The detailed mechanism of the OH-initiated atmospheric oxidation of α-pinene: a theoretical study

- Supporting information -

Jozef Peeters, Luc Vereecken, Gaia Fantechi

Contentsof this supporting information :

A) Methodology

The results below are calculated at the following level of theory :

Geometry : fully optimized at B3LYP-DFT/6-31G(d,p) 5d
Frequencies : calculated at B3LYP-DFT/6-31G(d,p) 5d (reported unscaled)
Energies : calculated at B3LYP-DFT/6-31G(d,p) 5d

B) Estimation of the hyperconjugation stabilization of the 2,2-di-Me-cyclobutoxy radical

The stabilization is estimated from the energy difference between the oxy radical, and the corresponding peroxy radical and alcohol. These differences are compared to those found for the 2-propoxy radical.

Structure	Energy (Hartree)	ZPE (Hartree)	Energy difference (Hartree)	Stabilisation (kcal/mol)
2,2-di-Me-cyclobutoxy	-310.408239709	.156910	0.000000	
2,2-di-Me-cyclobutylperoxy	-385.563701666	.162711	-75.149661	6.32
2,2-di-Me-cyclobutanol	-311.071175755	.171198	-0.648648	5.16
2-propoxy	-193.694679598	.094617	0.000000	
2-propylperoxy	-268.859561544	.099769	-75.159730	
2-propanol	-194.365221402	.108281	-0.656878	

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2,2-di-Me-cyclobutylO
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 E(UB+HF-LYP) =  -310.408239709     A.U.
 Cartesian coordinates:
     C      -0.024316      1.498286       0.231472
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C	0.618472	0.104858	0.033672
C	-0.916464	-0.361972	-0.585937
C	-1.452078	0.918769	0.107494
C	1.733069	-0.037007	-0.986608
C	0.920731	-0.618651	1.338796
H	0.093608	-0.548186	2.049115
H	1.125828	-1.678420	1.166660
H	1.806861	-0.166036	1.802135
H	1.926085	-1.090204	-1.215543
H	2.660898	0.392420	-0.585282
H	1.500175	0.483911	-1.920125
H	-2.172718	1.503684	-0.471704
H	-1.890051	0.659994	1.074693
H	-0.796409	-0.229334	-1.679508
H	0.220963	2.175082	-0.592938
H	0.225449	1.994748	1.174291
O	-1.247146	-1.565419	-0.204391

Rotational constants (GHZ): 3.2177152 2.5574238 2.1366409

Vibrational harmonic frequencies :

122.0904	195.3724	225.0257
246.0353	256.1684	344.4441
357.8292	376.4274	438.0648
479.6789	532.8738	747.5251
803.6693	861.1482	947.6846
960.5427	972.2655	990.8047
1012.3174	1051.3686	1085.4930
1166.4629	1199.3985	1243.3554
1254.3737	1281.7834	1295.4181
1313.1944	1403.8101	1416.0416
1431.9349	1483.3190	1490.0107
1496.9214	1503.7553	1508.6313
1517.1975	2917.4424	3030.0033
3041.2892	3062.8343	3075.4938
3098.6936	3112.0838	3116.5778
3125.3444	3138.5252	3145.0016

Zero-point correction= .156910 (Hartree/Particle)

2,2-di-Me-cyclobutylOO

E(UB+HF-LYP) = -385.563701666 A.U.

Cartesian coordinates:

C	1.218192	1.353556	-0.025745
C	0.925722	-0.185575	-0.032508
C	-0.541161	0.186494	-0.396150
C	-0.306398	1.629899	0.085747
C	1.672501	-1.024754	-1.067831
C	1.054984	-0.797137	1.369074
H	0.528618	-0.209830	2.127402
H	0.648150	-1.812498	1.396812
H	2.111885	-0.844327	1.653785
H	1.278722	-2.046983	-1.104663
H	2.738753	-1.087253	-0.821874
H	1.585733	-0.593278	-2.071006
H	-0.735982	2.430231	-0.520633
H	-0.632272	1.754778	1.121688
H	-0.761200	0.114281	-1.463980
H	1.632588	1.696018	-0.978748
H	1.851188	1.725189	0.784909
O	-1.552997	-0.581394	0.297878
O	-2.745656	-0.431259	-0.262780

Rotational constants (GHZ): 2.9846702 1.5583866 1.3635382
Vibrational harmonic frequencies :

17.6766	110.0324	189.4124
217.5347	243.8022	273.5875
340.6929	350.8086	372.3779
471.9372	504.0014	602.1234
751.4033	812.7782	876.5421
909.3748	940.4515	961.8929
975.7648	1010.4138	1017.3582
1052.4596	1129.8865	1184.9362
1189.7288	1210.0576	1235.1556
1253.2752	1271.5039	1291.7276
1323.5455	1362.6152	1416.8730
1434.0678	1490.9588	1497.0770
1503.2731	1511.6506	1517.1231
1520.2037	3035.5705	3047.6506
3070.4142	3087.2242	3105.3007
3107.0667	3110.2533	3117.1962
3121.7824	3127.0828	3146.2748

Zero-point correction= .162711 (Hartree/Particle)

2,2-di-MecyclobutylOH

E(RB+HF-LYP) = -311.071175755 A.U.
Cartesian coordinates:

C	0.281658	1.530069	0.173510
C	0.620365	0.012052	0.004285
C	-0.826708	-0.170849	-0.545283
C	-1.229466	1.183138	0.091364
C	1.753409	-0.339973	-0.958452
C	0.818037	-0.683212	1.356427
H	0.027095	-0.430329	2.068403
H	0.816641	-1.771006	1.239790
H	1.777147	-0.383877	1.794727
H	1.790427	-1.420312	-1.141692
H	2.725724	-0.038349	-0.551025
H	1.627006	0.161295	-1.924795
H	-1.879802	1.848022	-0.485215
H	-1.668493	1.025984	1.080830
H	-0.819771	-0.090382	-1.644149
H	0.617458	2.123723	-0.682906
H	0.634091	2.012515	1.090044
O	-1.473948	-1.357218	-0.132294
H	-2.359711	-1.366883	-0.516772

Rotational constants (GHZ): 3.1616971 2.5212177 2.0676518
Vibrational harmonic frequencies :

128.9789	207.6100	230.3363
242.1087	258.0643	280.2652
353.8025	369.2173	437.0837
538.5863	594.9976	722.9281
788.3266	874.8710	908.1962
948.9960	960.0858	968.0769
1000.2676	1020.9416	1118.6020
1145.1819	1178.6055	1189.1925
1222.4871	1244.2707	1263.8685
1282.2560	1313.4654	1344.7852
1413.2763	1424.4918	1438.5611
1489.6550	1496.6638	1503.3656
1513.8711	1515.9406	1520.4063
2986.8858	3030.2896	3044.9696

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    3062.1335             3069.6581             3099.1819
    3101.9416             3110.4365             3114.5847
    3125.6828             3130.8112             3817.7980
 Zero-point correction= 0.171198 (Hartree/Particle)


2-C3H7O
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 E(UB+HF-LYP) =  -193.694679598     A.U.
 Cartesian coordinates:
     C      -0.020844      0.126158       0.368740
     C      -1.356943     -0.461998      -0.101176
     O       0.224961      1.371953      -0.157016
     H       0.018485      0.157722       1.474222
     H      -2.183456      0.190632       0.194838
     H      -1.368693     -0.556316      -1.191464
     H      -1.526395     -1.449490       0.341917
     C       1.186850     -0.740802      -0.093818
     H       1.207079     -0.802406      -1.184821
     H       2.126265     -0.309559       0.257695
     H       1.072654     -1.746361       0.321268
 Rotational constants (GHZ):      9.5429646      7.9327385      4.9809727
 Vibrational harmonic frequencies :
     207.8535              247.7366              343.9322
     389.5265              410.7320              814.6141
     898.7315              923.4427              941.5725
    1046.7143             1101.2756             1162.7485
    1280.8874             1361.1767             1389.0443
    1414.5445             1483.6822             1495.3991
    1502.2961             1523.3140             2935.4698
    3046.0367             3059.5988             3121.3919
    3131.5527             3143.1282             3155.7745
 Zero-point correction= .094617 (Hartree/Particle)

2-C3H7OO
--------
 E(UB+HF-LYP) =  -268.859561544     A.U.
 Cartesian coordinates:
     C      -0.368451      0.020517      -0.341204
     C      -1.581255     -0.821356       0.023425
     O       0.773269     -0.634003       0.325849
     H      -0.152630     -0.037489      -1.413075
     H      -1.446508     -1.860163      -0.289985
     H      -1.754851     -0.803867       1.103869
     H      -2.471426     -0.423873      -0.472901
     C      -0.445693      1.471418       0.110457
     H      -0.643207      1.533024       1.185468
     H       0.496949      1.979121      -0.106104
     H      -1.251467      1.988060      -0.420178
     O       1.926173     -0.165783      -0.118745
 Rotational constants (GHZ):      7.8932224      4.0562004      2.9487738
 Vibrational harmonic frequencies :
     100.1510              202.9811              242.8568
     301.4484              341.9789              452.2476
     524.7843              799.8658              893.6734
     941.4575              952.9341             1130.9048
    1160.7290             1201.7932             1212.7398
    1346.9377             1370.7833             1413.3381
    1430.1968             1494.1567             1500.1705
    1505.4367             1523.2111             3055.2006
    3059.4132             3080.9540             3127.7483
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    3136.3389             3139.4886             3149.7011
 Zero-point correction= .099769 (Hartree/Particle)

2-C3H7OH
--------
 E(RB+HF-LYP) =  -194.365221402     A.U.
 Cartesian coordinates:
     C       0.000028      0.041211      -0.370597
     C       1.273055     -0.667195       0.098117
     O       0.000008      1.414583       0.023560
     H       0.000012      0.077972      -1.466937
     H       2.158529     -0.122072      -0.240683
     H       1.304090     -0.722558       1.194202
     H       1.326032     -1.691496      -0.286412
     C      -1.273081     -0.667194       0.098112
     H      -1.304161     -0.722538       1.194201
     H      -2.158452     -0.121993      -0.240791
     H      -1.326061     -1.691500      -0.286398
     H      -0.000067      1.436588       0.990544
 Rotational constants (GHZ):      8.4753024      7.9658189      4.7361452
 Vibrational harmonic frequencies :
     234.8912              273.8800              306.5266
     357.2081              426.0926              471.2648
     819.3706              924.4898              940.7973
     975.7984             1090.9722             1150.7407
    1194.4428             1318.8180             1368.1400
    1411.9450             1421.9874             1430.9210
    1497.0670             1498.5009             1511.5965
    1521.0825             3030.9809             3034.9874
    3055.1554             3097.8645             3108.2520
    3129.6885             3131.4854             3794.7463
 Zero-point correction= .108281 (Hartree/Particle)
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C) Reactions of the RO radical (Figure 1)

The RO radical can have the oxyradical function either on the same side as the -C(CH_3)$_2$- bridge (syn), or on the other side of the sixmembered ring (anti). Addition of the O_2 on the parent radical formed after H-abstraction in α-pinene is less sterically hindered on the anti side, so we calculated most of the barriers for the anti isomer. The 1,5-H-shift can only occur for the syn-isomer, for obvious geometrical reasons.
The RO syn isomer is 0.9 kcal/mol more stable than the anti isomer.

Structure	Energy (Hartree)	ZPE (Hartree)	Relative Energy (kcal/mol)
RO anti	-465.213183247	0.227426	0.00
TS for CH_3-elimination	-465.184667528	0.223558	15.47
TS for ringopening	-465.192971330	0.224566	10.89
RO syn	-465.214189702	0.227005	0.00
TS for 1,5-H-shift	-465.198062816	0.222040	7.00

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RO (anti)
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 E(UB+HF-LYP) =  -465.213183247     A.U.
 Cartesian coordinates:
     C      -1.274602      0.304197      -0.011047
     C      -0.041125      0.015070      -0.952834
     C       1.348458      0.204372      -0.266759
     C       1.290781     -0.425399       1.138169
     C       0.177786     -1.076551       1.509530
     C      -0.986161     -1.150844       0.551065
     C      -0.404851     -1.490125      -0.854816
     C       1.853650      1.658027      -0.254657
     C      -2.588618      0.364287      -0.810165
     C      -1.279800      1.484544       0.965784
     H      -0.037975      0.493245      -1.939232
     H       2.178245     -0.341946       1.756751
     H       0.091253     -1.503452       2.506487
     H      -1.828024     -1.729277       0.942438
     H       0.434031     -2.186528      -0.885240
     H      -1.163837     -1.800208      -1.573825
     H       1.146204      2.337101       0.225462
     H       2.812498      1.712521       0.268080
     H       2.009101      1.995172      -1.284789
     H      -2.693284     -0.439140      -1.541990
     H      -2.655993      1.314640      -1.352476
     H      -3.448792      0.311573      -0.132773
     H      -1.308600      2.435283       0.420478
     H      -0.417176      1.499637       1.631948
     H      -2.180651      1.445488       1.590488
     O       2.311236     -0.608698      -0.839679
 Rotational constants (GHZ):      1.7284350      1.0419038      0.9650374
 Vibrational harmonic frequencies :
     142.8253               179.2977               191.4651
     200.0864               205.9008               266.5952
     299.0607               324.4440               336.9881
     362.4915               395.9130               435.6651
     466.2074               487.6422               525.3285
     557.7443               629.6376               663.6928
     734.2208               760.5396               846.5518
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     858.3690              885.8196              919.0456
     930.3079              954.4836              960.0363
     966.9894              973.7110             1020.8110
    1025.6041             1050.2260             1088.6206
    1105.0105             1122.8970             1141.0986
    1170.7264             1189.2150             1212.9394
    1233.0445             1245.6631             1261.6261
    1284.5342             1302.0152             1342.7959
    1375.8745             1405.9288             1413.6343
    1432.2553             1494.4196             1498.1918
    1498.8458             1506.4813             1514.3887
    1530.5326             1533.6843             1646.3525
    3036.7790             3044.0050             3056.1530
    3065.3549             3090.2267             3091.5809
    3101.1795             3106.2385             3127.6696
    3141.2794             3152.4635             3158.2098
    3162.1502             3172.5763             3214.1660
 Zero-point correction= 0.227426 (Hartree/Particle)


RO (syn)
--------
 E(UB+HF-LYP) =  -465.214189702     A.U.
 Cartesian coordinates:
     C      -1.281424      0.272810      -0.057401
     C      -0.005453     -0.005731      -0.936318
     C       1.293543      0.300066      -0.133135
     C       1.240171     -0.411803       1.217545
     C       0.131976     -1.080861       1.553902
     C      -0.994553     -1.162160       0.544977
     C      -0.338390     -1.520939      -0.824960
     C      -2.567074      0.294542      -0.901814
     C      -1.304739      1.490817       0.868850
     H       0.045643      0.462844      -1.925208
     H       2.091583     -0.293798       1.883014
     H       0.029594     -1.565106       2.522111
     H      -1.847010     -1.750536       0.897287
     H       0.493111     -2.229389      -0.787595
     H      -1.049016     -1.851797      -1.584462
     H      -2.653145     -0.549968      -1.589524
     H      -2.614416      1.213052      -1.498000
     H      -3.447933      0.279942      -0.249612
     H      -1.375971      2.411466       0.279477
     H      -0.418963      1.569281       1.500844
     H      -2.182768      1.450155       1.525681
     C       2.557953     -0.128133      -0.948404
     H       3.462724      0.061802      -0.366681
     H       2.490700     -1.196059      -1.168968
     H       2.609081      0.435861      -1.882962
     O       1.496841      1.657575       0.018143
 Rotational constants (GHZ):      1.7249589      1.0442114       .9812790
 Vibrational harmonic frequencies :
     146.7336              168.4782              177.8527
     195.1306              212.4352              224.0106
     281.1195              308.2835              347.2573
     385.2893              399.5209              426.5624
     447.0147              479.4571              520.8821
     572.6140              627.4801              684.0210
     733.0119              761.0680              846.6848
     863.7477              897.0580              909.0465
     924.6768              950.9387              959.0790
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965.1470	975.2939	1000.9347
1021.8033	1034.6898	1057.1577
1090.6831	1130.0594	1146.9520
1170.6347	1200.4876	1211.2973
1218.9232	1243.4723	1263.0196
1286.3647	1295.7143	1345.2259
1379.9038	1394.7960	1416.2679
1434.8877	1481.4559	1492.5955
1497.4660	1504.7038	1512.1486
1522.7946	1526.9582	1693.4247
3037.2381	3043.8258	3062.5276
3073.7520	3083.7759	3091.1261
3097.9650	3104.2026	3127.7834
3140.9621	3144.6256	3150.8922
3152.5849	3172.3413	3195.5622

Zero-point correction= .227005 (Hartree/Particle)

TS for RO (anti) CH3-elimination

E(UB+HF-LYP) = -465.184667528 A.U.

Cartesian coordinates:

C	-1.225182	0.397572	-0.013545
C	-0.054741	-0.073263	-0.964450
C	1.337116	-0.214177	-0.313779
C	1.239931	-0.725319	1.097538
C	0.040574	-1.171789	1.505907
C	-1.145881	-1.068146	0.565355
C	-0.654579	-1.518364	-0.843462
C	2.050191	1.791739	-0.023073
C	-2.513572	0.651412	-0.819508
C	-1.070263	1.563943	0.966565
H	0.032619	0.376700	-1.957540
H	2.150027	-0.821849	1.681933
H	-0.090307	-1.629297	2.483720
H	-2.056394	-1.511265	0.980043
H	0.053400	-2.349341	-0.876610
H	-1.461858	-1.705380	-1.552264
H	1.483293	2.186113	0.810772
H	3.094101	1.566996	0.158349
H	1.819644	2.191742	-1.004345
H	-2.723195	-0.111468	-1.572198
H	-2.445016	1.613941	-1.339622
H	-3.378253	0.702648	-0.147882
H	-0.905281	2.506932	0.433342
H	-0.257215	1.417416	1.677084
H	-1.994857	1.679013	1.544999
O	2.332215	-0.489318	-1.033134

Rotational constants (GHZ): 1.6046710 1.0248803 0.9255902

Vibrational harmonic frequencies :

-459.8237	64.1042	115.4730
171.8243	194.8450	204.1605
259.2388	270.4193	280.7348
340.9774	369.5997	406.7644
433.1098	455.0150	495.3394
513.5912	572.7047	614.9276
643.4935	661.0610	691.4913
760.6462	769.9872	847.5277
865.7261	890.7900	939.5103
948.2874	969.4435	982.3116
993.9621	1005.6390	1026.3570

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   1055.5380             1078.8131             1137.3158
   1151.5385             1169.6367             1205.3636
   1215.4345             1235.7220             1253.3600
   1277.9031             1296.2784             1335.8808
   1379.2867             1410.4674             1427.6401
   1432.0453             1444.8571             1495.6079
   1505.3692             1509.7018             1513.7174
   1529.4700             1533.9191             1664.4290
   3038.8893             3045.4460             3086.0749
   3094.5457             3095.5822             3101.4480
   3102.8634             3127.6132             3134.4459
   3156.5511             3157.8491             3176.5659
   3207.5089             3285.2989             3301.4267
 Zero-point correction= 0.223558 (Hartree/Particle)


TS for RO (anti) ringopening
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 E(UB+HF-LYP) =  -465.192971330     A.U.
 Cartesian coordinates:
     C      -1.319202      0.335008      -0.037436
     C      -0.224905     -0.066753      -1.040713
     C       1.664247      0.104814      -0.180733
     C       1.318911     -0.398678       1.218532
     C       0.158290     -0.952849       1.585941
     C      -1.007657     -1.068724       0.635026
     C      -0.482913     -1.536415      -0.762769
     C       1.984143      1.597274      -0.313646
     C      -2.695116      0.333625      -0.750769
     C      -1.238740      1.608761       0.806935
     H      -0.016426      0.399200      -2.003190
     H       2.138616     -0.318154       1.933231
     H       0.033135     -1.315217       2.604113
     H      -1.854463     -1.603103       1.075437
     H       0.381918     -2.199250      -0.777473
     H      -1.270630     -1.954942      -1.399610
     H       1.229944      2.257093       0.115971
     H       2.931877      1.787991       0.206536
     H       2.132269      1.837571      -1.369360
     H      -2.858701     -0.549631      -1.371763
     H      -2.793754      1.217128      -1.390999
     H      -3.495668      0.372590      -0.003132
     H      -1.228073      2.498053       0.166337
     H      -0.358623      1.631125       1.448919
     H      -2.122684      1.681875       1.451066
     O       2.276114     -0.684838      -0.956037
 Rotational constants (GHZ):      1.6997914      0.9763220      0.9170475
 Vibrational harmonic frequencies :
    -410.4581              143.4177              165.7440
     171.2886              187.5665              213.4093
     251.1024              266.9287              305.7950
     314.2266              380.9390              386.7107
     412.7246              445.2558              461.1069
     504.9489              584.3561              627.2706
     673.8860              736.0919              784.1280
     805.5418              860.3960              867.8104
     911.9561              930.8904              945.7942
     967.0463              971.8543              981.3574
    1010.1417             1020.1754             1032.0574
    1055.8744             1116.4716             1146.9488
    1170.1496             1176.1285             1201.9051
```

```
    1207.2612             1231.5835             1263.5112
    1301.0889             1342.7552             1395.3593
    1399.9298             1407.4914             1427.4798
    1449.5809             1488.2098             1489.5781
    1499.6879             1505.8540             1509.0212
    1517.1917             1534.2869             1699.2423
    3040.9337             3043.9478             3046.5380
    3057.0824             3090.9548             3099.0976
    3108.0809             3121.4251             3140.5729
    3141.8400             3154.1842             3158.1572
    3163.1515             3173.5433             3175.0971
 Zero-point correction= 0.224566 (Hartree/Particle)


TS for RO (syn) 1,5-H-shift
---------------------------
 E(UB+HF-LYP) =  -465.198062816     A.U.
 Cartesian coordinates:
     C      -1.248852      0.301030      -0.015066
     C      -0.034288     -0.011848      -0.969477
     C       1.265211      0.251768      -0.153289
     C       1.244868     -0.590967       1.118041
     C       0.124882     -1.238926       1.456480
     C      -1.034135     -1.187260       0.484418
     C      -0.445583     -1.504058      -0.926940
     C      -2.575043      0.490947      -0.767566
     C      -1.025237      1.456214       0.946712
     H       0.005169      0.510419      -1.931732
     H       2.126784     -0.562658       1.753355
     H       0.036274     -1.798054       2.384730
     H      -1.916384     -1.735868       0.827467
     H       0.348484     -2.254460      -0.960976
     H      -1.203015     -1.750262      -1.675176
     H      -2.774491     -0.316174      -1.478080
     H      -2.568347      1.433474      -1.326614
     H      -3.413231      0.527230      -0.062547
     H      -1.564482      2.372575       0.695142
     H      -1.084931      1.222468       2.010812
     H       0.201469      1.765863       0.744879
     C       2.524046     -0.002032      -1.000760
     H       3.423292      0.172738      -0.403504
     H       2.539393     -1.034225      -1.362816
     H       2.540865      0.678362      -1.856841
     O       1.315992      1.622422       0.200825
 Rotational constants (GHZ):      1.7108400      1.0983732      1.0084398
 Vibrational harmonic frequencies :
    -1518.4073             175.3259             194.4223
     224.6739             236.6752             249.8277
     301.3417             351.7462             359.6205
     406.9630             429.3766             442.1989
     455.2988             500.3426             523.5064
     588.4237             632.8330             672.4816
     708.6251             737.8939             767.6883
     843.1152             866.2117             913.1354
     924.9012             935.9188             959.9339
     965.2724             978.6437             997.8394
    1025.0775            1052.6486            1067.9270
    1092.6367            1102.0159            1122.7980
    1148.6668            1168.3541            1196.3204
    1205.1534            1225.0670            1229.6385
    1250.4091            1263.0085            1275.5569
```

1300.7839	1341.0121	1393.6858
1406.8333	1418.4045	1463.8433
1492.7164	1501.2335	1507.9573
1509.8231	1524.9929	1546.8041
1695.0669	3039.4694	3053.4234
3071.6344	3080.9416	3089.3307
3091.8675	3104.9147	3119.3724
3132.6326	3134.5148	3135.9209
3171.3448	3172.2340	3193.8377

Zero-point correction= 0.222040 (Hartree/Particle)

D) 1,5-H-shift in 1-butanal-4-oxy ($^{\cdot}OCH_2CH_2CH_2CHO \rightarrow HOCH_2CH_2CH_2C^{\cdot}O$)

Structure	Energy (Hartree)	ZPE (Hartree)	Relative Energy (kcal/mol)
1-butanal-4-oxy	-307.000120476	0.103996	
TS for 1,5-H-shift	-306.997857461	0.101691	-0.026

The slightly negative barrier appears after the ZPE correction ; even a small scaling factor below 1.000 on the zero-point energies would lead to a positive barrier. This result should not be taken on face value, since it is unphysical to have a negative barrier, but it indicates that the barrier for the hydrogen shift is very low, and that the rate is mainly governed by the Arrhenius pre-exponential factor.

```
1-butanal-4-O
-------------
 E(UB+HF-LYP) =  -307.000120476     A.U.
 Point group : CS
 Cartesian coordinates:
     C      -0.793993     -1.951219       0.000000
     C       0.393290     -1.011708       0.000000
     C       0.000000      0.464354       0.000000
     C       1.261265      1.381433       0.000000
     O       0.806406      2.671291       0.000000
     H      -0.525397     -3.032091       0.000000
     H       1.012375     -1.267797       0.873000
     H       1.012375     -1.267797      -0.873000
     H      -0.606372      0.696816      -0.879000
     H      -0.606372      0.696816       0.879000
     H       1.856030      1.146675       0.901000
     H       1.856030      1.146675      -0.901000
     O      -1.951661     -1.598347       0.000000
 Rotational constants (GHZ):     11.1574020      1.5389130      1.3875056
 Vibrational harmonic frequencies :
      74.7770 (  A")      112.5171 (  A")      147.6772 (  A')
     181.8766 (  A")      303.5626 (  A')      388.7039 (  A')
     527.4241 (  A")      681.2006 (  A")      693.0643 (  A')
     856.9590 (  A")      891.8103 (  A')      939.5252 (  A')
    1028.5390 (  A")     1063.6020 (  A')     1123.3409 (  A')
    1175.9322 (  A")     1268.7252 (  A')     1270.8222 (  A")
    1304.5313 (  A")     1321.1559 (  A')     1381.9293 (  A')
    1424.6992 (  A')     1464.4196 (  A')     1510.1935 (  A')
    1554.2163 (  A')     1835.0748 (  A')     2896.3115 (  A')
    2941.4457 (  A')     2981.7835 (  A")     3020.1821 (  A')
    3048.7228 (  A")     3092.0142 (  A')     3142.0379 (  A")
 Zero-point correction= .103996 (Hartree/Particle)

TS for 1-butanal-4-O 1,5-H-shift
--------------------------------
 E(UB+HF-LYP) =  -306.997857461     A.U.
 Cartesian coordinates:
     C       1.188546     -0.240507       0.054109
     C       0.496190      1.107990       0.190246
     C      -0.943836      1.032730      -0.329901
     C      -1.675049     -0.207672       0.235198
     O      -1.036985     -1.392012      -0.126079
     H       1.101312      1.870632      -0.310171
     H       0.496576      1.338668       1.266175
     H      -0.942398      0.972388      -1.423721
```

```
     H      -1.491567      1.937347      -0.045113
     H      -2.688966     -0.237215      -0.196375
     H      -1.788556     -0.100824       1.330688
     H       0.346139     -1.100168       0.070644
     O       2.358529     -0.462497      -0.072676
 Rotational constants (GHZ):      6.1172063      2.6082214      1.9462376
 Vibrational harmonic frequencies :
    -539.3557              91.4340             225.5753
     283.5158             410.8697             475.9617
     506.0695             709.9788             772.8648
     847.4385             913.5012             948.9797
     995.1537            1037.0730            1088.2842
    1160.7945            1182.0277            1219.5918
    1269.1080            1324.2805            1361.0217
    1381.9835            1451.8052            1490.7153
    1500.5726            1856.3331            1887.3431
    2939.0952            2999.8999            3027.4219
    3061.5153            3104.6937            3112.4582
 Zero-point correction= .101691 (Hartree/Particle)
```

E) Acetone elimination from RO2 (Figure 1)

We did not perform calculation on the RO2 radical itself (see figure 1), but rather replaced the -CHO function by a hydrogen to reduce the computational demands somewhat.

Structure	Energy (Hartree)	ZPE (Hartree)	Relative Energy (kcal/mol)
RO2	-502.370660440	0.222028	
TS for acetone elimination	-502.363994160	0.219858	2.82

```
RO2
---
 E(UB+HF-LYP) =  -502.370660440     A.U.
 Cartesian coordinates:
     C       4.028285     -0.472807      -0.661381
     C       2.834815     -0.032942       0.167698
     O       2.942115      0.223645       1.358191
     C       1.531897      0.067505      -0.549984
     C       0.417892      0.470582       0.080375
     C      -0.937211      0.628999      -0.540818
     C      -1.441495      2.077042      -0.377890
     C      -1.998123     -0.396632       0.014248
     H      -0.866136      0.414949      -1.614484
     C      -2.179609     -0.347685       1.546534
     C      -1.606725     -1.846333      -0.415614
     O      -3.204059     -0.203603      -0.616854
     H       4.191875      0.223206      -1.492943
     H       3.843651     -1.458838      -1.104565
     H       4.920204     -0.512816      -0.035263
     H       1.513786     -0.188383      -1.608378
     H       0.521817      0.724831       1.135894
     H      -0.782514      2.774568      -0.902863
     H      -1.473895      2.381783       0.673273
     H      -2.447843      2.167810      -0.797090
     H      -2.489606      0.648989       1.871594
     H      -1.253488     -0.609281       2.066705
     H      -2.959278     -1.055369       1.838889
     H      -0.627162     -2.077437       0.011779
     H      -1.548542     -1.919809      -1.504208
     H      -2.345669     -2.560915      -0.048056
 Rotational constants (GHZ):      2.0100352       .5074137       .4879405
 Vibrational harmonic frequencies :
      36.3222               51.7315               75.5099
     118.2983              131.1401              145.8307
     211.5324              225.9652              236.9579
     244.1138              265.1008              294.6107
     329.6601              344.7382              375.9267
     408.8218              449.9485              492.7414
     544.4306              589.9464              617.0053
     713.2713              862.5475              874.3023
     901.4282              913.7818              923.3861
     942.8273              975.8836              987.6373
    1025.1483             1037.9948             1051.7888
    1074.7805             1132.3192             1166.9665
    1173.3561             1194.0645             1214.9057
    1282.1980             1332.2030             1343.2193
    1373.4710             1382.8865             1398.4606
    1409.6403             1412.8872             1476.7597
    1480.1941             1487.5445             1496.5469
```

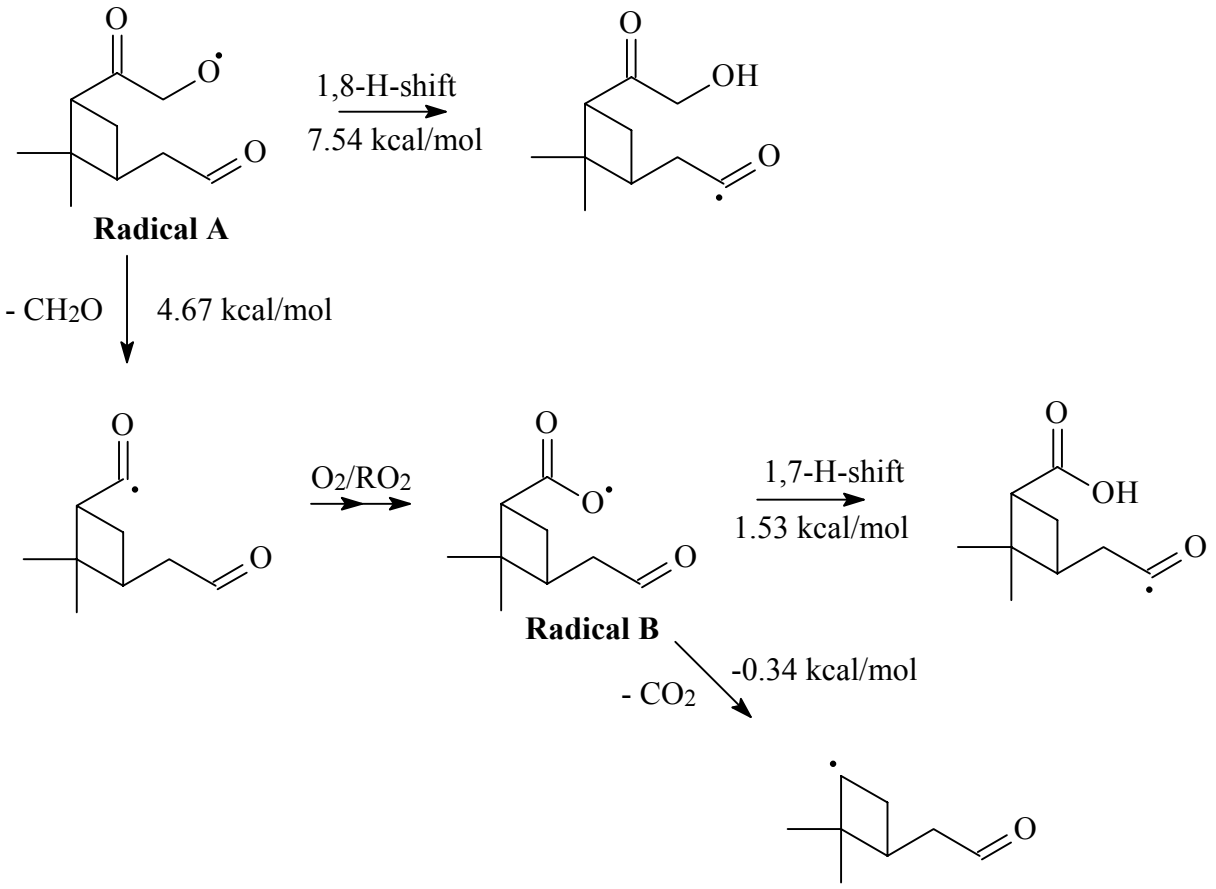
```
    1499.8687             1511.8509             1513.1738
    1524.0609             1688.7089             1790.6699
    3042.5451             3047.9664             3051.8774
    3059.2005             3062.5902             3101.9791
    3123.3434             3132.4132             3137.5549
    3143.4580             3146.9787             3156.9536
    3158.2427             3164.2058             3168.7384
 Zero-point correction= .222028 (Hartree/Particle)

TS for RO2 acetone elimination
------------------------------
 E(UB+HF-LYP) =  -502.363994160     A.U.
 Cartesian coordinates:
     C       3.910030     -0.639042      -0.568088
     C       2.759818      0.046525       0.145635
     O       2.901186      0.564835       1.244742
     C       1.450530      0.057199      -0.562003
     C       0.372552      0.681923      -0.032455
     C      -0.943862      0.770633      -0.652371
     C      -1.677830      2.082503      -0.448616
     C      -2.011089     -0.630084       0.094376
     H      -0.964531      0.426408      -1.686199
     C      -1.960264     -0.438315       1.617798
     C      -1.342981     -1.922325      -0.393150
     O      -3.123131     -0.320956      -0.485693
     H       4.097192     -0.161246      -1.537276
     H       3.663681     -1.687838      -0.772788
     H       4.809600     -0.586615       0.045922
     H       1.387353     -0.436299      -1.529963
     H       0.513912      1.164755       0.934149
     H      -1.148983      2.881938      -0.982089
     H      -1.711948      2.365755       0.607969
     H      -2.698723      2.019017      -0.825645
     H      -2.372055      0.532221       1.902215
     H      -0.949365     -0.543470       2.020761
     H      -2.588555     -1.211126       2.075289
     H      -0.314647     -2.026830      -0.039113
     H      -1.365624     -1.973324      -1.484779
     H      -1.923164     -2.768497      -0.007612
 Rotational constants (GHZ):      1.8644276      0.5355055      0.5004297
 Vibrational harmonic frequencies :
    -539.2270              34.6056               50.9233
      73.8359             124.5460              128.3882
     166.8426             196.3089              209.7190
     220.9179             234.2308              259.8134
     269.6099             329.8943              347.9167
     371.9415             412.5478              464.0550
     478.5214             520.5442              584.7722
     612.6356             766.9755              864.0296
     886.0039             906.0547              921.7953
     962.3089             972.7154              997.0114
    1015.8159            1038.3343             1051.0874
    1061.6406            1106.1344             1147.9289
    1173.2555            1203.0891             1216.4173
    1291.4481            1325.7178             1376.6947
    1388.1101            1390.7885             1403.4533
    1408.8134            1421.0338             1476.4966
    1485.3069            1487.5742             1489.6425
    1498.4901            1504.3863             1506.6008
    1512.3418            1615.8613             1775.9491
    3043.4391            3045.1474             3048.8782
```

```
   3053.5918             3102.8882             3106.5906
   3118.2597             3122.6386             3140.4706
   3148.9742             3153.7992             3166.1826
   3168.7807             3169.8532             3175.3473
Zero-point correction= 0.219858 (Hartree/Particle)
```

F) The "Jenkin mechanism"

These reaction steps were proposed by Jenkin et al. (Atmos. Environ. 34, 2837 (2000)) to explain pinic acid formation in the ozone-initiated oxidation of α-pinene. We performed some calculations on a subsection of the mechanism.



Structure	Energy (Hartree)	ZPE (Hartree)	Relative Energy (kcal/mol)
Radical A	-615.660619202	0.233160	0.00
TS for CH_2O-elimination	-615.651118722	0.231101	4.67
TS for 1,8-H-shift	-615.647876547	0.232434	7.54
Radical B	-576.376388898	0.205826	0.00
TS for CO_2-elimination	-576.374859649	0.203752	-0.34
TS for 1,7-H-shift	-576.371803105	0.203678	1.53

The negative barrier for the CO_2 elimination from radical B should not be taken on face value, but rather as an indication of a very low barrier.

```
Radical A
---------
 E(UB+HF-LYP) =  -615.660619202     A.U.
 Cartesian coordinates:
     C       1.067094      0.721230       0.996747
     H       1.166278      1.583151       1.667713
     C       2.488412      0.203103       0.734461
```

C	2.645463	-1.077874	-0.059979
H	2.949922	-0.000843	1.714453
H	3.103240	0.969423	0.250087
H	1.996991	-1.925439	0.252247
C	0.107629	1.155183	-0.172833
C	-0.043890	-0.206970	1.559983
C	0.046646	2.652707	-0.465750
C	0.284771	0.364413	-1.474742
H	0.257160	-0.718593	-1.323212
H	-0.516968	0.613229	-2.178453
H	1.235527	0.619346	-1.953119
H	-0.802531	2.886959	-1.117090
H	0.958630	2.985286	-0.975430
H	-0.059301	3.239795	0.453125
H	-0.179632	-0.214173	2.645057
H	0.026255	-1.233010	1.197888
C	-1.070383	0.601174	0.735209
H	-1.488251	1.434327	1.311990
C	-2.246191	-0.036206	0.035607
O	3.453746	-1.218672	-0.952272
O	-3.062449	0.586332	-0.591593
C	-2.442363	-1.640697	0.141221
H	-3.384565	-1.851162	-0.388732
H	-2.580827	-1.757266	1.239104
O	-1.354429	-2.248586	-0.328031

Rotational constants (GHZ): 1.1179405 0.5789669 0.4796857

Vibrational harmonic frequencies :

36.5324	48.3481	72.3890
80.4740	102.8782	142.7178
182.3000	198.9322	220.5478
247.4189	250.9836	290.2276
305.6500	339.4279	351.5666
404.8357	454.1999	479.3422
502.8745	531.3977	593.3507
636.8577	677.8244	735.8957
775.8654	810.5976	886.0524
893.7843	925.2052	959.3507
980.6776	985.5978	1008.3690
1035.1122	1064.5811	1100.6178
1129.0307	1145.0932	1155.5492
1168.8199	1193.5172	1224.1662
1238.2461	1248.3546	1259.7697
1280.3811	1294.2517	1318.7146
1332.9320	1350.8090	1401.6226
1417.6378	1436.2607	1441.6548
1461.7133	1496.3362	1503.1034
1512.2578	1517.1961	1520.2011
1525.0859	1827.0334	1833.4371
2870.0421	2913.4100	3004.4055
3014.2176	3034.3625	3046.1946
3049.1479	3067.8499	3085.0537
3094.2939	3105.2388	3111.3748
3117.2078	3129.3948	3157.2403

Zero-point correction= 0.233160 (Hartree/Particle)

TS for Radical A 1,8-H-shift

E(UB+HF-LYP) = -615.647876547 A.U.

Cartesian coordinates:

C	0.566466	-1.443740	-0.543500
H	0.600887	-2.457374	-0.955239

C	1.930350	-1.214816	0.138922
C	2.429182	0.221128	0.163559
H	2.716123	-1.802503	-0.346568
H	1.888061	-1.544696	1.186641
H	1.643789	1.021041	0.424759
C	-0.783281	-1.235455	0.250098
C	0.101343	-0.407420	-1.609341
C	-1.685096	-2.472097	0.150157
C	-0.697170	-0.785645	1.709512
H	-0.093454	0.114268	1.842328
H	-1.700490	-0.562957	2.088397
H	-0.282715	-1.586457	2.333527
H	-2.692900	-2.247377	0.515942
H	-1.282244	-3.294683	0.753357
H	-1.773702	-2.826586	-0.882865
H	-0.065528	-0.828295	-2.603996
H	0.760499	0.456656	-1.734412
C	-1.209190	-0.135872	-0.820165
H	-2.110629	-0.449872	-1.353313
C	-1.532384	1.260781	-0.309369
O	3.567648	0.548277	-0.052179
O	-2.675788	1.539222	0.008384
C	-0.434563	2.335659	-0.180983
H	-0.950242	3.270309	0.105670
H	0.038263	2.543370	-1.158811
O	0.506932	2.095003	0.805199

Rotational constants (GHZ): 0.9695610 0.7278503 0.5199934

Vibrational harmonic frequencies :

-55.9253	36.8333	57.1607
106.0661	154.8011	171.2236
200.4236	213.7754	234.3737
262.3669	293.6117	312.6088
327.6087	365.5715	378.5810
415.1810	456.5577	466.7946
494.2092	584.2390	609.0964
630.1472	755.9728	777.3668
797.8532	844.7846	892.7305
896.7162	954.5870	964.4653
982.8827	1004.4530	1016.5593
1046.7158	1056.9313	1073.1688
1104.4453	1142.8875	1155.9216
1172.6459	1190.8152	1227.9623
1238.3654	1258.5189	1264.0473
1287.5621	1302.5415	1317.5476
1334.9831	1355.0304	1373.1765
1381.7650	1404.3376	1418.0650
1439.0313	1459.6365	1498.9416
1506.2847	1509.0531	1518.3287
1534.6345	1786.1851	1850.1867
2194.3423	2942.7956	2981.2873
3032.4334	3037.7045	3042.6281
3065.8240	3076.4792	3090.2383
3101.3711	3101.7276	3105.5257
3113.7318	3123.3542	3148.1785

Zero-point correction= 0.232434 (Hartree/Particle)

TS for Radical A CH2O elimination

E(UB+HF-LYP) = -615.651118722 A.U.

Cartesian coordinates:

C	1.016083	0.900039	0.938796

H	1.153672	1.819787	1.520191
C	2.415210	0.317141	0.701297
C	2.528945	-1.016433	-0.015664
H	2.873923	0.159172	1.691146
H	3.057373	1.029444	0.171762
H	1.814351	-1.806921	0.294463
C	0.039629	1.240656	-0.249287
C	-0.098473	0.053110	1.609723
C	-0.029331	2.715231	-0.643350
C	0.200117	0.360551	-1.494392
H	0.174073	-0.708466	-1.267381
H	-0.605533	0.567614	-2.208495
H	1.146231	0.583362	-1.997865
H	-0.871362	2.904507	-1.318709
H	0.886997	3.013191	-1.166244
H	-0.143498	3.364084	0.231612
H	-0.231752	0.177637	2.687675
H	-0.040640	-1.010149	1.375231
C	-1.136178	0.767103	0.714301
H	-1.594000	1.634900	1.204619
C	-2.266267	0.006194	0.076585
O	3.376205	-1.242794	-0.853704
O	-3.280499	0.404848	-0.389799
C	-2.051565	-2.160634	-0.078910
H	-2.618061	-2.118651	-1.026671
H	-2.686890	-2.246573	0.825957
O	-0.848693	-2.469640	-0.052982

Rotational constants (GHZ): 1.0059948 0.6102765 0.4737375

Vibrational harmonic frequencies :

-165.6295	38.8770	42.9388
63.4201	83.2296	97.5599
131.2664	177.3238	189.2261
215.0607	243.9433	252.4095
270.6365	308.1626	332.2686
351.3199	387.1281	403.0818
443.7581	478.6949	513.0444
589.2786	628.3479	664.7292
703.6172	758.7722	805.5024
874.1131	909.4637	962.6932
966.3984	979.2460	1003.7831
1020.2603	1048.9512	1095.9097
1099.8355	1122.7936	1145.9653
1163.2018	1191.2215	1225.3138
1240.7607	1245.9529	1261.7349
1278.6297	1319.6748	1330.9505
1339.2167	1401.6956	1420.0459
1441.6430	1448.1474	1460.3868
1476.6997	1500.4487	1504.5761
1515.0108	1521.0561	1535.8667
1638.8960	1821.9652	1928.9611
2908.7009	2944.4082	2984.5555
3004.3750	3035.4100	3043.6505
3047.2178	3055.9100	3086.5556
3092.7709	3105.9955	3110.6643
3112.1188	3137.0188	3157.2749

Zero-point correction= 0.231101 (Hartree/Particle)

Radical B

E(UB+HF-LYP) = -576.376388898 A.U.

Cartesian coordinates:

C	0.846458	0.617073	0.996646
H	0.822122	1.464589	1.692494
C	2.327745	0.311145	0.728304
C	2.657387	-0.934596	-0.067192
H	2.819445	0.176717	1.705236
H	2.818698	1.158590	0.237953
H	2.181101	-1.874273	0.292698
C	-0.164236	0.944939	-0.162880
C	-0.131314	-0.464602	1.529050
C	-0.416357	2.427335	-0.430028
C	0.112510	0.202000	-1.474905
H	0.232393	-0.876485	-1.336364
H	-0.717832	0.346828	-2.174550
H	1.020908	0.583037	-1.950749
H	-1.275738	2.564144	-1.095903
H	0.453346	2.888105	-0.912590
H	-0.617211	2.974657	0.497294
H	-0.264663	-0.537092	2.611180
H	0.067055	-1.464696	1.136105
C	-1.263323	0.224656	0.728524
H	-1.811388	0.964776	1.320131
C	-2.250280	-0.645910	0.028126
O	3.422126	-0.955599	-1.006711
O	-3.319902	-0.216616	-0.496963
O	-2.107196	-1.885428	-0.155927

Rotational constants (GHZ): 1.4680178 0.6055381 0.5503887

Vibrational harmonic frequencies :

41.8201	46.5473	74.4639
87.1909	132.0916	185.7792
206.1391	238.3510	242.6239
260.3766	306.7459	340.0362
356.1304	400.7114	443.7617
466.8263	581.5134	585.4773
623.1354	660.9510	724.7226
787.9016	818.1451	888.8185
914.0056	959.5080	964.4398
981.6380	1002.6883	1022.6211
1045.5416	1093.7102	1121.0266
1134.5345	1155.9745	1187.6436
1192.4300	1229.5753	1251.4235
1258.3731	1281.0860	1314.6015
1329.5035	1348.8731	1404.4410
1420.1627	1438.8052	1442.6724
1462.2244	1495.7516	1503.6443
1508.9206	1516.6209	1523.1795
1592.4133	1830.3954	2895.4870
3007.3203	3036.0841	3047.0052
3051.9245	3086.0693	3087.3170
3096.8924	3107.7970	3111.1158
3119.1540	3132.1648	3140.0781

Zero-point correction= 0.205826 (Hartree/Particle)

TS for Radical B 1,7-H-shift

E(UB+HF-LYP) = -576.371803105 A.U.

Cartesian coordinates:

C	0.339149	-1.347787	-0.692046
H	0.265387	-2.382555	-1.044174
C	1.798019	-1.132528	-0.285949
C	2.198976	0.294107	0.070349
H	2.461124	-1.426850	-1.111347

H	2.083714	-1.762314	0.566599
H	1.337411	1.096447	0.015965
C	-0.815835	-1.002341	0.325963
C	-0.254592	-0.315667	-1.693245
C	-1.887966	-2.099917	0.313473
C	-0.442113	-0.673522	1.773324
H	0.280454	0.140759	1.864243
H	-1.334584	-0.367280	2.330039
H	-0.029174	-1.556695	2.274248
H	-2.785607	-1.773272	0.849592
H	-1.515527	-3.009313	0.799512
H	-2.184877	-2.363857	-0.707460
H	-0.751621	-0.774449	-2.550820
H	0.440074	0.438844	-2.073392
C	-1.256306	0.195346	-0.615579
H	-2.309292	0.149876	-0.904135
C	-1.031564	1.600073	-0.104232
O	3.303147	0.628101	0.401498
O	-1.958787	2.380242	0.117157
O	0.175128	2.052166	0.123694

Rotational constants (GHZ): 1.1072010 0.8778872 0.6371774

Vibrational harmonic frequencies :

-204.2034	38.1343	79.6153
156.1881	181.9990	207.1789
230.5579	253.7013	276.4936
292.4156	306.1545	335.5022
377.9165	386.7331	398.9728
474.6467	546.6211	605.0549
628.6933	697.3850	729.7463
781.7572	800.8960	870.8198
916.1980	931.7739	954.1673
974.2878	994.2404	1014.9616
1041.7211	1082.0504	1106.2469
1135.8146	1168.3451	1186.8167
1225.4593	1246.0174	1262.3333
1281.3179	1308.6014	1311.6696
1321.7847	1335.1439	1380.5994
1406.2317	1418.0613	1434.8308
1440.7719	1496.4416	1500.0921
1503.7226	1516.2361	1524.8895
1607.7629	1819.0934	1860.7576
3034.3702	3036.1120	3046.7702
3062.4857	3078.8724	3079.8652
3101.9365	3105.8270	3108.5305
3113.8933	3132.8641	3137.2057

Zero-point correction= 0.203678 (Hartree/Particle)

TS for Radical B CO2 elimination

E(UB+HF-LYP) = -576.374859649 A.U.

Cartesian coordinates:

C	0.861496	0.496315	1.067582
H	0.837715	1.249748	1.861942
C	2.341091	0.245884	0.727143
C	2.676226	-0.908149	-0.194373
H	2.860159	0.027041	1.673910
H	2.798215	1.149891	0.311358
H	2.223671	-1.887865	0.077497
C	-0.177515	0.951362	-0.041204
C	-0.092300	-0.671900	1.471709
C	-0.467219	2.447006	-0.140958

C	0.104835	0.358607	-1.428865
H	0.240050	-0.726911	-1.403905
H	-0.736851	0.569062	-2.094858
H	1.005147	0.801668	-1.864076
H	-1.357771	2.620538	-0.753895
H	0.371301	2.977176	-0.606771
H	-0.641848	2.889710	0.845550
H	-0.220109	-0.891915	2.534079
H	0.114027	-1.602033	0.939457
C	-1.183683	0.136472	0.792189
H	-1.852628	0.709712	1.436129
C	-2.435045	-0.777068	-0.197225
O	3.426271	-0.819792	-1.141497
O	-3.100435	0.087990	-0.730105
O	-2.251884	-1.962823	-0.039947

Rotational constants (GHZ): 1.4237809 0.6019336 0.5476462

Vibrational harmonic frequencies :

-96.6421	28.6816	52.7911
73.7806	80.2457	130.9179
181.8772	208.1960	236.3054
241.0050	258.9687	290.6294
314.2672	364.1969	429.7990
436.2825	465.4927	561.0594
589.3293	614.8996	670.9309
695.6035	795.6637	817.9450
847.5253	923.0248	958.8323
976.8440	983.2426	1011.9912
1020.1896	1040.5905	1101.9864
1109.7612	1135.5128	1172.9779
1193.4041	1226.8336	1238.1263
1259.6879	1272.4798	1280.5898
1301.3657	1333.2386	1397.3569
1414.7563	1434.2482	1439.5771
1462.4440	1494.0927	1501.3766
1505.5692	1514.6275	1529.7056
1829.9382	1932.1057	2898.5395
3010.2736	3039.7765	3056.0948
3068.6880	3096.7927	3100.2325
3109.9207	3119.8990	3128.3599
3133.7283	3136.5067	3154.9136

Zero-point correction= 0.203752 (Hartree/Particle)

G) Ring-opening in the 1,5-H-shifted syn RO1 radical (Figure 4)

After the 1,5-H-shift in RO, the four-membered ring can break, forming an allyl-resonance stabilised radical.

Structure	Energy (Hartree)	ZPE (Hartree)	Relative Energy (kcal/mol)
1,5-H-shifted syn RO1 radical	-465.209745291	0.225251	0.0
TS for ringopening	-465.196847811	0.224457	7.6

```
minimumOH
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 E(UB+HF-LYP) =  -465.209745291     A.U.
 Cartesian coordinates:
     C      -1.318437      0.316539      -0.003515
     C      -0.039603      0.010581      -0.919237
     C       1.285756      0.245783      -0.164915
     C       1.203508     -0.443809       1.191846
     C       0.089166     -1.096938       1.540385
     C      -1.053420     -1.146862       0.547327
     C      -0.427688     -1.491731      -0.835304
     C      -2.594083      0.407469      -0.862314
     C      -1.310148      1.445526       0.957283
     H      -0.009208      0.499202      -1.898938
     H       2.068611     -0.378977       1.851150
     H      -0.009173     -1.585284       2.507010
     H      -1.913587     -1.720049       0.905799
     H       0.379456     -2.228199      -0.829212
     H      -1.161594     -1.780183      -1.589579
     H      -2.674834     -0.385565      -1.609339
     H      -2.618343      1.365609      -1.393666
     H      -3.483244      0.359553      -0.224527
     C       2.494909     -0.256562      -0.973199
     H       3.422985     -0.079378      -0.415385
     H       2.438731     -1.327862      -1.184127
     H       2.559128      0.289242      -1.919618
     O       1.411629      1.671791      -0.013528
     H      -0.691188      1.432909       1.843755
     H      -1.791226      2.381559       0.691363
     H       2.210685      1.843113       0.503399
 Rotational constants (GHZ):      1.7202820      1.0502828      0.9835924
 Vibrational harmonic frequencies :
     143.2202               155.3054               186.8499
     193.0896               214.7945               225.3158
     234.2527               293.1732               309.5428
     366.6364               389.2045               404.6126
     428.1539               453.6273               475.5951
     516.2542               579.4596               590.0737
     642.0545               689.7764               744.2802
     768.7719               825.4608               866.1884
     904.8413               915.1779               933.8685
     946.9534               970.5606               977.3819
     981.9867              1021.1886              1064.6423
    1083.0928              1095.8913              1105.9399
    1131.0360              1166.6773              1177.2649
    1186.1683              1213.5302              1250.1516
    1257.9164              1266.2804              1302.2580
    1345.8498              1375.9316              1402.4926
    1415.6931              1416.7963              1470.8550
```

1500.5651	1504.6581	1506.6543
1508.5075	1533.3912	1698.1533
3037.8664	3045.5672	3076.4233
3085.0048	3092.6618	3106.8834
3107.4027	3130.0361	3135.4562
3144.5397	3149.2264	3169.9097
3183.5784	3281.9379	3799.3237

Zero-point correction= 0.225251 (Hartree/Particle)

TS for ring breaking in minimumOH

E(UB+HF-LYP) = -465.196847811 A.U.

Cartesian coordinates:

C	-1.340689	0.487156	-0.025770
C	-0.085015	0.114164	-0.881661
C	1.273460	0.268567	-0.146036
C	1.233906	-0.520064	1.156090
C	0.161412	-1.271555	1.468635
C	-0.937276	-1.389120	0.502651
C	-0.427935	-1.389753	-0.936165
C	-2.663330	0.436853	-0.793758
C	-1.322028	1.430262	1.014526
H	-0.034084	0.654710	-1.836079
H	2.075008	-0.405746	1.838158
H	0.080368	-1.753869	2.440712
H	-1.804726	-1.980538	0.790234
H	0.407680	-2.074610	-1.113492
H	-1.203857	-1.611717	-1.669788
H	-2.854887	-0.511884	-1.299000
H	-2.679814	1.222854	-1.560098
H	-3.501674	0.623457	-0.116058
C	2.444965	-0.174973	-1.042007
H	3.393196	-0.051424	-0.503856
H	2.376542	-1.223844	-1.339252
H	2.479894	0.448831	-1.941316
O	1.448576	1.675239	0.119557
H	-0.404900	1.746538	1.488579
H	-2.260100	1.779845	1.437646
H	2.317925	1.786250	0.528124

Rotational constants (GHZ): 1.6670630 1.0414514 0.9568238

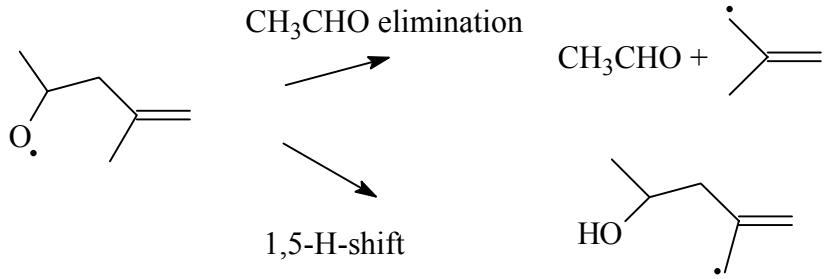
Vibrational harmonic frequencies :

-663.9123	144.3343	157.0658
172.6277	214.4214	237.6370
264.3334	290.0530	314.4749
361.5801	377.0452	386.3176
433.5924	447.8185	464.0121
489.5716	536.2639	585.9978
616.1192	704.0335	737.7607
743.8919	778.0620	838.6150
896.8779	907.3051	936.7966
947.5394	954.0425	967.5713
990.7512	1019.9879	1047.7246
1059.8757	1072.9831	1091.9309
1112.7594	1134.5202	1187.0077
1195.4993	1235.1099	1242.0180
1296.5118	1317.7497	1341.5306
1362.3522	1381.4591	1411.2369
1423.4358	1425.9138	1493.9723
1500.5304	1506.6888	1509.5520
1517.4371	1533.0928	1652.8746
3036.6143	3036.8792	3042.6754

```
   3074.4208             3104.5015             3104.6903
   3127.2730             3139.0270             3142.8996
   3151.4436             3159.3544             3161.7465
   3178.8226             3295.3775             3799.2912
Zero-point correction= 0.224457 (Hartree/Particle)
```

H) Allyl-assisted 1,5-H-shift and CH_3CHO elimination

The following oxyradical can undergo both an allyl-assisted 1,5-H-shift, and an allyl-assisted CH_3CHO elimination :



Structure	Energy (Hartree)	ZPE (Hartree)	Relative Energy (kcal/mol)
Oxyradical	-310.409239808	0.156348	0.0
TS for 1,5-H-shift	-310.394893550	0.152248	6.4
TS for CH_3CHO elimination	-310.398344188	0.153522	5.1

```
Oxyradical
----------
 E(UB+HF-LYP) =  -310.409239808     A.U.
 Cartesian coordinates:
     C       1.147695     -0.050885      -0.365449
     C       2.537897     -0.577914       0.090617
     C       0.030954     -0.601779       0.568656
     O       1.238947      1.314581      -0.304381
     H       0.967766     -0.409043      -1.396420
     H       2.545791     -1.668610       0.006686
     H       3.326106     -0.166466      -0.543486
     H       2.728043     -0.289228       1.127280
     H       0.229770     -0.211982       1.575656
     H       0.124262     -1.693125       0.602077
     C      -1.355419     -0.213764       0.112369
     C      -1.707399      1.247221       0.206635
     C      -2.208945     -1.127490      -0.365845
     H      -1.659431      1.595681       1.246003
     H      -0.984142      1.858577      -0.350439
     H      -2.709166      1.449684      -0.181492
     H      -1.944779     -2.179829      -0.427784
     H      -3.204502     -0.854635      -0.704933
 Rotational constants (GHZ):      4.6807394      1.6670823      1.3479145
 Vibrational harmonic frequencies :
      66.3477              102.5366              172.5984
     215.9318              224.0202              278.5832
     314.5851              416.3170              433.7034
     484.8708              541.8595              713.6834
     829.7980              862.4558              879.8468
     927.3557              933.5820              948.5112
     996.1818             1029.8892             1057.8076
    1079.9812             1141.8174             1191.4586
    1287.4832             1296.9173             1325.9603
    1366.5353             1397.2911             1427.9986
    1454.8959             1476.7041             1485.3241
```

```
    1488.9440             1504.7208             1512.5982
    1722.5967             2945.0485             3021.1544
    3035.1894             3058.1174             3072.9663
    3092.1221             3127.8733             3143.5763
    3152.0353             3154.0400             3234.8884
 Zero-point correction= 0.156348 (Hartree/Particle)

TS for 1,5-H-shift
------------------
 E(UB+HF-LYP) =  -310.394893550     A.U.
 Cartesian coordinates:
     C       1.082564     -0.123239      -0.373728
     C       2.500437     -0.527007       0.054298
     C       0.006444     -0.765942       0.562179
     O       1.006082      1.271955      -0.328583
     H       0.895295     -0.499218      -1.396152
     H       2.616967     -1.614829       0.004347
     H       3.240298     -0.067404      -0.606176
     H       2.695950     -0.191870       1.077171
     H       0.257571     -0.491649       1.595357
     H       0.040627     -1.856421       0.476121
     C      -1.333487     -0.206618       0.170378
     C      -1.389662      1.259088       0.286662
     C      -2.308391     -0.950301      -0.390673
     H      -1.248795      1.651872       1.297384
     H      -0.250082      1.545830      -0.193645
     H      -2.194880      1.762021      -0.250295
     H      -2.210415     -2.026470      -0.500727
     H      -3.238630     -0.503395      -0.729412
 Rotational constants (GHZ):      4.8072131      1.7995707      1.4541669
 Vibrational harmonic frequencies :
    -1533.4921              117.9344              133.5175
     233.2481              274.3713              395.6228
     418.4305              431.9428              482.0150
     500.3486              558.4892              680.1682
     684.5584              843.2079              874.0897
     912.6212              926.9812              933.1504
     993.0671             1027.8125             1061.0032
    1090.3185             1100.3001             1133.8378
    1223.5682             1272.6891             1294.2964
    1324.5249             1356.7631             1379.2568
    1406.3823             1448.4019             1476.1011
    1491.2582             1501.2930             1513.0705
    1599.7990             1664.3535             2949.5781
    3039.0906             3050.3636             3086.7983
    3106.9127             3127.7830             3138.8808
    3156.1428             3171.1202             3243.8747
 Zero-point correction= 0.152248 (Hartree/Particle)

TS for CH3CHO elimination
-------------------------
 E(UB+HF-LYP) =  -310.398344188     A.U.
 Cartesian coordinates:
     C       1.350566      0.044883      -0.474344
     C       2.591925     -0.533038       0.204743
     C      -0.104136     -0.597546       0.734203
     O       1.183158      1.297536      -0.496969
     H       0.987862     -0.557540      -1.332048
     H       2.529403     -1.616590       0.342886
     H       3.456647     -0.323704      -0.436190
     H       2.764947     -0.045100       1.167712
```

H	0.218554	-0.047230	1.614438
H	0.146802	-1.656328	0.751655
C	-1.385140	-0.238995	0.158716
C	-1.836899	1.189594	0.316702
C	-2.106698	-1.154037	-0.535353
H	-1.936050	1.457316	1.375333
H	-1.075128	1.850245	-0.114165
H	-2.794950	1.371472	-0.176673
H	-1.757929	-2.175193	-0.661792
H	-3.063127	-0.902808	-0.983404

Rotational constants (GHZ): 4.3820283 1.5636340 1.3239193

Vibrational harmonic frequencies :

-508.8519	60.2837	110.7699
161.9903	186.4220	199.9635
239.4342	358.0573	412.7679
440.3099	483.2293	529.8503
669.5607	798.7239	849.9182
878.1717	901.9083	930.3321
947.2174	997.7577	1027.5085
1070.2894	1088.8860	1099.1216
1139.1182	1322.6685	1365.1568
1401.0302	1412.6617	1441.7842
1475.5111	1485.4566	1490.6699
1499.4405	1516.4074	1527.0349
1624.3721	2912.5555	3038.8442
3044.5736	3098.8954	3113.4959
3130.6054	3135.6544	3141.7949
3157.5791	3223.2978	3247.2456

Zero-point correction= 0.153522 (Hartree/Particle)

I) Ring-opening 2,2-di-Me-cyclobutoxy

Structure	Energy (Hartree)	ZPE (Hartree)	Relative Energy (kcal/mol)
2,2-di-Me-cyclobutoxy	-310.408239709	0.156910	
TS for ring opening	-310.408152427	0.156139	-0.43

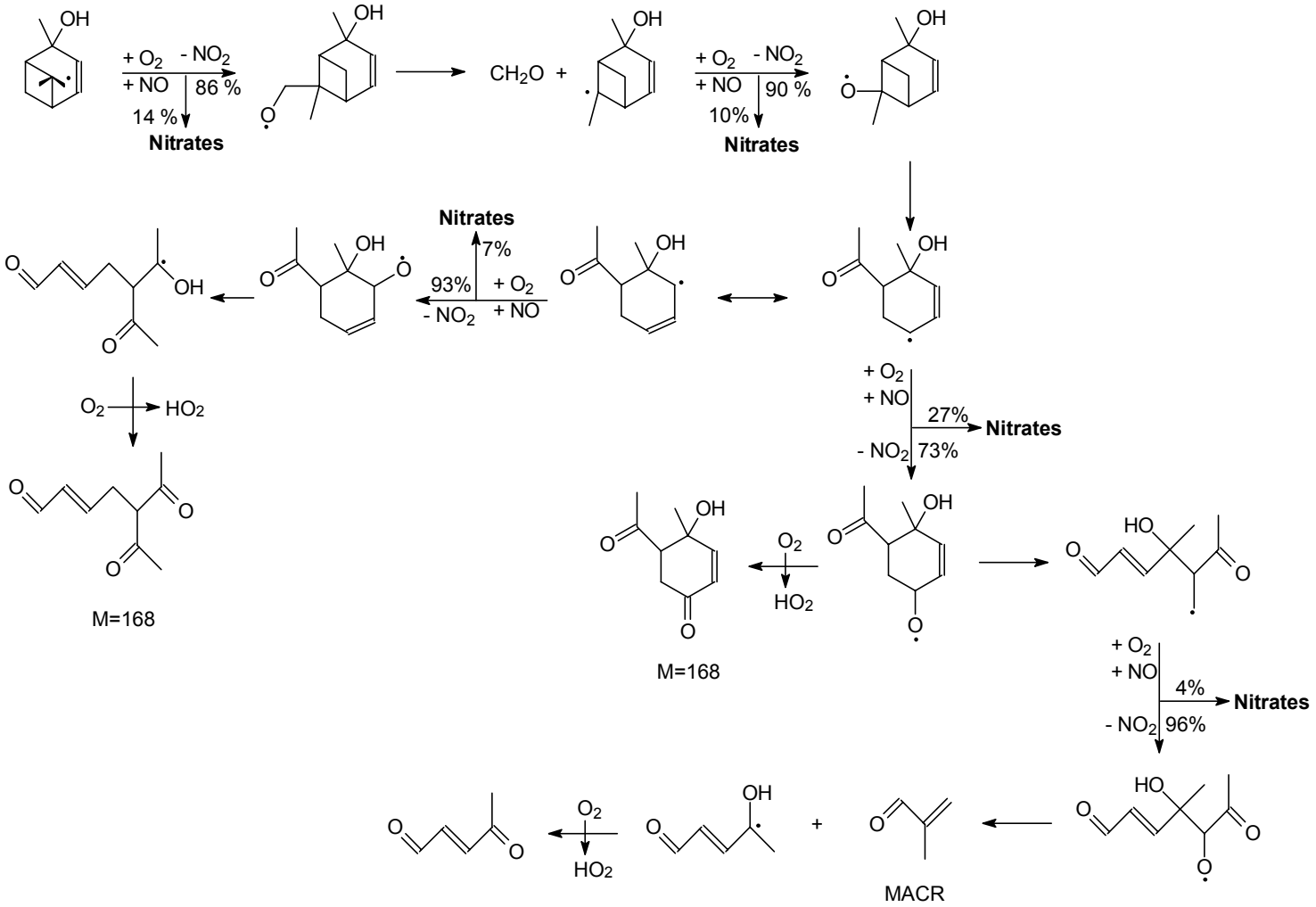
The negative barrier for the ring opening should not be taken on face value, but rather as an indication of a very low barrier.

```
2,2-di-Me-cyclobutoxy
---------------------

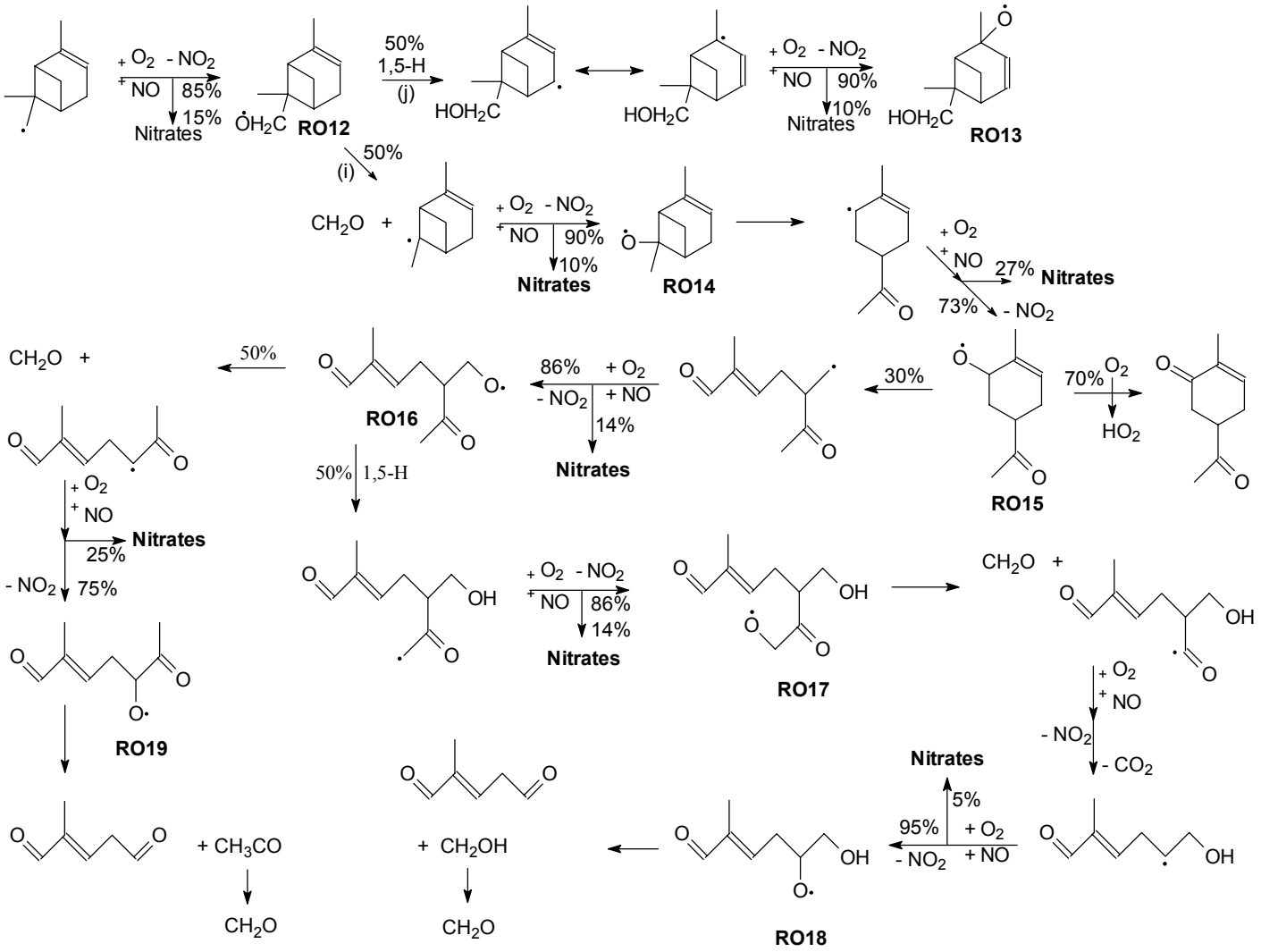
See section B


TS for ring opening in 2,2-di-Me-cyclobutoxy
-------------------------------------------
 E(UB+HF-LYP) =  -310.408152427     A.U.
 Cartesian coordinates:
     C       0.017476      1.490069       0.242285
     C       0.655647      0.102524       0.043705
     C      -0.972782     -0.349819      -0.589722
     C      -1.424571      0.948997       0.124296
     C       1.735395     -0.061650      -1.003469
     C       0.932113     -0.656431       1.327633
     H       0.108725     -0.572455       2.040506
     H       1.101148     -1.718371       1.132243
     H       1.834481     -0.244070       1.799312
     H       1.897001     -1.117847      -1.241921
     H       2.684402      0.341213      -0.621782
     H       1.495562      0.472227      -1.927573
     H      -2.128966      1.567489      -0.440836
     H      -1.862150      0.697522       1.093596
     H      -0.813977     -0.206025      -1.678505
     H       0.271662      2.168498      -0.578025
     H       0.274684      1.979450       1.187322
     O      -1.315280     -1.526222      -0.204089
 Rotational constants (GHZ):      3.2265329      2.5056039      2.1084228
 Vibrational harmonic frequencies :
    -269.8697              121.1392              191.4335
     227.3624              236.5540              280.7788
     340.9238              374.6229              429.2894
     477.6358              529.6179              747.2461
     804.4562              860.6130              947.9232
     963.5859              969.9839              991.2089
    1009.1406             1038.0343             1098.5585
    1156.1455             1197.9748             1248.7055
    1259.0914             1289.5249             1312.9406
    1337.1703             1412.1610             1428.4737
    1443.8963             1480.9462             1488.2138
    1494.4805             1503.2646             1505.6902
    1515.6063             2900.8920             3023.1760
    3034.6823             3060.0848             3071.8354
    3095.0968             3109.1656             3115.0763
    3127.9831             3137.1615             3147.6987
 Zero-point correction= 0.156139 (Hartree/Particle)
```

J) Figure 3b


OH
+ O2 - NO2
+ NO 86 %
14 %
Nitrates
CH2O +
+ O2 - NO2
+ NO 90 %
10%
Nitrates
Nitrates
7%
93%
+ O2
- NO2 + NO
+ O2
+ NO
27%
Nitrates
- NO2 73%
O2
HO2
M=168
M=168
HO
+ O2
+ NO
4%
Nitrates
- NO2 96%
MACR

K) Figure 5b


+ O2 - NO2
+ NO
85%
15%
Nitrates
RO12
50%
1,5-H
(j)
HOH2C
+ O2 - NO2
+ NO
90%
10%
Nitrates
RO13
50%
(i)
CH2O +
RO14
+ O2
+ NO
27%
Nitrates
73%
- NO2
30%
70%
O2
HO2
RO15
86%
+ O2
- NO2
+ NO
14%
Nitrates
RO16
50%
50% 1,5-H
CH2O +
+ O2
+ NO
Nitrates
25%
- NO2
75%
RO19
OH
RO17
CH2O +
+ O2
+ NO
- NO2
- CO2
Nitrates
5%
95%
+ O2
- NO2
+ NO
RO18
+ CH3CO
CH2O
+ CH2OH
CH2O