

Supporting Information of

Pressure-dependent branching in initial decomposition of gamma-valerolactone: a quantum chemical/RRKM study

Lili Ye*, Wei Li, Fei Qi

Key Laboratory for Power Machinery and Engineering of MOE, Shanghai Jiao Tong University,
Shanghai 200240, P. R. China

Table S1. Normal Mode Frequencies of Major Stationary Points on C₅H₈O₂ Surface at

B2PLYPD3/cc-pVTZ Level^a

	Frequencies (cm ⁻¹)
gamma-valerolactone (GVL)	123 153 238 302 458 516 533 611 667 812 836 910 962 977 1017 1092 1119 1143 1193 1224 1249 1316 1334 1377 1406 1429 1479 1499 1510 1514 1847 3042 3059 3072 3076 3131 3135 3144 3155
4-pentenoic acid (4PA)	46 80 118 228 315 394 495 524 609 665 697 812 856 937 955 1022 1046 1062 1122 1182 1221 1281 1319 1326 1371 1419 1467 1471 1492 1706 1809 3058 3064 3101 3112 3152 3179 3242 3758
3-pentenoic acid (3PA)	20 82 131 204 237 305 417 502 574 655 744 787 863 935 978 1004 1055 1078 1133 1154 1250 1309 1337 1359 1403 1426 1490 1493 1506 1738 1812 3043 3070 3095 3112 3125 3156 3164 3756
5-methyl-4,5-dihydro-2-furanol	75 225 248 306 357 439 482 630 649 674 690 844 921 949 997 1012 1076 1121 1154 1178 1223 1268 1311 1353 1396 1425 1466 1499 1512 1521 1723 3013 3050 3057 3085 3131 3140 3260 3844
γ-GBL radical	128 242 490 518 554 677 748 810 856 959 1015 1035 1132 1150 1175 1234 1293 1335 1377 1473 1500 1865 3004 3087 3110 3158 3249
CH ₃	511 1427 1427 3144 3326 3326
allyl	430 539 565 804 827 944 1030 1050 1191 1288 1433 1520 1536 3166 3166 3172 3268 3271
•CH ₂ COOH	307 424 556 583 646 775 917 998 1206 1373 1481 1745 3202 3327 3772
TS1	1635i 78 171 320 375 431 451 487 590 639 757 851 873 914 954 977 996 1009 1102 1167 1240 1249 1294 1326 1335 1349 1446 1459 1488 1504 1584 1764 3053 3079 3111 3149 3153 3207 3250
TS2	398i 55 114 158 178 220 285 362 421 520 653 731 858 917 930 964 1002 1030 1059 1060 1106 1225 1299 1320 1394 1448 1455 1482 1504 1613 1770 3044 3105 3142

* Corresponding author: yell@sjtu.edu.cn

	3143 3160 3218 3241 3260
TS3	2063i 118 231 255 311 449 461 564 609 701 779 822 905 938 971 1019 1066 1087 1143 1159 1222 1257 1297 1346 1389 1427 1459 1497 1508 1514 1597 1878 3050 3061 3077 3118 3135 3145 3168
TS4	1228i 62 126 168 194 311 376 402 437 502 558 627 682 696 787 864 979 1021 1045 1068 1088 1102 1212 1340 1413 1434 1449 1477 1501 1532 1801 2056 3055 3126 3153 3167 3180 3282 3295
TS5	556i 40 82 169 196 224 267 288 413 473 518 605 664 850 872 908 960 1022 1032 1078 1131 1263 1285 1362 1404 1478 1484 1489 1521 1578 2053 3046 3055 3113 3141 3159 3176 3236 3271
TS6	1937i 60 68 109 194 328 378 441 541 621 671 672 731 867 912 961 974 1028 1035 1106 1181 1241 1270 1300 1337 1367 1425 1469 1500 1708 1767 2050 2932 3054 3096 3136 3151 3159 3246
TS7	1778i 47 75 148 202 313 362 405 410 527 603 611 717 760 856 876 946 957 978 1042 1120 1154 1263 1299 1338 1374 1451 1469 1492 1709 1760 2029 3018 3093 3131 3154 3164 3244 3788
TS8	781i 42 55 106 226 275 413 441 473 521 579 628 638 666 764 874 881 957 1078 1129 1195 1250 1261 1285 1307 1329 1378 1472 1477 1539 1800 2660 3066 3132 3132 3166 3198 3276 3752
TS9	1326i 91 161 195 289 341 371 419 522 593 681 748 841 883 937 985 1057 1085 1104 1141 1248 1275 1297 1333 1357 1433 1499 1508 1521 1614 1659 1910 3056 3105 3120 3123 3134 3150 3236

^aThe numbers in bold represent the internal torsional modes that are treated as 1D hindered rotors.

● Cartesian coordinates of major species and transition states on C₅H₈O₂ potential energy surface

GVL

C	-0.941452	1.216173	0.052263
C	-1.219812	-0.275748	-0.009352
O	-0.050471	-0.952946	0.162580
C	1.048170	-0.037334	0.401949
C	0.564715	1.301079	-0.159922
O	-2.268384	-0.831753	-0.174299
H	1.036975	2.145845	0.334907
H	1.172646	0.031550	1.485337
C	2.296824	-0.597526	-0.232870
H	0.797261	1.353087	-1.223721
H	-1.545752	1.741737	-0.679978
H	-1.234985	1.567149	1.042765
H	3.135187	0.076470	-0.058480
H	2.543082	-1.569984	0.187287
H	2.155763	-0.708130	-1.306772

4PA

C	-2.926173	-0.229349	-0.586316
C	-1.725024	-0.446453	-0.059366
C	-0.967152	0.555689	0.757286
C	0.338053	0.995672	0.093323
C	1.369386	-0.099831	0.026650
O	1.307628	-1.170309	0.580592
O	2.428427	0.263918	-0.734811
H	-1.588738	1.435360	0.923670
H	-1.234562	-1.398966	-0.217799
H	-0.730937	0.128142	1.732747
H	0.793484	1.820750	0.644822
H	0.163937	1.364289	-0.917326
H	-3.445452	0.709097	-0.440816
H	-3.429716	-0.983567	-1.173057
H	3.049005	-0.478337	-0.707946

3PA

C	1.466148	-0.291402	0.048538
C	0.898524	0.908585	-0.019351
C	-0.575448	1.206266	0.091784
C	-1.422400	-0.037679	0.119717
O	-1.739081	-0.650833	1.109084
O	-1.787075	-0.427556	-1.125294
H	1.526953	1.781385	-0.157282
H	0.843393	-1.166307	0.198717
H	-0.884033	1.829822	-0.746876
H	-0.771537	1.757377	1.011439
H	-2.299349	-1.241171	-1.012857
C	2.937579	-0.536623	-0.058487
H	3.164177	-1.194708	-0.898707
H	3.485930	0.393534	-0.196633
H	3.317291	-1.027692	0.838671

5-methyl-4,5-dihydro-2-furanol

C	-0.827938	1.217814	-0.069632
C	-1.125974	-0.085026	-0.007963
O	-0.082872	-0.926785	0.153056
C	1.079947	-0.082673	0.417854
C	0.671911	1.343299	-0.009547
O	-2.290300	-0.751427	-0.087197
H	1.025891	2.076685	0.714310
H	1.228167	-0.115562	1.498697
C	2.271815	-0.664484	-0.300438

H	1.109065	1.604260	-0.978596
H	-1.529112	2.018475	-0.224074
H	3.159957	-0.071136	-0.084178
H	2.455801	-1.689083	0.016180
H	2.103613	-0.656575	-1.376104
H	-2.986573	-0.114950	-0.274752

TS1

O	0.276331	-1.018734	-0.669109
C	-1.480614	0.234761	-0.312359
C	-0.634665	1.291426	0.299007
C	0.813301	1.198883	-0.222452
C	1.202954	-0.279452	-0.090532
C	-2.044588	-0.812871	0.420347
O	2.182747	-0.658716	0.515499
H	-1.069948	2.259753	0.039052
H	-1.673282	0.304922	-1.374088
H	-0.647953	1.195050	1.383732
H	1.484456	1.843456	0.338200
H	0.841819	1.480582	-1.274707
H	-2.048245	-0.740078	1.499483
H	-2.808902	-1.425976	-0.034135
H	-0.888901	-1.294599	0.087278

TS2

O	2.471146	-0.084846	0.344851
C	0.749800	1.031811	0.281135
C	-1.162613	1.311402	-0.342747
C	-1.577335	0.014750	-0.463990
O	0.712393	-1.251712	-0.592304
C	1.302350	-0.307059	-0.084825
C	-2.088163	-0.809694	0.651394
H	-0.965373	1.882394	-1.237712
H	-1.501565	-0.469400	-1.426229
H	-1.440962	1.872772	0.539804
H	0.608696	1.193646	1.340890
H	1.153057	1.884923	-0.245401
H	-3.099795	-1.153040	0.423811
H	-1.463151	-1.698301	0.744403
H	-2.103455	-0.267793	1.594263

TS3

C	0.972484	1.137676	-0.002066
C	1.111957	-0.269244	-0.085132

O	0.015411	-0.983134	-0.213503
C	-1.087950	-0.001081	-0.406038
C	-0.532680	1.330970	0.150976
O	2.265359	-0.735583	0.204878
H	-0.929661	2.175289	-0.408286
H	-1.229346	0.063681	-1.484850
C	-2.314853	-0.548597	0.273302
H	-0.836240	1.448257	1.192893
H	2.237472	0.497395	0.616675
H	1.497788	1.697561	-0.766692
H	-3.141509	0.148360	0.138875
H	-2.603329	-1.509976	-0.145860
H	-2.135078	-0.669181	1.339991

TS4

C	-0.967085	1.139591	-0.701477
C	-1.512124	-0.021909	-0.225909
O	0.106541	-1.085450	0.226970
C	1.074527	-0.239074	0.313812
C	0.754291	1.033432	0.882703
O	-2.404873	-0.671155	0.151335
H	-0.002037	1.065311	1.647175
H	1.606436	-0.054678	1.484441
C	2.251753	-0.361638	-0.629052
H	1.435426	1.870365	0.797375
H	-0.223773	1.088112	-1.477546
H	-1.630453	1.991316	-0.685947
H	3.063105	0.318637	-0.375416
H	2.621580	-1.383352	-0.615880
H	1.908206	-0.145288	-1.641096

TS5

C	0.601043	1.691277	0.216083
C	1.488579	-0.249554	0.139882
O	-0.050047	-1.166809	-0.542613
C	-1.135858	-0.520616	-0.511209
C	-0.687961	1.622320	-0.260898
O	2.490539	-0.797574	0.194354
H	-0.878268	1.897679	-1.286587
H	-1.579953	-0.232464	-1.465791
C	-2.073129	-0.725302	0.652605
H	-1.510611	1.731003	0.426242
H	0.792157	1.768936	1.276513
H	1.405438	2.033451	-0.418667

H	-2.932826	-0.059972	0.607538
H	-2.431178	-1.756087	0.634776
H	-1.544749	-0.576233	1.593265

TS6

C	-2.850446	0.602159	-0.158981
C	-1.599537	0.254509	-0.443823
C	-0.914112	-0.966698	0.089293
C	0.255994	-0.619936	1.002534
C	1.577353	0.125355	-0.132816
O	1.821203	-0.543443	-1.074963
O	1.868835	1.217087	0.429726
H	-1.631860	-1.587309	0.626822
H	-1.010470	0.889750	-1.097044
H	-0.520950	-1.561551	-0.736976
H	0.813883	-1.481308	1.359175
H	-0.121897	-0.099589	1.904297
H	-3.471287	-0.007609	0.484206
H	-3.293208	1.499746	-0.564468
H	0.899984	0.586378	1.048643

TS7

C	2.851866	0.037503	-0.754713
C	1.771208	0.390230	-0.067026
C	1.040859	-0.509797	0.883979
C	-0.403902	-0.766421	0.470791
C	-1.241348	0.346395	0.254846
O	-1.401857	1.500890	0.240806
O	-2.295923	-0.613811	-0.892498
H	1.546829	-1.473761	0.931182
H	1.370944	1.390821	-0.186317
H	1.079107	-0.082328	1.891143
H	-0.909969	-1.548499	1.030551
H	-1.186189	-1.133710	-0.648763
H	3.280086	-0.951995	-0.663165
H	3.340932	0.725492	-1.428414
H	-3.051591	-1.010107	-0.439947

TS8

C	-2.986545	0.400447	-0.566137
C	-1.792391	0.168198	0.196119
C	-0.779874	-0.837623	0.049482
C	0.501322	-0.754634	0.816831
C	1.442067	0.187125	0.093618

O	1.489429	1.382345	0.255793
O	2.200718	-0.459216	-0.823300
H	-2.370010	-0.624054	0.806163
H	-1.524811	0.967465	0.882677
H	-0.937285	-1.655188	-0.639620
H	0.965610	-1.732849	0.916865
H	0.339217	-0.331299	1.808161
H	-3.300106	-0.300333	-1.326485
H	-3.715912	1.086645	-0.168760
H	2.714651	0.223499	-1.278421

TS9

C	1.489911	0.029379	0.375763
C	0.666915	0.987795	-0.234107
C	-0.635524	1.225074	0.244212
C	-1.500404	-0.327230	-0.032458
O	-2.670417	-0.122084	-0.233102
O	-0.756223	-1.317564	0.092016
H	0.892758	1.275905	-1.256815
H	1.426272	-0.015964	1.461756
H	-1.241022	1.948298	-0.279725
H	-0.758725	1.255890	1.322987
H	0.544615	-0.803736	0.154201
C	2.820809	-0.368527	-0.215340
H	3.078071	-1.389811	0.058623
H	2.799143	-0.310823	-1.302511
H	3.621769	0.278471	0.141754