

***Ab Initio* Pressure-Dependent Reaction Kinetics of Methyl Propanoate Radicals**

Supporting Information

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Table S1. Optimized geometries, rotational constants, and vibrational frequencies with internal rotations projected out of the reactants, transition states (TSs), and products obtained using DFT-M08-HX/cc-pVTZ. The parameters V_i ($i = 0 - 10$) for rotational potential energy surfaces fitted with $V = V_0 + V_1 \cos(\Delta\theta) + V_2 \cos(2\Delta\theta) + V_3 \cos(3\Delta\theta) + V_4 \cos(4\Delta\theta) + V_5 \cos(5\Delta\theta) + V_6 \sin(\Delta\theta) + V_7 \sin(2\Delta\theta) + V_8 \sin(3\Delta\theta) + V_9 \sin(4\Delta\theta) + V_{10} \sin(5\Delta\theta)$ are also given in order.

CH₃CH₂C(=O)OCH₂:

Cartesian Coordinates (Å)

C	-1.0659467212	2.4023774746	-1.8540730004
C	-1.2416806875	0.9897339718	-1.3229276117
C	-0.0187928988	0.5103207732	-0.5903606060
O	0.9919202592	1.1274627954	-0.4245112684
O	-0.1986028557	-0.7513359210	-0.1206604122
C	0.8266897147	-1.3247365486	0.5626634735
H	-0.2182093426	2.4541475658	-2.5402483594
H	-1.9627438597	2.7314428928	-2.3820862641
H	-0.8656375311	3.0997858536	-1.0382048661
H	-2.0896293303	0.9126703936	-0.6338639658
H	-1.4471634651	0.2722452724	-2.1246201538
H	0.6181921728	-2.3140405650	0.9296461230
H	1.7244376956	-0.7518624085	0.7241927312

Frequencies (cm⁻¹):

206.54 215.71 361.49 461.05 603.74 660.98 802.05 856.03 1009.51 1084.85
 1110.05 1153.80 1192.69 1267.74 1272.81 1382.44 1406.97 1446.15 1448.93
 1477.73 1485.82 1854.88 3049.17 3052.19 3088.19 3133.66 3136.994
 3206.42 3363.64

Rotational constants (GHz): 9.88174 2.24964 1.87456

V_i ($i = 0 - 10$) (cm⁻¹) for rotations:

HC3-C2C1: 360.38 2.36 -3.55 -365.75 3.68 -2.11 -0.01 0.00 0.30 0.02 0.00
 C3C2-C1O1: 368.02 -166.45 -127.32 -79.07 0.66 8.46 7.35 9.57 11.25 2.69 1.30
 C2C1-O2C4: 2373.9 -952.94 -1400.81 -103.37 57.51 18.260.00 0.00 -0.01 0.00 -0.01
 C1O2-C4H: 727.24 -10.70 -865.99 -6.96 142.70 29.11 0.00 -0.02 -0.02 0.00 0.00

CH₃CHC(=O)OCH₃:

Cartesian Coordinates (Å)

C	-1.0755276004	2.4299527174	-1.8974516884
C	-1.0591535405	1.0175565811	-1.4672645720
C	-0.0408049660	0.5346256906	-0.5590745153
O	0.8480326910	1.2102952821	-0.0904264892
O	-0.1848558513	-0.7754812265	-0.2808126886

C 0.7927789837 -1.2994965608 0.6089992131
H -0.9934053425 2.5118294397 -2.9881326734
H -2.0201449946 2.9155211761 -1.6235972790
H -0.2500656463 2.9751615002 -1.4371737590
H -1.8009628576 0.3101488595 -1.8156028096
H 0.7588184264 -0.7766176289 1.5682278027
H 1.7953692438 -1.1850204298 0.1889990262
H 0.5522971844 -2.3534360806 0.7404433623

Frequencies (cm⁻¹):

216.14 348.13 469.18 558.24 676.54 737.97 877.02 997.07 1026.83 1077.94
1161.98 1208.63 1217.15 1238.49 1382.39 1423.04 1454.65 1459.07 1474.17
1486.02 1502.21 1754.23 3011.50 3045.07 3062.07 3123.84 3136.58 3163.13
3216.27

Rotational constants (GHz): 10.24225 2.18459 1.84174

V_i ($i = 0 - 10$) (cm⁻¹) for rotations:

HC3-C2C1: 92.43 4.13 1.06 -94.61 -1.25 -4.15 0.00 0.00 0.00 0.01 0.00

C3C2-C1O1: 1734.75 -231.30 -1689.05 66.79 173.37 -26.46 0.01 -0.01 0.03 -0.04 0.06

C2C1-O2C4: 2664.13 -1169.87 -1363.45 -134.86 -5.83 3.52 -0.04 0.02 -0.03 0.04 -0.04

C1O2-C4H: 214.84 -0.98 -1.30 -202.04 1.11 0.85 -1.63 2.15 0.00 2.00 -1.56

CH₂CH₂C(=O)OCH₃:

Cartesian Coordinates (Å)

C -1.0044322529 2.3962629334 -1.8979165999
C -1.2385116188 1.0664658049 -1.2920270779
C -0.0067494120 0.4962545797 -0.6291842800
O 1.0672409565 1.0259241070 -0.5732255749
O -0.2595428865 -0.7047952966 -0.0949789708
C 0.8530411340 -1.3161832220 0.5532088187
H -0.0259044453 2.8484541994 -1.8330608279
H -1.8075106944 2.9117939572 -2.4031703036
H -2.0364623296 1.0850186265 -0.5348039089
H -1.5850219268 0.3252492223 -2.0276095713
H 1.2107370021 -0.6871339099 1.3716836987
H 1.6719745884 -1.4656912736 -0.1542924025
H 0.4964156353 -2.2720778484 0.9330940404

Frequencies (cm⁻¹):

223.63 353.97 449.68 460.45 599.57 658.41 872.41 916.60 1013.32 1043.44
1132.61 1183.02 1207.12 1221.01 1248.66 1391.81 1424.97 1443.41 1467.85
1474.47 1487.36 1847.66 2997.99 3022.25 3049.95 3130.84 3167.64 3183.22
3298.28

Rotational constants (GHz): 9.92294 2.26296 1.88542

V_i ($i = 0 - 10$) (cm⁻¹) for rotations:

HC3-C2C1: 286.53 -1.71 -289.23 -13.47 -7.00 14.54 0.04 -0.01 -0.04 0.00 0.04

C3C2-C1O1: 423.66 -183.62 -188.21 -85.04 30.63 4.30 11.17 17.93 15.62 -1.57 3.30

C2C1-O2C4: 2896.54 -1172.48 -1651.01 -115.44 37.34 -28.24 0.02 0.00 0.00 0.00 -0.02

C1O2-C4H: 201.61 -0.85 -1.26 -189.17 1.06 0.72 -1.40 2.08 0.00 1.95 -1.35

TS1 (R1):

Cartesian Coordinates (Å)

C -2.0040029311 -0.4499461439 -0.7802557317
 C -1.2971115347 -0.6399518802 0.5627887197
 C -0.1170283446 0.2806164512 0.6846573762
 O -0.0127989156 1.4322721015 0.4493873527
 O 1.2405339178 -0.7085471498 -0.1611732506
 C 2.1234252130 0.0025082575 -0.6399199592
 H -1.3349630338 -0.7246072710 -1.5997138142
 H -2.8977570790 -1.0747987073 -0.8414739666
 H -2.2953588440 0.5941967039 -0.9121226381
 H -1.9617600559 -0.3900837404 1.3958162871
 H -0.9511148515 -1.6653925433 0.6985424017
 H 3.1597976617 -0.3525298272 -0.6720693310
 H 1.8878530278 1.0174493791 -0.9865039558

Frequencies (cm⁻¹): 751.68i

148.12 195.76 222.86 258.20 376.27 484.28 621.91 775.67 878.30 990.57
 1018.23 1038.98 1099.57 1235.73 1257.35 1324.13 1382.65 1413.59 1445.56
 1475.61 1486.08 1580.19 1894.21 3008.28 3041.12 3063.92 3118.07 3122.21
 3126.80 3138.83

Rotational constants (GHz): 5.81730 2.42057 2.06608

 V_i ($i = 0 - 10$) (cm⁻¹) for rotations:

HC3-C2C1: 632.67 -30.34 -23.80 -399.07 -26.72 -30.46 9.36 -19.93 -292.35 36.61 7.57
 C3C2-C1O1: 97.27 -9.35 12.28 -110.08 12.73 -8.83 -16.72 -18.85 22.61 6.17 -4.94

TS2 (R2):

Cartesian Coordinates (Å)

C 2.4105360164 0.0625644229 0.2037378715
 C 1.2431300043 0.7037338163 0.1072030452
 C -0.0165070238 -0.0729139691 0.0594167538
 O -0.0940744107 -1.2720207798 0.0997402304
 O -1.0832594284 0.7304321753 -0.0361765513
 C -2.3348264674 0.0519074469 -0.0847235815
 H 3.3481455171 0.5992906343 0.2971230491
 H 2.9914156967 -0.3220964022 -1.6779965456
 H 2.4178182143 -1.0179589344 0.3198001833
 H 1.1664659013 1.7831059477 0.0415542893
 H -2.4799963671 -0.5447199865 0.8190235252
 H -2.3738856796 -0.6136125800 -0.9503424700
 H -3.0978576435 0.8246742686 -0.1605336494

Frequencies (cm⁻¹): 626.09i

142.79 204.85 245.21 291.29 509.34 598.74 636.52 906.72 1016.54 1031.67
 1092.98 1119.29 1146.95 1156.32 1359.26 1393.15 1394.32 1409.45 1461.57
 1480.29 1488.27 2124.91 2934.35 2997.89 3026.68 3040.73 3089.45 3129.53
 3261.50

Rotational constants (GHz): 5.93363 2.15703 1.75989
 V_i ($i = 0 - 10$) (cm^{-1}) for rotations:
 HC3-C2C1: 175.93 -0.06 -2.64 -183.49 2.69 0.36 -0.47 -0.42 -13.42 -0.04 -0.39
 C3C2-C1O1: 580.73 -91.03 -459.40 19.74 -114.57 43.97 -227.63 321.95 -70.28 -96.53
 62.56
 C1O2-C4H: 155.77 5.05 -2.08 -144.88 0.14 -10.43 11.77 5.30 -52.07 4.26 5.30

TS3 (R3):

Cartesian Coordinates (Å)

C 2.4105360164 0.0625644229 0.2037378715
 C 1.2431300043 0.7037338163 0.1072030452
 C -0.0165070238 -0.0729139691 0.0594167538
 O -0.0940744107 -1.2720207798 0.0997402304
 O -1.0832594284 0.7304321753 -0.0361765513
 C -2.3348264674 0.0519074469 -0.0847235815
 H 3.3481455171 0.5992906343 0.2971230491
 H 2.9914156967 -0.3220964022 -1.6779965456
 H 2.4178182143 -1.0179589344 0.3198001833
 H 1.1664659013 1.7831059477 0.0415542893
 H -2.4799963671 -0.5447199865 0.8190235252
 H -2.3738856796 -0.6136125800 -0.9503424700
 H -3.0978576435 0.8246742686 -0.1605336494

Frequencies (cm^{-1}): 887.10i

215.44 274.73 355.81 365.05 479.50 606.44 676.27 844.87 884.90 1008.14
 1025.77 1060.27 1076.64 1207.98 1221.72 1249.12 1325.05 1414.97 1465.28
 1474.47 1486.30 1655.16 1822.85 3049.36 3129.97 3142.08 3168.04 3205.00
 3245.34

Rotational constants (GHz): 9.75649 2.22265 1.87981

V_i ($i = 0 - 10$) (cm^{-1}) for rotations:

C3C2-C1O1: 1200.38 -38.19 -1211.09 -60.19 125.58 -5.6 -13.30 -16.04 0.14 16.96 -1.15
 C2C1-O2C4: 3007.17 -1238.68 -1576.26 -234.41 23.57 19.43 -7.99 1.66 -8.79 3.33 0.69
 C1O2-C4H: 203.17 1.86 2.40 -191.07 -2.10 -1.75 0.02 -0.02 0.35 -0.01 0.02

TS4 (R4):

Cartesian Coordinates (Å)

C -1.9647382244 0.1678077696 0.5264748503
 C 0.2686553003 0.4712536715 0.2525924845
 O 0.7078571807 1.4408088985 -0.2642314571
 O 0.8069338328 -0.7286875940 0.3301175667
 C 2.1005143493 -0.8493239928 -0.2960181354
 H -2.0815624735 1.2455398575 0.5801547511
 H -1.7790624928 -0.3502772040 1.4626602547
 H 2.8097473595 -0.1694165719 0.1803606315
 H 2.0211406439 -0.6035546816 -1.3571097515
 H 2.4064032075 -1.8845421738 -0.1595853034
 C -2.3249602301 -0.5143649923 -0.5760058689

H -2.2967062843 -1.5983020622 -0.6026538480
H -2.6090442937 -0.0020545710 -1.4889621533
Frequencies (cm⁻¹): 371.09i
156.68 203.79 296.63 433.39 743.47 776.73 874.93 917.70 936.93 971.09
1135.94 1187.01 1199.55 1233.81 1318.76 1445.58 1446.14 1468.80 1479.85
1593.71 1873.12 3053.17 3132.93 3140.15 3145.98 3177.49 3218.88 3244.93
Rotational constants (GHz): 8.12115 1.77736 1.50509
 V_i ($i = 0 - 10$) (cm⁻¹) for rotations:
HC3-C2C1: 3573.03 -139.47 -4202.84 169.84 854.47 -59.13 154.21 5.16 50.73 -182.16
-1.91
C3C2-C1O1: 98.51 -3.48 -79.19 1.23 -23.75 2.01 -121.41 4.65 12.37 2.70 14.25
C2C1-O2C4: 1729.94 -264.26 -1507.20 40.25 46.81 -22.38 22.40 126.08 -42.37 1.00
-34.28
C1O2-C4H: 142.04 -0.39 -0.92 -133.04 0.74 0.39 -0.63 1.59 -3.83 1.48 -0.57

TS5 (R5):

Cartesian Coordinates (Å)
C 2.4409241940 -0.0010643441 0.1612658085
C 1.2792322309 0.6567325695 0.0595511768
C 0.0025410164 -0.1148592647 0.0220163671
O -0.0791319964 -1.3098191232 -0.0503527249
O -1.0565708935 0.6974420940 0.0877990803
C -2.3174465537 0.0346173456 0.0461341635
H 2.4485658935 -1.0852096487 0.1077884092
H 3.3829107407 0.5227875880 0.2708134072
H 1.2003071715 1.7297728566 0.1992701955
H 0.9835794925 1.0705408857 -1.7860621997
H -2.4114566737 -0.6585983931 0.8852122857
H -2.4192884060 -0.5282287158 -0.8847221595
H -3.0737436161 0.8151637699 0.1068575405
Frequencies (cm⁻¹): 1008.36i
225.79 347.52 371.60 393.43 481.99 573.33 670.52 685.51 822.22 883.90
1034.09 1058.50 1069.71 1207.13 1238.50 1246.67 1319.82 1417.10 1465.59
1485.15 1486.36 1640.39 1837.09 3050.31 3132.53 3150.08 3169.34 3193.90
3251.01
Rotational constants (GHz): 9.54131 2.29320 1.92400
 V_i ($i = 0 - 10$) (cm⁻¹) for rotations:
C3C2-C1O1: 1220.95 -63.87 -1166.01 -72.36 92.56 -1.64 -57.13 66.18 -73.72 -22.74 5.63
C2C1-O2C4: 2943.41 -1184.48 -1630.32 -159.63 24.18 27.37 97.74 9.18 26.66 -1.89
-38.08
C1O2-C4H: 197.61 1.70 2.38 -185.43 -2.10 -1.56 -0.06 -0.09 1.12 -0.07 -0.04

TS6(R6):

Cartesian Coordinates (Å)
C 0.3168348579 -1.4116370581 0.0641415820
C 0.6321956440 0.0602522368 0.0262104500

O	1.7115221917	0.5594492349	0.0229925951
O	-0.5073599211	0.8048529206	-0.0265642340
C	-1.6529039424	0.0165826628	-0.1662694450
H	0.2980153266	-1.7881609839	1.0882499645
H	-2.2979575799	0.0379291177	0.7104713846
H	-0.9862632287	-1.1801049794	-0.1894428527
C	1.0825583745	-2.2628638414	-0.9100742092
H	-2.1558761379	0.1733819942	-1.1190509667
H	2.1587913000	-2.1509911474	-0.7324958110
H	0.8912682793	-1.9586609943	-1.9423669523
H	0.8251934161	-3.3180666128	-0.8052500253

Frequencies (cm⁻¹): 1716.88i

82.98 170.86 235.10 430.92 516.79 597.89 660.36 710.22 817.79 847.56
 1014.33 1071.96 1082.60 1118.07 1140.71 1171.66 1217.07 1321.07 1382.93
 1397.69 1470.60 1472.41 1478.47 1730.96 1908.73 3024.62 3087.62 3095.52
 3112.87 3133.74 3192.35

Rotational constants (GHz): 5.05404 3.26146 2.15299

V_i ($i = 0 - 10$) (cm⁻¹) for rotations:

HC3-C2C1: 250.36 -3.22 2.76 -248.76 -2.59 3.17 0.59 1.53 6.06 1.70 0.79

TS7 (R7):

Cartesian Coordinates (Å)

C	-0.6064729205	1.4039561365	-1.0202172917
C	-0.6120383756	0.5636014470	0.2457796465
C	-1.9521496469	1.4095714811	-1.6985111190
O	-0.0898373825	0.8836320540	1.2681966760
O	-1.2806069777	-0.6149413604	0.1762506028
C	-1.7620275759	-1.0577901533	-1.0549936956
H	-2.7626836034	1.8618169302	-1.1304911021
H	-1.9585828853	1.6736123508	-2.7525490790
H	-2.1685267886	0.0735588536	-1.6420979921
H	0.1471074136	0.9769634105	-1.6936680393
H	-0.2545894594	2.3946277986	-0.7244078662
H	-0.9860069382	-1.4703238733	-1.7037243711
H	-2.6134985694	-1.7160728452	-0.9041935391

Frequencies (cm⁻¹): 1655.16i

125.14 181.44 302.49 461.87 474.96 546.06 600.84 634.52 712.04 793.06
 843.95 979.58 1083.16 1101.98 1126.65 1167.55 1191.51 1228.64 1282.37
 1328.62 1409.08 1444.66 1456.43 1479.23 1590.14 1885.11 3051.55 3080.92
 117.25 3124.26 3203.91 3213.95

Rotational constants (GHz): 4.86289 3.73000 2.32220

TS8 (R8):

Cartesian Coordinates (Å)

C	-1.1499923064	1.1053935935	-1.2435861438
C	0.0091992949	0.5028608326	-0.6022904997

O 1.1108512646 1.0001199671 -0.5648955417
 O -0.2768807614 -0.6975324555 -0.0641519022
 C 0.8296225776 -1.3401144260 0.5574372719
 H -2.1150610638 0.6254683414 -1.1584566524
 H -0.8754333746 1.3416420435 -2.4427877373
 H 1.2295138779 -0.7219327064 1.3650593296
 H 1.6273723201 -1.5196108375 -0.1678809524
 H 0.4525396118 -2.2832421311 0.9503050787
 C -1.0417104634 2.4811025186 -1.7585753089
 H -0.0935118958 2.9875527869 -1.6504321082
 H -1.9259392511 2.9951460128 -2.1011611437
 Frequencies (cm^{-1}): 1771.00i
 211.20 341.15 424.39 470.29 666.22 696.60 719.80 836.31 872.82 1045.52
 1063.37 1165.52 1205.49 1210.51 1218.46 1239.97 1396.10 1434.85 1473.41
 1478.48 1490.02 1783.06 2254.76 3045.47 3124.66 3162.43 3182.58 3228.02
 3313.99
 Rotational constants (GHz): 10.21699 2.23604 1.87362
 V_i ($i = 0 - 10$) (cm^{-1}) for rotations:
 C3C2-C1O1: 1933.30 -182.0 -1844.61 19.39 65.11 -6.47 -74.31 -454.35 -7.96 164.32
 9.68
 C2C1-O2C4: 2577.01 -1140.30 -1330.99 -91.77 -12.49 -4.89 21.42 40.82 12.94 -4.39
 -0.92
 C1O2-C4H: 198.01 -0.81 -1.23 -184.82 0.98 0.78 1.47 -2.06 5.49 -1.87 1.21

CH₂CHC(=O)OCH₃:

Cartesian Coordinates (Å)

C -2.4807788369 0.1009397324 -0.0003451166
 C -1.3092773613 0.7160454905 0.0001501943
 C -0.0555301483 -0.0813120564 -0.0001870541
 O 0.0066200294 -1.2808358994 -0.0009959446
 O 1.0234606156 0.7106078529 0.0005257228
 C 2.2684759740 0.0182704714 0.0002823407
 H -3.4149873126 0.6516057807 -0.0000245435
 H -2.5177967170 -0.9850697982 -0.0010825256
 H -1.2070054711 1.7959031968 0.0008959536
 H 2.3508467053 -0.6165709521 -0.8850898051
 H 2.3539800124 -0.6118229641 0.8888033551
 H 3.0428738504 0.7834099355 -0.0030433077
 Frequencies (cm^{-1}):
 93.80 157.82 200.52 226.97 353.45 479.18 536.41 677.36 846.89 888.37
 1024.68 1032.20 1064.09 1080.26 1183.19 1212.95 1257.00 1342.18 1425.69
 1471.60 1474.40 1492.41 1728.55 1839.61 3061.93 3141.50 3158.25 3181.08
 3213.16 3259.82
 Rotational constants (GHz): 10.48470 2.35133 1.94406

CH₃CH₂C(=O):

Cartesian Coordinates (Å)

C -1.2255335741 1.0012964357 -1.3337057635
C 0.0198111240 0.5221736988 -0.6079017180
O 1.0126360215 1.1223022957 -0.4344072291
H -2.0531957149 0.8955184684 -0.6253629521
H -1.4183317491 0.2724323683 -2.1271195748
C -1.0880393838 2.4231681985 -1.8653452151
H -0.2533898373 2.4925217445 -2.5659905721
H -2.0004130810 2.7340710609 -2.3786968215
H -0.8925425153 3.1213653193 -1.0488799835

Frequencies (cm⁻¹):

239.63 307.72 626.27 813.84 967.22 979.29 1057.94 1210.46 1300.05
1364.00 1430.13 1440.69 1499.48 1981.83 2930.20 3051.73 3087.78 3131.30
3162.63

Rotational constants (GHz): 18.38124 5.97112 4.77108

CH₃CHC(=O):

Cartesian Coordinates (Å)

C -1.0352250594 2.3501306201 -1.9424237752
C -1.4107608189 1.2871471212 -0.9416724274
C -0.7994233843 1.1378886430 0.2045146706
O -0.2570670736 1.0075171899 1.2182292482
H -0.7321043174 1.9040635152 -2.8936218515
H -1.8765302143 3.0209633264 -2.1369201500
H -0.2038301141 2.9563641904 -1.5787537413
H -2.2170079180 0.5904857937 -1.1347855434

Frequencies (cm⁻¹):

148.99 206.25 529.38 581.21 658.03 912.12 1056.90 1088.64 1153.20
1406.85 1429.79 1474.42 1507.47 2255.30 3047.68 3113.75 3141.96 3219.08

Rotational constants (GHz): 39.10652 4.52983 4.16523

CH₃OC(=O):

Cartesian Coordinates (Å)

C -0.1114909733 0.5599880783 -0.4457146736
O 0.7790735742 1.3023421077 -0.2274310697
O -0.2311547423 -0.7136885214 -0.1738110075
C 0.9094415644 -1.2988468010 0.4990131268
H 1.0796387712 -0.7826657032 1.4455799604
H 1.7939482901 -1.2066780932 -0.1339752254
H 0.6568377658 -2.3435228573 0.6650032590

Frequencies (cm⁻¹):

125.75 287.52 383.67 774.14 939.71 1162.19 1172.71 1212.67 1451.08
1473.28 1482.60 1907.62 3069.73 3159.54 3197.77

Rotational constants (GHz): 22.89380 6.95663 5.52272

C₂H₄:

Cartesian Coordinates (Å)

C -0.0000040206 0.0000000000 0.6608666159
 C -0.0000039690 -0.0000000000 -0.6608630323
 H 0.9249482460 0.0000000000 1.2297919412
 H 0.9249455055 -0.0000000000 -1.2297937627
 H -0.9249558528 -0.0000000000 1.2297954190
 H -0.9249530960 0.0000000000 -1.2297971812

Frequencies (cm⁻¹):

824.42 980.68 999.49 1066.55 1236.71 1378.83 1458.74 1710.62 3142.5
 3160.75 3225.10 3250.39

Rotational constants (GHz): 146.39864 30.45566 25.21096

CH₃Ö:

Cartesian Coordinates (Å)

O 2.8667811568 0.8727562898 -0.0523202298
 C 3.6652088441 -0.2266505047 0.0592907106
 H 3.7919285759 -0.6076073026 -0.9719841500
 H 3.2020879278 -1.0378906611 0.6391035628
 H 4.6719941554 0.0086724586 0.4332816665

Frequencies (cm⁻¹): 157.42624 28.04537 27.86464

Rotational constants (GHz): 157.42624 28.04537 27.86464

HCHO:

Cartesian Coordinates (Å)

O -3.4491859551 0.7400574936 -0.0848227758
 C -3.8406097535 -0.3610279393 0.1559066736
 H -3.2487730621 -1.2633110513 -0.1023018825
 H -4.8172094494 -0.5410110529 0.6507842548

Frequencies (cm⁻¹):

1203.97 1267.46 1526.73 1877.47 2914.31 2989.20

Rotational constants (GHz): 282.34278 39.49701 34.64984

Table S2. Phenomenological rate coefficients for the β-scission and isomerization

reactions of the MP-m, MP-α, and MP-β radicals in modified Arrhenius form ($k =$

$AT^n \exp(-\frac{E_a}{RT})$), obtained with CCSD(T)/CBS(T-Q)//M08-HX/cc-pVTZ energies.

Pressure	A(s ⁻¹)	n	E _a (cal/mol)
R1: CH ₃ CH ₂ C(=O)OĈH ₂ → CH ₃ CH ₂ ĈC(=O) + HCHO			
<i>p</i> = 7.6 Torr	6.29 × 10 ³⁵	-7.51	37323
<i>p</i> = 30 Torr	2.49 × 10 ³⁷	-7.79	39027
<i>p</i> = 1 atm	4.09 × 10 ³⁶	-7.17	41154
<i>p</i> = 10 atm	3.93 × 10 ³⁰	-5.19	39705
<i>p</i> = 100 atm	1.09 × 10 ²²	-2.56	36322

High-pressure limit	1.50×10^{16}	-0.79	33807
R2: $\text{CH}_3\dot{\text{C}}\text{HC}(=\text{O})\text{OCH}_3 \rightarrow \text{CH}_3\text{CHC}(=\text{O}) + \text{CH}_3\dot{\text{O}}$			
$p = 7.6 \text{ Torr}$	7.31×10^{44}	-10.59	59290
$p = 30 \text{ Torr}$	8.48×10^{50}	-12.02	63522
$p = 1 \text{ atm}$	4.92×10^{51}	-11.52	67970
$p = 10 \text{ atm}$	4.64×10^{42}	-8.52	65980
$p = 100 \text{ atm}$	1.87×10^{30}	-4.69	61162
High-pressure limit	2.98×10^{21}	-2.03	57362
R3: $\text{CH}_3\dot{\text{C}}\text{HC}(=\text{O})\text{OCH}_3 \rightarrow \text{CH}_2\text{CHC}(=\text{O})\text{OCH}_3 + \text{H}$			
$p = 7.6 \text{ Torr}$	1.68×10^{48}	-11.27	53032
$p = 30 \text{ Torr}$	7.57×10^{48}	-11.19	54908
$p = 1 \text{ atm}$	1.67×10^{43}	-8.98	55799
$p = 10 \text{ atm}$	7.56×10^{32}	-5.69	52537
$p = 100 \text{ atm}$	1.09×10^{21}	-2.07	47597
High-pressure limit	2.28×10^{13}	0.24	44220
R4: $\dot{\text{C}}\text{H}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3\text{O}\dot{\text{C}}(=\text{O})$			
$p = 7.6 \text{ Torr}$	1.66×10^{36}	-7.70	35100
$p = 30 \text{ Torr}$	7.33×10^{38}	-8.27	37326
$p = 1 \text{ atm}$	4.32×10^{41}	-8.61	41453
$p = 10 \text{ atm}$	1.16×10^{38}	-7.28	41630
$p = 100 \text{ atm}$	2.21×10^{30}	-4.82	39253
High-pressure limit	3.63×10^{16}	-0.63	33508
R5: $\dot{\text{C}}\text{H}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_3 \rightarrow \text{CH}_2\text{CHC}(=\text{O})\text{OCH}_3 + \text{H}$			
$p = 7.6 \text{ Torr}$	6.02×10^{53}	-13.35	48375
$p = 30 \text{ Torr}$	6.32×10^{51}	-12.56	48316
$p = 1 \text{ atm}$	3.90×10^{39}	-8.44	45168
$p = 10 \text{ atm}$	1.90×10^{36}	-7.12	45853
$p = 100 \text{ atm}$	2.16×10^{28}	-4.53	43826
High-pressure limit	5.50×10^{11}	0.54	37097
R6: $\text{CH}_3\dot{\text{C}}\text{HC}(=\text{O})\text{OCH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{O}\dot{\text{C}}\text{H}_2$			
$p = 7.6 \text{ Torr}$	2.93×10^{37}	-8.22	36641
$p = 30 \text{ Torr}$	3.23×10^{38}	-8.33	38372
$p = 1 \text{ atm}$	2.75×10^{35}	-7.02	39691
$p = 10 \text{ atm}$	1.15×10^{28}	-4.65	37563
$p = 100 \text{ atm}$	3.39×10^{18}	-1.74	33663
High-pressure limit	1.01×10^{10}	0.82	29865
R7: $\dot{\text{C}}\text{H}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{O}\dot{\text{C}}\text{H}_2$			
$p = 7.6 \text{ Torr}$	6.01×10^{26}	-5.41	23534
$p = 30 \text{ Torr}$	1.05×10^{29}	-5.91	25556
$p = 1 \text{ atm}$	7.55×10^{29}	-5.83	28216
$p = 10 \text{ atm}$	7.08×10^{25}	-4.45	27677
$p = 100 \text{ atm}$	2.92×10^{18}	-2.14	25037
High-pressure limit	6.03×10^6	1.39	20012
R8: $\dot{\text{C}}\text{H}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_3 \rightarrow \text{CH}_3\dot{\text{C}}\text{HC}(=\text{O})\text{OCH}_3$			
$p = 7.6 \text{ Torr}$	3.07×10^{36}	-8.20	32048

$p = 30$ Torr	2.92×10^{41}	-9.48	36436
$p = 1$ atm	1.80×10^{47}	-10.79	43638
$p = 10$ atm	1.02×10^{43}	-9.28	43970
$p = 100$ atm	7.28×10^{27}	-4.63	37970
High-pressure limit	9.32×10^7	1.38	29295

Table S3. Phenomenological rate coefficients for unimolecular dissociation reactions of the MP-m, MP- α , and MP- β radicals in modified Arrhenius form ($k = AT^n \exp(-\frac{E_a}{RT})$), obtained with CCSD(T)/CBS(T-Q)//M08-HX/cc-pVTZ energies.

R9: $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\dot{\text{O}}\text{CH}_2 \rightarrow \text{CH}_3\text{CHC}(=\text{O}) + \text{CH}_3\dot{\text{O}}$			
$p = 7.6$ Torr	1.85×10^{34}	-7.64	49305
$p = 30$ Torr	5.30×10^{41}	-9.51	54201
$p = 1$ atm	1.66×10^{50}	-11.26	64100
$p = 10$ atm	3.72×10^{44}	-9.20	66455
$p = 100$ atm	6.73×10^{23}	-2.95	59847
R10: $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\dot{\text{O}}\text{CH}_2 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3\text{O}\dot{\text{C}}(=\text{O})$			
$p = 7.6$ Torr	2.84×10^{44}	-10.15	42564
$p = 30$ Torr	1.35×10^{48}	-11.04	46067
$p = 1$ atm	4.10×10^{51}	-11.61	53200
$p = 10$ atm	9.19×10^{45}	-9.68	54799
$p = 100$ atm	1.79×10^{30}	-4.94	50607
R11: $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\dot{\text{O}}\text{CH}_2 \rightarrow \text{CH}_2\text{CHC}(=\text{O})\text{OCH}_3 + \text{H}$			
$p = 7.6$ Torr	1.66×10^{44}	-10.21	47070
$p = 30$ Torr	4.45×10^{43}	-9.78	48713
$p = 1$ atm	5.70×10^{50}	-11.26	58799
$p = 10$ atm	4.51×10^{44}	-9.13	61038
$p = 100$ atm	3.61×10^{20}	-2.00	51717
R12: $\text{CH}_3\dot{\text{C}}\text{HC}(=\text{O})\text{OCH}_3 \rightarrow \text{CH}_3\text{CH}_2\dot{\text{C}}(=\text{O}) + \text{HCHO}$			
$p = 7.6$ Torr	4.26×10^{56}	-13.43	54316
$p = 30$ Torr	7.76×10^{58}	-13.84	57780
$p = 1$ atm	2.14×10^{57}	-12.86	63593
$p = 10$ atm	2.02×10^{48}	-9.96	63904
$p = 100$ atm	2.44×10^{23}	-2.63	53959
R13: $\text{CH}_3\dot{\text{C}}\text{HC}(=\text{O})\text{OCH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3\text{O}\dot{\text{C}}(=\text{O})$			
$p = 7.6$ Torr	1.41×10^{62}	-15.19	57479
$p = 30$ Torr	3.59×10^{64}	-15.64	61458
$p = 1$ atm	2.24×10^{62}	-14.41	68182
$p = 10$ atm	1.42×10^{53}	-11.38	68883
$p = 100$ atm	5.55×10^{34}	-5.81	63739

R14: $\dot{\text{C}}\text{H}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_3 \rightarrow \text{CH}_3\text{CH}_2\dot{\text{C}}(=\text{O}) + \text{HCHO}$			
$p = 7.6 \text{ Torr}$	3.00×10^{64}	-16.21	49969
$p = 30 \text{ Torr}$	1.52×10^{57}	-13.84	48377
$p = 1 \text{ atm}$	8.58×10^{50}	-11.56	50909
$p = 10 \text{ atm}$	1.59×10^{42}	-8.75	50890
$p = 100 \text{ atm}$	2.86×10^{26}	-4.03	46518
R15: $\dot{\text{C}}\text{H}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_3 \rightarrow \text{CH}_3\text{CHC}(=\text{O}) + \text{CH}_3\dot{\text{O}}$			
$p = 7.6 \text{ Torr}$	6.40×10^{54}	-14.00	56647
$p = 30 \text{ Torr}$	2.52×10^{59}	-15.05	60487
$p = 1 \text{ atm}$	9.56×10^{51}	-12.10	63705
$p = 10 \text{ atm}$	1.43×10^{40}	-8.19	63094
$p = 100 \text{ atm}$	2.71×10^{26}	-3.89	60825