.24E-08	1.58E-08	1.85E-08	1.37	1.49	1.27E-08
900	3.22E-06	3.78E-06	4.41E-06	1.29	1.37	3.29E-06
1000	2.77E-04	3.09E-04	3.57E-04	1.24	1.29	2.82E-04
1100	1.06E-02	1.14E-02	1.30E-02	1.2	1.23	1.08E-02
1200	2.24E-01	2.30E-01	2.67E-01	1.16	1.19	2.28E-01
1300	2.96E+00	2.96E+00	3.43E+00	1.14	1.16	3.00E+00
1400	2.71E+01	2.64E+01	3.09E+01	1.12	1.14	2.74E+01
1500	1.85E+02	1.79E+02	2.07E+02	1.11	1.12	1.87E+02
1600	9.95E+02	9.37E+02	1.09E+03	1.09	1.1	9.97E+02
1700	4.40E+03	4.09E+03	4.80E+03	1.08	1.09	4.36E+03
1800	1.65E+04	1.52E+04	1.78E+04	1.07	1.08	1.60E+04
1900	5.39E+04	4.93E+04	5.77E+04	1.07	1.07	5.10E+04
2000	1.56E+05	1.42E+05	1.67E+05	1.06	1.07	1.42E+05

Table 8S. Unimolecular rate constants k_6 (s^{-1}) of R6 for the reported **MePr** reaction channels obtained by means of TST, TST/W, TST/Eck, W(T), Eck (T) and RRKM theories ($T = 400$ – 2000 K, $P = 1$ atm)

k_6 , R6, $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OCH}_3 \rightarrow \text{HC}(\text{O})\text{OCH}_3 + \text{CH}_2=\text{CH}_2$						
T K	TST	TST/W	TST/Eck	W	Eck	RRKM
400	3.03E-44	6.88E-44	1.89E-43	2.27	6.24	3.11E-44
500	1.44E-32	2.61E-32	3.86E-32	1.81	2.68	1.47E-32
600	9.26E-25	1.44E-24	1.76E-24	1.56	1.9	9.43E-25
700	3.62E-19	5.10E-19	5.72E-19	1.41	1.58	3.68E-19
800	5.78E-15	7.63E-15	8.15E-15	1.32	1.41	5.86E-15
900	1.09E-11	1.36E-11	1.43E-11	1.25	1.31	1.10E-11
1000	4.60E-09	5.52E-09	5.70E-09	1.2	1.24	4.65E-09
1100	6.51E-07	7.62E-07	7.75E-07	1.17	1.19	6.57E-07
1200	4.05E-05	4.62E-05	4.70E-05	1.14	1.16	4.09E-05
1300	1.34E-03	1.50E-03	1.51E-03	1.12	1.13	1.35E-03
1400	2.70E-02	2.97E-02	3.00E-02	1.1	1.11	2.72E-02
1500	3.65E-01	3.98E-01	4.02E-01	1.09	1.1	3.67E-01
1600	3.57E+00	3.86E+00	3.89E+00	1.08	1.09	3.58E+00
1700	2.67E+01	2.86E+01	2.88E+01	1.07	1.08	2.66E+01
1800	1.60E+02	1.70E+02	1.71E+02	1.06	1.07	1.57E+02
1900	7.95E+02	8.43E+02	8.43E+02	1.06	1.06	7.67E+02
2000	3.37E+03	3.54E+03	3.54E+03	1.05	1.05	3.15E+03

Table 9S. Unimolecular rate constants k_7 (s^{-1}) of R7 for the reported **MePr** reaction channels obtained by means of TST, TST/W, TST/Eck, W(T), Eck (T) and RRKM theories ($T = 400$ – 3000 K, $P = 1$ atm).

$k_7, R7, CH_3CH_2C(O)OCH_3 \rightarrow CH_2CH_2C(O)O \text{ Cyc} + CH_4$						
T K	TST	TST/W	TST/Eck	W	Eck	RRKM
400	2.12E-37	2.57E-37	2.65E-37	1.21	1.25	2.22E-37
500	2.38E-27	2.71E-27	2.74E-27	1.14	1.15	2.48E-27
600	1.25E-20	1.36E-20	1.38E-20	1.09	1.1	1.30E-20
700	8.12E-16	8.69E-16	8.69E-16	1.07	1.07	8.39E-16
800	3.37E-12	3.54E-12	3.57E-12	1.05	1.06	3.47E-12
900	2.23E-09	2.32E-09	2.32E-09	1.04	1.04	2.29E-09
1000	4.05E-07	4.17E-07	4.21E-07	1.03	1.04	4.16E-07
1100	2.88E-05	2.97E-05	2.97E-05	1.03	1.03	2.96E-05
1200	1.01E-03	1.03E-03	1.03E-03	1.02	1.02	1.04E-03
1300	2.06E-02	2.10E-02	2.10E-02	1.02	1.02	2.11E-02
1400	2.74E-01	2.79E-01	2.79E-01	1.02	1.02	2.81E-01
1500	2.59E+00	2.64E+00	2.64E+00	1.02	1.02	2.65E+00
1600	1.85E+01	1.87E+01	1.87E+01	1.01	1.01	1.89E+01
1700	1.05E+02	1.06E+02	1.07E+02	1.01	1.02	1.07E+02
1800	4.91E+02	4.96E+02	5.01E+02	1.01	1.02	4.97E+02
1900	1.96E+03	1.98E+03	2.00E+03	1.01	1.02	1.96E+03
2000	6.97E+03	7.04E+03	7.04E+03	1.01	1.01	6.72E+03

Table 10S. Unimolecular rate constants k_8 (s^{-1}) of R8 for the reported **MePr** reaction channels obtained by means of TST, TST/W, TST/Eck, W(T), Eck(T) and RRKM theories ($T = 400\text{--}2000$ K, $P = 1$ atm).

k_8 , R8, MePr \rightarrow [CH ₃ CH=C(OH)OCH ₃]						
T K	TST	TST/W	TST/Eck	W	Eck	RRKM
400	2.11E-29	6.60E-29	1.42E-27	3.13	67.24	1.95E-29
500	5.14E-21	1.21E-20	3.51E-20	2.36	6.82	4.90E-21
600	2.05E-15	4.00E-15	6.60E-15	1.95	3.22	1.99E-15
700	2.10E-11	3.57E-11	4.70E-11	1.7	2.24	2.05E-11
800	2.15E-08	3.29E-08	3.91E-08	1.53	1.82	2.12E-08
900	4.79E-06	6.80E-06	7.62E-06	1.42	1.59	4.73E-06
1000	3.63E-04	4.86E-04	5.26E-04	1.34	1.45	3.60E-04
1100	1.26E-02	1.61E-02	1.70E-02	1.28	1.35	1.25E-02
1200	2.44E-01	3.03E-01	3.15E-01	1.24	1.29	2.42E-01
1300	2.99E+00	3.59E+00	3.71E+00	1.2	1.24	2.98E+00
1400	2.57E+01	3.01E+01	3.08E+01	1.17	1.2	2.56E+01
1500	1.66E+02	1.91E+02	1.96E+02	1.15	1.18	1.66E+02
1600	8.54E+02	9.65E+02	9.82E+02	1.13	1.15	8.48E+02
1700	3.62E+03	4.05E+03	4.09E+03	1.12	1.13	3.57E+03
1800	1.31E+04	1.45E+04	1.47E+04	1.11	1.12	1.28E+04
1900	4.14E+04	4.51E+04	4.60E+04	1.09	1.11	3.97E+04
2000	1.17E+05	1.28E+05	1.29E+05	1.09	1.1	1.09E+05

Table 11S. Unimolecular rate constants k_9 (s^{-1}) of R9 for the reported **MePr** reaction channels obtained by means of TST, TST/W, TST/Eck, W(T), Eck (T) and RRKM theories ($T = 400\text{--}2000$ K, $P = 1$ atm)

k_9 , R9, MePr \rightarrow CH ₃ CH ₂ OCH ₃ + CO						
T K	TST	TST/W	TST/Eck	W	Eck	RRKM
400	2.82E-44	3.92E-44	4.34E-44	1.39	1.54	3.25E-44
500	8.84E-33	1.11E-32	1.16E-32	1.25	1.31	1.02E-32
600	4.27E-25	5.04E-25	5.12E-25	1.18	1.2	4.97E-25
700	1.35E-19	1.53E-19	1.54E-19	1.13	1.14	1.57E-19
800	1.82E-15	2.00E-15	2.02E-15	1.1	1.11	2.13E-15
900	3.00E-12	3.24E-12	3.24E-12	1.08	1.08	3.51E-12
1000	1.13E-09	1.20E-09	1.21E-09	1.06	1.07	1.33E-09
1100	1.46E-07	1.53E-07	1.55E-07	1.05	1.06	1.71E-07
1200	8.41E-06	8.75E-06	8.83E-06	1.04	1.05	9.85E-06
1300	2.60E-04	2.70E-04	2.70E-04	1.04	1.04	3.04E-04
1400	4.93E-03	5.08E-03	5.08E-03	1.03	1.03	5.77E-03
1500	6.32E-02	6.51E-02	6.51E-02	1.03	1.03	7.40E-02
1600	5.90E-01	6.02E-01	6.08E-01	1.02	1.03	6.90E-01
1700	4.23E+00	4.31E+00	4.31E+00	1.02	1.02	4.95E+00
1800	2.44E+01	2.49E+01	2.49E+01	1.02	1.02	2.85E+01
1900	1.17E+02	1.19E+02	1.19E+02	1.02	1.02	1.36E+02
2000	4.82E+02	4.92E+02	4.92E+02	1.02	1.02	5.56E+02

Table 12S. Unimolecular rate constants k_{10} (s^{-1}) of R10 for the reported **MePr** reaction channels obtained by means of TST, TST/W, TST/Eck, W(T), Eck (T) and RRKM theories ($T = 400\text{--}2000$ K, $P = 1$ atm).

k_{10} , R10, MePr \rightarrow CH ₃ CH ₂ CH ₃ + CO ₂						
T K	TST	TST/W	TST/Eck	W	Eck	RRKM
400	4.06E-40	3.12E-40	4.06E-40	1.1	1	2.65E-40
500	1.21E-29	8.90E-30	1.21E-29	1.06	1	8.06E-30
600	1.22E-22	8.76E-23	1.22E-22	1.04	1	8.21E-23
700	1.26E-17	8.97E-18	1.26E-17	1.03	1	8.56E-18
800	7.37E-14	5.20E-14	7.37E-14	1.02	1	5.04E-14
900	6.35E-11	4.52E-11	6.35E-11	1.02	1	4.37E-11
1000	1.43E-08	1.02E-08	1.43E-08	1.02	1	9.84E-09
1100	1.20E-06	8.44E-07	1.20E-06	1.01	1	8.32E-07
1200	4.86E-05	3.41E-05	4.86E-05	1.01	1	3.37E-05
1300	1.11E-03	7.87E-04	1.11E-03	1.01	1	7.74E-04
1400	1.63E-02	1.15E-02	1.63E-02	1.01	1	1.14E-02
1500	1.68E-01	1.19E-01	1.68E-01	1.01	1	1.17E-01
1600	1.29E00	9.15E-01	1.29E00	1.01	1	9.00E-01
1700	7.79E00	5.53E+00	7.79E00	1.01	1	5.44E+00
1800	3.86E+01	2.69E+01	3.86E+01	1	1	2.70E+01
1900	1.62E+02	1.13E+02	1.62E+02	1	1	1.13E+02
2000	5.87E+02	4.10E+02	5.87E+02	1	1	4.09E+02

Table 13S. Branching ratios (Γ) of complex fission reactions (R1-R10) in the overall reaction of MePr decomposition.

<i>TK</i>	$\Gamma1$	$\Gamma2$	$\Gamma3$	$\Gamma4$	$\Gamma5$	$\Gamma6$	$\Gamma7$	$\Gamma8$	$\Gamma9$	$\Gamma10$
400	0.00	0.00	0.18	0.00	2.22	0.00	0.00	97.59	0.00	0.00
500	0.00	0.00	1.78	0.00	11.15	0.00	0.00	85.28	0.00	0.00
600	0.00	0.00	3.18	0.00	16.77	0.00	0.00	62.69	0.00	0.00
700	0.00	0.00	2.86	0.00	12.37	0.00	0.00	34.98	0.00	0.00
800	0.00	0.00	1.84	0.00	7.48	0.00	0.00	16.61	0.00	0.00
900	0.00	0.00	1.15	0.00	4.53	0.00	0.00	8.18	0.00	0.00
1000	0.00	0.00	0.76	0.00	2.96	0.00	0.00	4.50	0.00	0.00
1100	0.00	0.00	0.54	0.01	2.09	0.00	0.00	2.75	0.00	0.00
1200	0.00	0.00	0.42	0.01	1.58	0.00	0.00	1.87	0.00	0.00
1300	0.00	0.00	0.33	0.01	1.27	0.00	0.00	1.37	0.00	0.00
1400	0.00	0.00	0.28	0.02	1.07	0.00	0.00	1.06	0.00	0.00
1500	0.00	0.00	0.25	0.03	0.93	0.00	0.01	0.87	0.00	0.00
1600	0.00	0.00	0.22	0.04	0.83	0.00	0.01	0.72	0.00	0.00
1700	0.00	0.00	0.20	0.09	0.76	0.00	0.01	0.63	0.00	0.00
1800	0.00	0.00	0.19	0.06	0.71	0.00	0.01	0.57	0.00	0.00
1900	0.00	0.00	0.18	0.08	0.67	0.00	0.01	0.51	0.00	0.00
2000	0.00	0.00	0.17	0.09	0.65	0.00	0.01	0.48	0.00	0.00

Table 14S. Branching ratios (Γ) of simple bond fission (R11-R17) in the overall reaction of MePr decomposition.

<i>TK</i>	<i>Γ_{11}</i>	<i>Γ_{12}</i>	<i>Γ_{13}</i>	<i>Γ_{14}</i>	<i>Γ_{15}</i>	<i>Γ_{16}</i>	<i>Γ_{17}</i>
400	0.01	0.00	0.00	0.01	0.00	0.00	0.00
500	0.93	0.00	0.00	0.86	0.00	0.00	0.00
600	8.22	0.07	0.00	9.07	0.00	0.00	0.00
700	21.82	0.46	0.00	27.51	0.00	0.00	0.00
800	30.55	1.19	0.01	42.33	0.00	0.00	0.00
900	33.60	2.11	0.02	50.42	0.00	0.00	0.00
1000	34.03	3.13	0.03	54.58	0.00	0.01	0.00
1100	33.70	4.20	0.06	56.64	0.00	0.01	0.00
1200	32.97	5.28	0.10	57.75	0.00	0.02	0.00
1300	32.10	6.36	0.14	58.37	0.00	0.02	0.01
1400	31.17	7.44	0.20	58.71	0.00	0.03	0.01
1500	30.39	8.45	0.26	58.76	0.01	0.04	0.02
1600	29.92	9.41	0.34	58.44	0.01	0.05	0.02
1700	28.82	10.37	0.42	58.59	0.02	0.06	0.03
1800	28.24	11.30	0.51	58.28	0.02	0.07	0.05
1900	27.50	12.13	0.60	58.15	0.03	0.08	0.06
2000	26.97	12.95	0.70	57.76	0.04	0.10	0.08

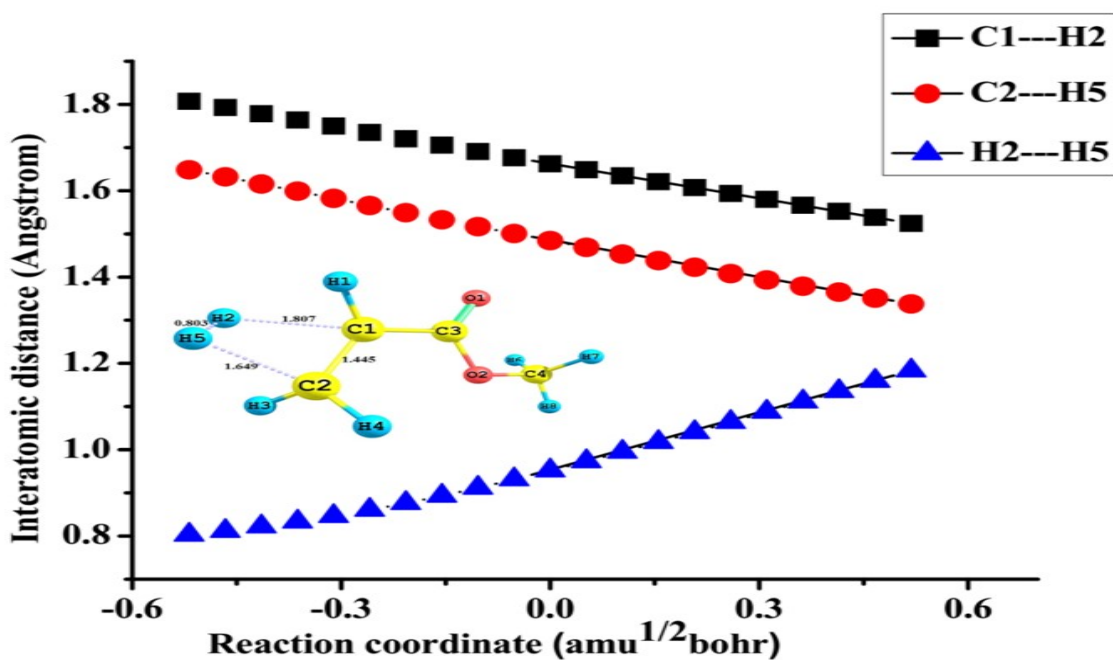


Fig. 1S. Variation of bond distances along the reaction coordinate for TS1, formation of methyl acrylate and hydrogen.

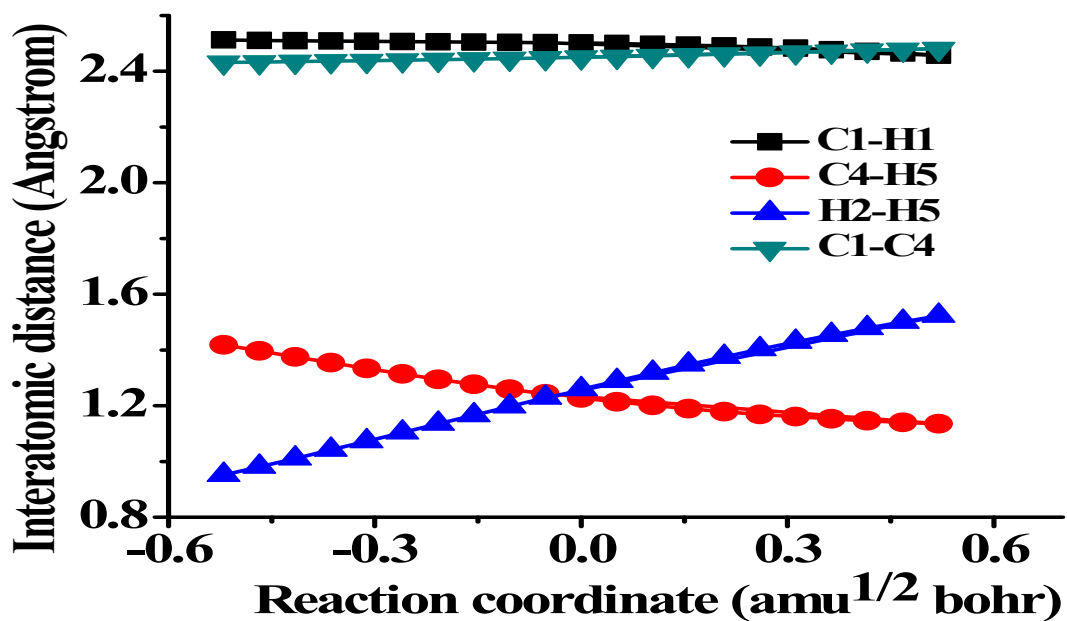


Fig. 2S. Variation of bond distances along the reaction coordinate for TS2, formation of lactone and hydrogen.

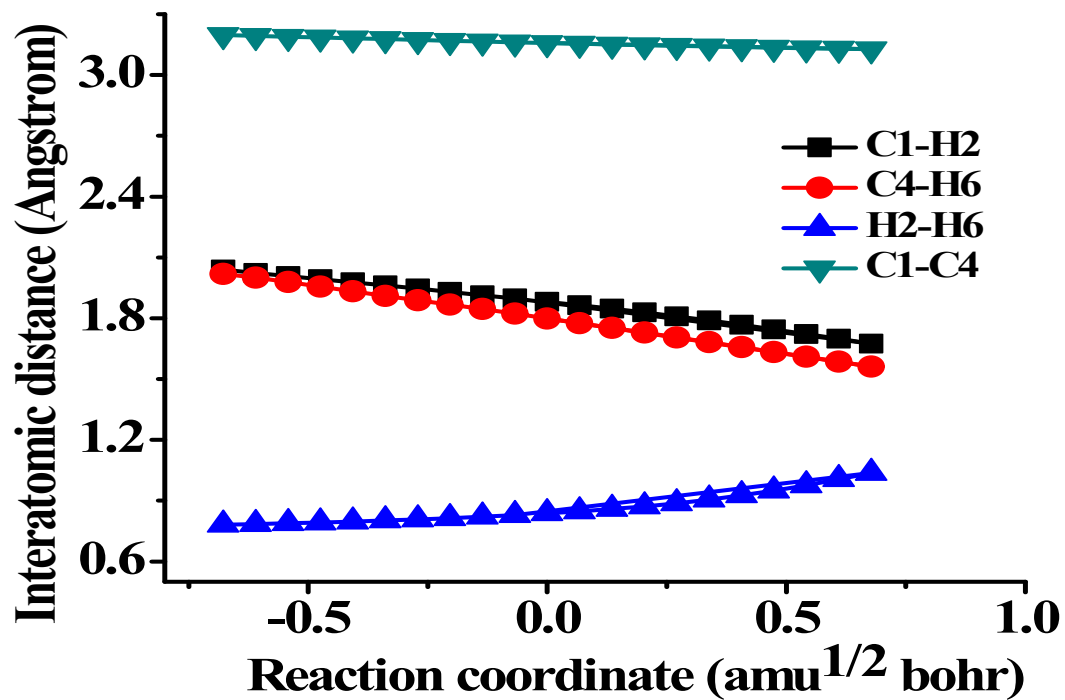


Fig. 3S. Variation of bond distances along the reaction coordinate for TS3, formation of lactone and hydrogen.

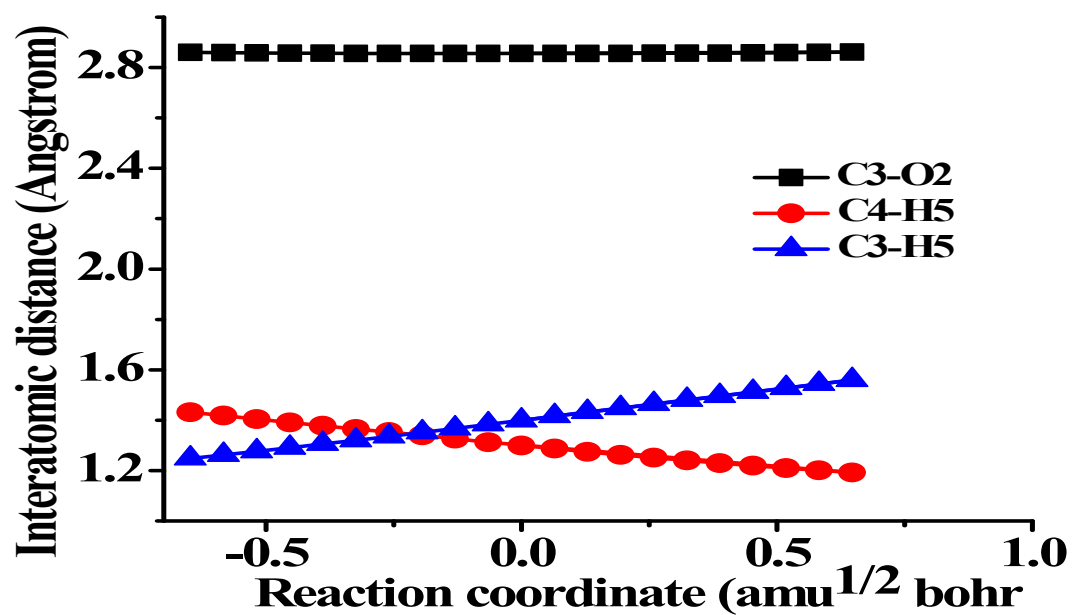


Fig. 4S. Variation of bond distances along the reaction coordinate for TS4, formation of propanal and formaldehyde.

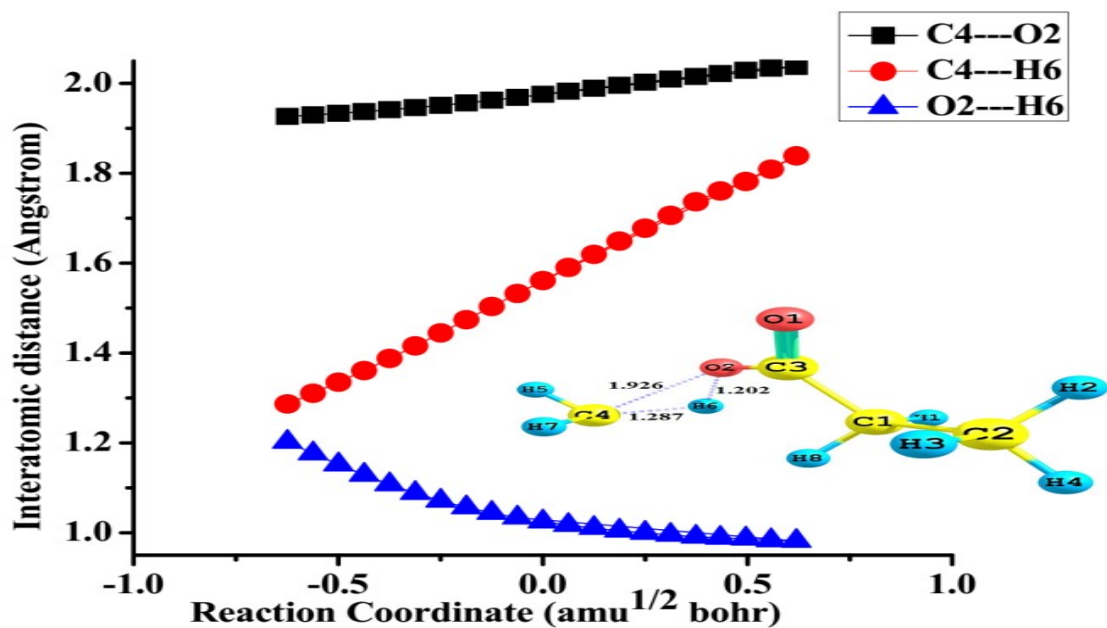


Fig. 5S. Variation of bond distances along the reaction coordinate for TS5, formation of propanoic acid and methene.

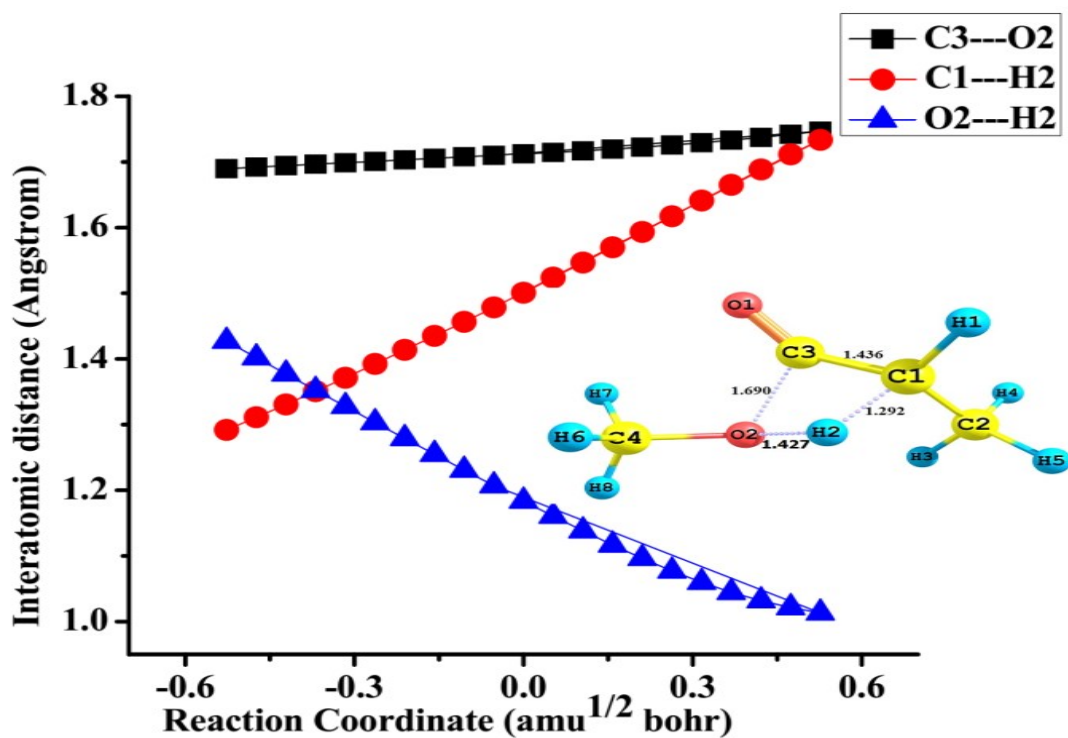


Fig. 6S. Variation of bond distances along the reaction coordinate for TS6, formation of propenone and methanol.

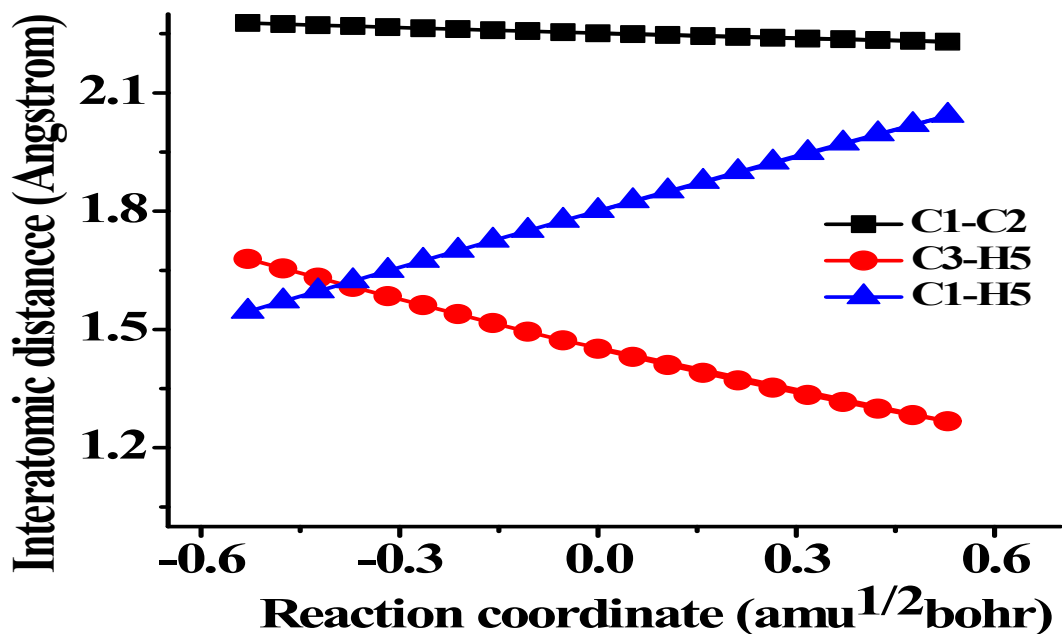


Fig. 7S. Variation of bond distances along the reaction coordinate for TS7, formation of methoxynal and ethene.

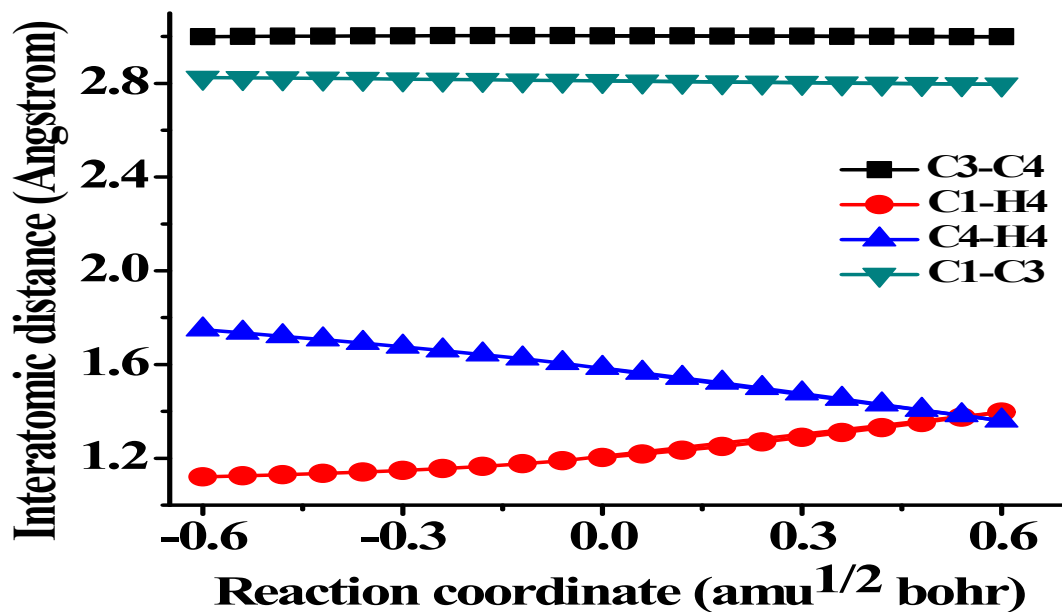


Fig. 8S. Variation of bond distances along the reaction coordinate for TS8, formation of lactone and methane.

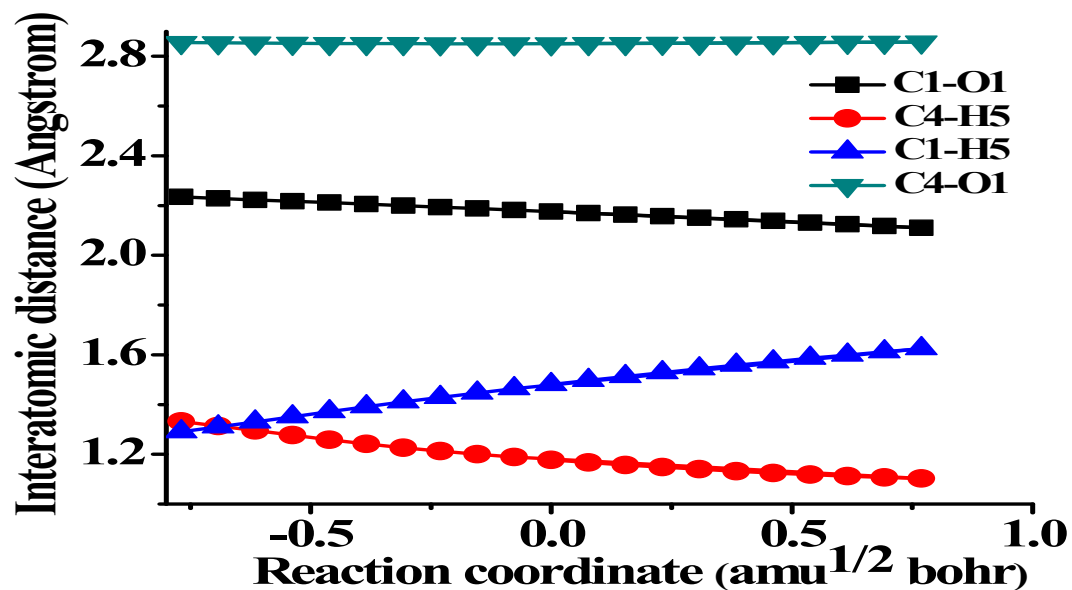


Fig. 9S. Variation of bond distances along the reaction coordinate for TS9, formation of lactone and methane.

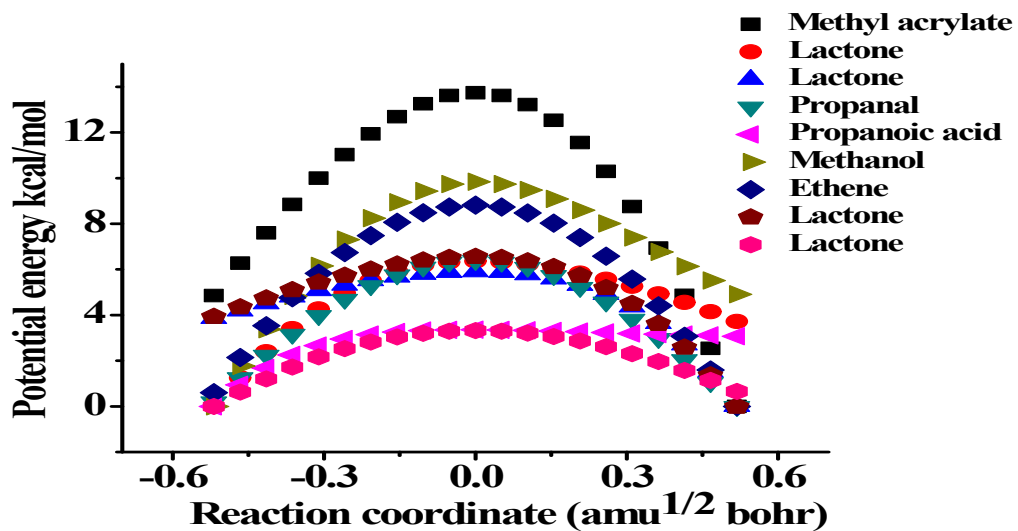
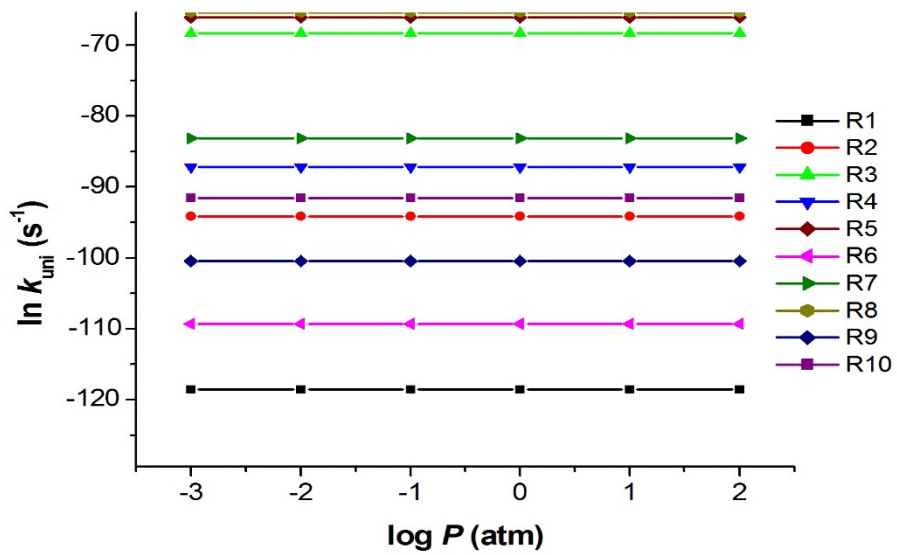
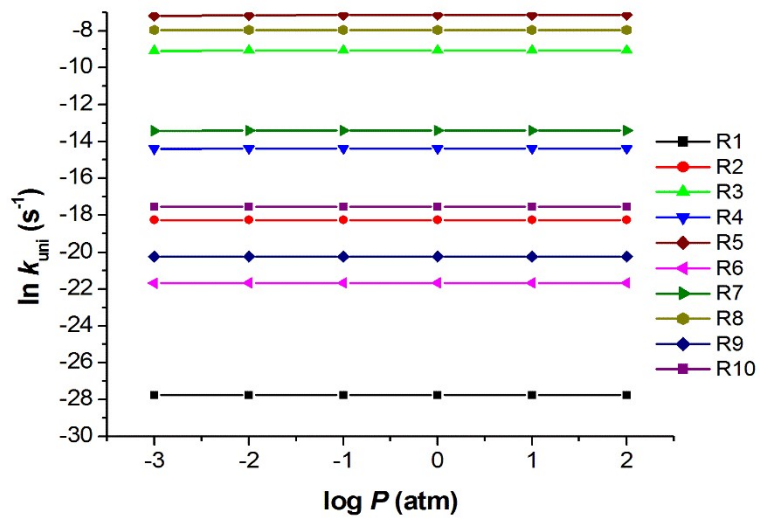


Fig. 10S. Potential energy profile along MEP from the IRC calculation of MePr decomposition reactions.



a) $T=400 \text{ K}$



b) $T=1000 \text{ K}$

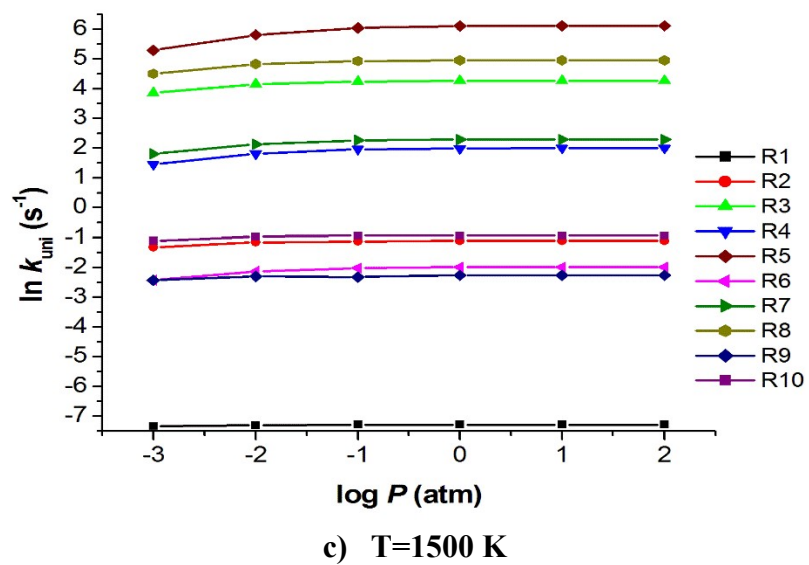


Fig. 11S. Calculated pressure-dependent RRKM rate constants for R1–R10 at 400 K, 1000 K, and 1500 K