Supplementary Material (ESI) for *Physical Chemistry Chemical Physics*

Autoxidation of α-Pinene at High Oxygen Pressure

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SUPPORTING INFORMATION

computational results

Contents:

1,4-H shift, fate of $R_{(a)}$-OO-$_{(b)}R_{(c)}$-OO$^{\bullet}$

Ground state

Cartesian Coordinates (Å):

C	-0.183027	2.238774	0.042158
C	0.266735	0.831653	-0.339722
C	1.070134	0.174515	0.777411
O	-0.806418	0.007371	-0.778851
O	-1.750684	-0.122451	0.336080
C	-2.525272	-1.264069	0.025052
H	0.683472	2.885840	0.191089
H	-0.792527	2.657218	-0.758814
H	0.893656	0.867606	-1.235824
H	-3.061424	-1.130461	-0.918385
O	1.672212	-1.078034	0.351119
O	2.650136	-0.884097	-0.509904
H	-1.905421	-2.163270	-0.021471
H	-3.239697	-1.342491	0.845975
H	1.874771	0.830074	1.111504
H	0.429822	-0.104778	1.612217
H	-0.776040	2.232711	0.956769

Energy (Hartree): -458.65831854
ZPE (Hartree): 0.135436
Rotational constants (GHz): 3.725797/1.159593/1.042200

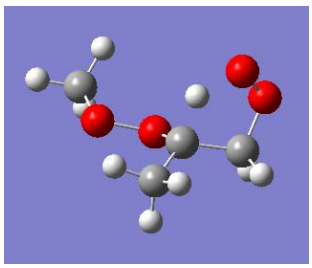
Transition state

Cartesian Coordinates (Å):

C	-0.076366	1.942568	-0.017592
C	0.306626	0.482883	-0.140938
C	1.173944	-0.107943	0.986282
O	-0.717280	-0.367781	-0.534286
O	-1.807132	-0.280254	0.496182
C	-2.988782	-0.593628	-0.209317
H	0.815248	2.565419	0.107958
H	-0.598872	2.264239	-0.923314
H	1.284492	0.256329	-0.918982
H	-3.211688	0.149553	-0.985011
O	2.125927	-0.963816	0.284280
O	2.435404	-0.318864	-0.859827
H	-2.935591	-1.591624	-0.661687
H	-3.778137	-0.581582	0.549731
H	1.727850	0.679477	1.506879
H	0.651952	-0.758262	1.689574
H	-0.743141	2.118893	0.833458

Energy (Hartree): -458.60968854
ZPE (Hartree): 0.130008
Rotational constants (GHz): 3.725797/1.159593/1.042200
Imaginary frequency (i cm^{-1}): -1932.80

Level: UB3LYP/6-311++G(df,pd)



1,7-H shift, fate of $R_{(a)}$-OO-$_{(b)}R_{(c)}$-OO$^{\bullet}$

Ground state

Cartesian Coordinates (Å):

C	-1.887753	-1.514130	-0.919186
C	-1.436571	-0.095005	-0.500464
C	-2.576627	0.744477	0.155570
O	-0.389934	-0.159823	0.475021
O	0.787803	-0.658174	-0.262149
H	-1.017647	-2.168050	-0.816026
H	-1.057763	0.476390	-1.353672
C	1.906593	-0.462062	0.614483
C	3.022578	-1.292736	0.025586
C	2.319009	1.016408	0.713564
H	2.855010	-2.359249	-0.098800
O	-3.287572	1.455596	-0.954938
C	-3.664895	-0.155311	0.763232
H	-4.339409	0.432963	1.392401
O	-2.514849	2.301856	-1.607388
H	1.509598	1.615072	1.136811
H	-2.164870	-1.516031	-1.980528
C	-4.290855	-1.085679	-0.313351
H	-5.222040	-1.525798	0.055746
H	-4.453831	-0.682643	-1.316303
C	-3.074077	-2.017656	-0.080954
H	-3.220066	-3.095542	-0.200196
C	-2.077926	1.811400	1.123726
H	-1.333588	2.447548	0.642174
H	-2.922379	2.429643	1.443099
H	-1.626733	1.347766	2.002738
C	-3.009695	-1.437309	1.362525
H	-2.033808	-1.350589	1.845765
H	-3.708879	-1.945904	2.032150
C	4.176174	-0.699743	-0.315699
C	4.273508	0.801412	-0.089170
H	5.241872	1.209964	-0.391518
C	3.738324	1.114679	1.344117
H	3.966227	2.138622	1.656404
H	4.004718	0.418232	2.145789
C	5.361486	-1.427643	-0.879163
H	5.167336	-2.498019	-0.990179
H	5.635587	-1.023522	-1.862349
H	6.242238	-1.302106	-0.235755
C	2.969448	1.470626	-0.621025
H	3.061730	2.559710	-0.669361
H	2.541521	1.089195	-1.551609
H	1.619270	-0.843671	1.606099

Energy (Hartree): -924.4297925
ZPE (Hartree): 0.369032
Rotational constants (GHz): 0.7396962/0.1763457/0.1614746

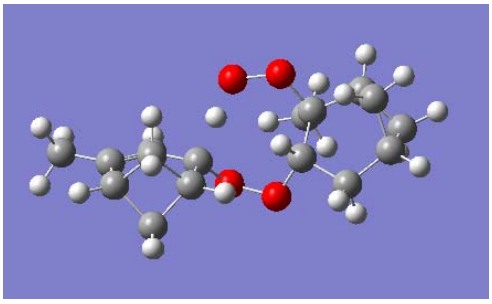
Transition state

Cartesian Coordinates (Å):

C	-1.887753	-1.514130	-0.919186
C	-1.436571	-0.095005	-0.500464
C	-2.576627	0.744477	0.155570
O	-0.389934	-0.159823	0.475021
O	0.787803	-0.658174	-0.262149
H	-1.017647	-2.168050	-0.816026
H	-1.057763	0.476390	-1.353672
C	1.906593	-0.462062	0.614483
C	3.022578	-1.292736	0.025586
C	2.319009	1.016408	0.713564
H	2.855010	-2.359249	-0.098800
O	-3.287572	1.455596	-0.954938
C	-3.664895	-0.155311	0.763232
H	-4.339409	0.432963	1.392401
O	-2.514849	2.301856	-1.607388
H	1.509598	1.615072	1.136811
H	-2.164870	-1.516031	-1.980528
C	-4.290855	-1.085679	-0.313351
H	-5.222040	-1.525798	0.055746
H	-4.453831	-0.682643	-1.316303
C	-3.074077	-2.017656	-0.080954
H	-3.220066	-3.095542	-0.200196
C	-2.077926	1.811400	1.123726
H	-1.333588	2.447548	0.642174
H	-2.922379	2.429643	1.443099
H	-1.626733	1.347766	2.002738
C	-3.009695	-1.437309	1.362525
H	-2.033808	-1.350589	1.845765
H	-3.708879	-1.945904	2.032150
C	4.176174	-0.699743	-0.315699
C	4.273508	0.801412	-0.089170
H	5.241872	1.209964	-0.391518
C	3.738324	1.114679	1.344117
H	3.966227	2.138622	1.656404
H	4.004718	0.418232	2.145789
C	5.361486	-1.427643	-0.879163
H	5.167336	-2.498019	-0.990179
H	5.635587	-1.023522	-1.862349
H	6.242238	-1.302106	-0.235755
C	2.969448	1.470626	-0.621025
H	3.061730	2.559710	-0.669361
H	2.541521	1.089195	-1.551609
H	1.619270	-0.843671	1.606099

Energy (Hartree): -924.392577
ZPE (Hartree): 0.363204
Rotational constants (GHz): 0.7396962/0.1763457/0.1614746
Imaginary frequency (i cm^{-1}): 1773.17

Level: UB3LYP/6-311++G(df,pd)//6-31G(d,p) 5d



O-O bond strength of *i*Pr-OO-*i*Pr, reaction (12)

Ground state (*i*PrO•)

Cartesian Coordinates (Å):

O	0.001016	1.422527	0.145457
C	-0.000227	0.125691	-0.292189
H	0.000803	0.266954	-1.397643
C	-1.286273	-0.626524	0.077703
H	-2.161870	-0.057595	-0.234829
H	-1.313583	-1.608962	-0.397345
H	-1.334593	-0.768516	1.159481
C	1.285584	-0.627886	0.077771
H	1.310681	-1.610753	-0.396416
H	2.161548	-0.060378	-0.236233
H	1.334377	-0.768653	1.159617

Energy (Hartree): -193.7574595
ZPE (Hartree): 0.093371
Rotational constants (GHz): 9.2302332/8.0520724/4.8444991

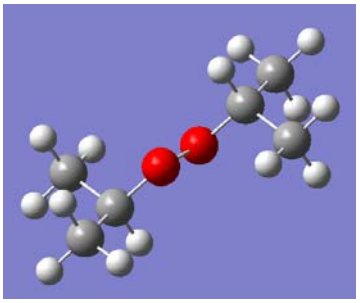
Ground state (*i*Pr-OO-*i*Pr)

Cartesian Coordinates (Å):

O	0.535595	-0.417109	0.274862
O	-0.535545	0.411502	-0.283918
C	-1.749247	-0.018801	0.338368
H	-1.592791	0.003746	1.423488
C	-2.143950	-1.425240	-0.097553
H	-1.357025	-2.137993	0.145575
H	-3.058741	-1.734869	0.413204
H	-2.321739	-1.454532	-1.175082
C	-2.774065	1.037297	-0.055389
H	-3.739517	0.798549	0.394118
H	-2.467208	2.026200	0.286482
H	-2.898927	1.066269	-1.139797
C	1.750754	0.021501	-0.338761
H	1.598788	0.007476	-1.424653
C	2.139934	1.425323	0.110352
H	3.055646	1.741864	-0.394489
H	1.351840	2.137826	-0.129733
H	2.313837	1.446130	1.188719
C	2.776734	-1.035194	0.050312
H	2.473925	-2.021917	-0.301307
H	3.743455	-0.790064	-0.392995
H	2.897094	-1.073144	1.134951

Energy (Hartree): -387.566410725
ZPE (Hartree): 0.194658
Rotational constants (GHz): 3.9685956/1.0323613/0.8638754

Level: UB3LYP/6-311++G(df,pd)



O-O bond strength of *i*Pr-OO-*i*Pr-OOH, reaction (12)

Ground state (*i*PrO•)

Cartesian Coordinates (Å):

O	0.001016	1.422527	0.145457
C	-0.000227	0.125691	-0.292189
H	0.000803	0.266954	-1.397643
C	-1.286273	-0.626524	0.077703
H	-2.161870	-0.057595	-0.234829
H	-1.313583	-1.608962	-0.397345
H	-1.334593	-0.768516	1.159481
C	1.285584	-0.627886	0.077771
H	1.310681	-1.610753	-0.396416
H	2.161548	-0.060378	-0.236233
H	1.334377	-0.768653	1.159617

Energy (Hartree): -193.7574595
ZPE (Hartree): 0.093371
Rotational constants (GHz): 9.2302332/8.0520724/4.8444991

Ground state (•OiPrOOH)

Cartesian Coordinates (Å):

O	0.433229	1.337494	-0.064408
C	0.892712	0.112452	-0.379661
H	0.861459	-0.058517	-1.469219
C	-0.211321	-0.918931	0.181045
H	0.086184	-1.912769	-0.158656
H	-0.226498	-0.852559	1.270126
C	2.257971	-0.233731	0.214445
H	2.559708	-1.248627	-0.054531
H	3.007455	0.457812	-0.171955
H	2.238873	-0.141881	1.301657
O	-1.464260	-0.675115	-0.365543
O	-2.052840	0.440123	0.327990
H	-1.492389	1.177785	0.003290

Energy (Hartree): -344.1559506
ZPE (Hartree): 0.102357
Rotational constants (GHz): 7.2679274/2.3891557/1.9680857

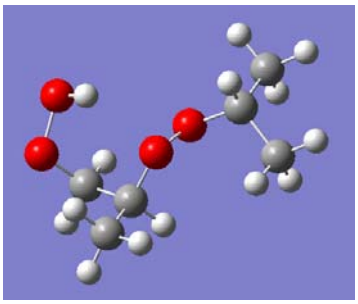
Ground state (*i*Pr-OO-*i*Pr-OOH)

Cartesian Coordinates (Å):

O	0.914255	-0.418515	0.220519
O	-0.048435	0.387982	-0.527916
C	-0.990888	0.926088	0.414753
H	-0.428959	1.386616	1.235424
C	-1.885466	-0.175035	0.990503
H	-1.297523	-0.915354	1.535747
H	-2.618219	0.271257	1.669796
C	-1.767352	1.981444	-0.360722
H	-2.477456	2.474268	0.305632
H	-1.092421	2.735628	-0.765323
H	-2.327253	1.528267	-1.178561
C	2.213785	-0.154071	-0.332579
H	2.146824	-0.295800	-1.417275
C	2.689131	1.259137	-0.023485
H	3.666441	1.434749	-0.478464
H	1.994052	1.996850	-0.423954
H	2.780407	1.407013	1.055033
C	3.101037	-1.234297	0.271508
H	2.725988	-2.227900	0.026003
H	4.114720	-1.137534	-0.120815
H	3.143253	-1.136190	1.358094
O	-2.661395	-0.821931	-0.010318
O	-1.864160	-1.870551	-0.612488
H	-1.213455	-1.357350	-1.119576

Energy (Hartree): -537.9611887
ZPE (Hartree): 0.2035175
Rotational constants (GHz): 2.0408830/0.7577310/0.6118704

Level: UB3LYP/6-311++G(df,pd)



Alkoxyl addition to C=C double bond, reaction (14)

Ground state (alkoxyl part)

Cartesian Coordinates (Å):

O	0.001016	1.422527	0.145457
C	-0.000227	0.125691	-0.292189
H	0.000803	0.266954	-1.397643
C	-1.286273	-0.626524	0.077703
H	-2.161870	-0.057595	-0.234829
H	-1.313583	-1.608962	-0.397345
H	-1.334593	-0.768516	1.159481
C	1.285584	-0.627886	0.077771
H	1.310681	-1.610753	-0.396416
H	2.161548	-0.060378	-0.236233
H	1.334377	-0.768653	1.159617

Energy (Hartree): -193.75745952
ZPE (Hartree): 0.093371
Rotational constants (GHz): 9.2302332/8.0520724/4.8444991

Ground state (olefin part)

Cartesian Coordinates (Å):

C	-1.088562	-0.326155	0.205896
C	-0.863775	1.164582	-0.246797
C	-2.413330	-0.899567	-0.323404
C	-0.980716	-0.676586	1.691845
C	0.125688	-0.642247	-0.756603
C	0.298061	1.814673	0.530249
C	1.445550	-0.288902	-0.082778
C	-0.310988	0.603192	-1.587092
C	2.576770	-1.275464	-0.136796
C	1.513585	0.910981	0.512361
H	-1.743217	1.818494	-0.278192
H	-2.440016	-1.987292	-0.188572
H	-2.584439	-0.695326	-1.382997
H	-3.259358	-0.479206	0.233498
H	-1.057275	-1.761348	1.835688
H	-1.805279	-0.217622	2.251146
H	-0.041632	-0.348034	2.139641
H	0.148723	-1.622973	-1.243931
H	0.540599	2.790535	0.084132
H	-0.002373	2.028696	1.566734
H	0.488681	1.166791	-2.075897
H	-1.094847	0.387856	-2.314912
H	3.471353	-0.894889	0.365128
H	2.843905	-1.517910	-1.174139
H	2.296203	-2.224396	0.339789
H	2.425278	1.249583	1.001599

Energy (Hartree): -390.77632255
ZPE (Hartree): 0.236219
Rotational constants (GHz): 1.9316695/1.2152402/1.1164088

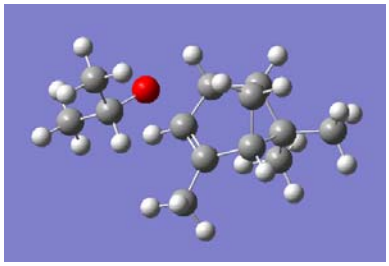
Transition state

Cartesian Coordinates (Å):

C	-3.038636	-0.657547	0.829363
H	-3.270549	-1.120533	1.794515
C	-2.000469	0.434115	0.942994
C	-1.562693	0.991253	-0.237886
H	-0.959946	1.892869	-0.224106
C	-2.288804	0.635914	-1.519876
H	-2.779208	1.533724	-1.922181
H	-1.552179	0.317044	-2.264931
C	-1.495949	0.839600	2.291671
H	-0.980981	0.003722	2.786634
H	-0.800928	1.682100	2.238017
H	-2.327557	1.119973	2.952569
C	1.266745	-0.017131	0.191407
H	0.978572	-0.195274	1.243854
O	0.161432	-0.157204	-0.649354
C	2.248364	-1.140338	-0.201693
H	1.767446	-2.116748	-0.100831
C	1.930582	1.364270	0.087085
H	1.246082	2.158354	0.403195
C	-3.318482	-0.483426	-1.269775
C	-4.253843	-0.142703	-0.052706
C	-2.651148	-1.568410	-0.378886
H	-3.191586	-2.516216	-0.379514
H	-1.584663	-1.739160	-0.529159
C	-4.751342	1.293452	0.130561
H	-5.452126	1.558608	-0.670336
H	-5.291078	1.394759	1.079967
H	-3.945831	2.030653	0.129097
C	-5.465945	-1.082640	0.033292
H	-5.964928	-0.979033	1.004103
H	-6.198501	-0.825931	-0.741358
H	-5.208173	-2.136364	-0.095265
H	-3.804911	-0.793684	-2.201673
H	2.562852	-1.017233	-1.243017
H	3.138439	-1.115180	0.436387
H	2.825991	1.427565	0.716202
H	2.220289	1.563203	-0.950352

Energy (Hartree): -584.5312123
ZPE (Hartree): 0.332594
Rotational constants (GHz): 1.352403/0.390847/0.370940
Imaginary frequency (i cm^{-1}): 222.6651

Level: UB3LYP/6-311++G(df,pd)//6-31G(d,p) 5d



1,6-H shift, scheme 3 (R2→R3)

Ground state

Cartesian Coordinates (Å):

C	-2.211530	-0.810200	0.202036
H	-2.963276	-1.541724	-0.115208
H	-2.477329	-0.370807	1.164747
O	-2.263692	0.255603	-0.789066
O	-2.258422	1.457479	-0.231495
C	-0.825361	-1.447400	0.239790
H	-0.897637	-2.351250	0.859393
H	-0.540055	-1.767324	-0.772920
O	0.139749	-0.603930	0.823849
C	0.929716	0.198387	-0.085075
C	1.161905	1.540218	0.595353
H	1.727116	2.215158	-0.053716
H	0.197034	2.000070	0.819615
H	1.713928	1.406145	1.530037
C	2.178653	-0.573234	-0.446770
H	1.993248	-1.593325	-0.785086
C	3.434667	-0.131513	-0.392964
H	4.267432	-0.767057	-0.679448
H	3.684808	0.873443	-0.066549
H	0.345344	0.365906	-1.001388

Energy (Hartree): -460.9110292
ZPE (Hartree): 0.166377
Rotational constants (GHz): 2.9365987/0.9134491/0.7808714

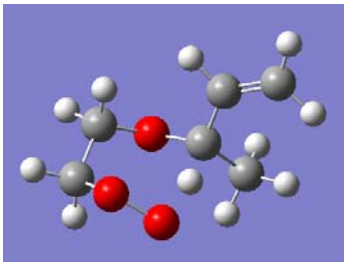
Transition state

Cartesian Coordinates (Å):

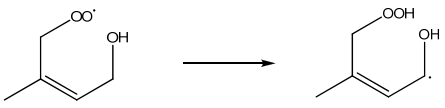
C	2.265867	0.071354	-0.182495
H	3.153393	-0.044323	-0.817124
H	2.563818	0.467080	0.795261
O	1.749919	-1.251689	-0.026503
O	0.860217	-1.241946	1.084391
C	1.280824	1.003544	-0.879350
H	1.773718	1.954002	-1.108584
H	0.966360	0.548298	-1.828055
O	0.151235	1.359462	-0.072555
C	-0.795212	0.366706	0.213872
C	-1.563134	0.773197	1.453710
H	-2.257353	-0.009022	1.767748
H	-0.863420	0.968170	2.269616
H	-2.135013	1.688375	1.259794
C	-1.515994	-0.198913	-0.935261
H	-1.049300	-0.056059	-1.907267
C	-2.655320	-0.913532	-0.877834
H	-3.105325	-1.315164	-1.779715
H	-3.169117	-1.123459	0.054932
H	-0.070918	-0.618640	0.654886

Energy (Hartree): -460.8849482
ZPE (Hartree): 0.160762
Rotational constants (GHz): 2.3054401/1.1462498/1.0834411
Imaginary frequency (i cm^{-1}): 1667.54

Level: UB3LYP/6-311++G(df,pd)//6-31G(d,p) 5d



The barrier of this 1,6-H shift (i.e. 13.0 kcal mol^{-1}) is similar to the barrier of the reaction depicted below in the frame of isoprene oxidation (i.e. 14.3 kcal mol^{-1} on B3LYP/6-31+G(d,p) level; Table S4 in ESI; Peeters et al, *PCCP*, 2009, **11**, 5935). They also performed CBS-APNO calculations (ibid.) and the barrier increased to 16.3 kcal mol^{-1}, other CBS-APNO energy barriers were only ≈1 kcal mol^{-1} above the DFT value. Thus, a isodesmic correction of 1.5 kcal mol^{-1} might be applied to DFT-derived 1,6-H shifts. For the herein reported reaction the corrected barrier would then be 14.5 kcal mol^{-1}. The lower barrier might be partially attributed to the stabilizing hyperconjugation of the cyclobutyl group.



O_2 elimination, scheme 3 (R5→R3)

R5

Cartesian Coordinates (Å):

C	3.83760400	-1.01777900	-0.89266200
H	4.67983300	-1.42685000	-0.33600900
C	2.90939000	-0.29235200	0.06797900
C	1.68913200	0.26546400	-0.69122500
H	1.28864200	-0.55984400	-1.28994100
C	2.00048400	1.46205200	-1.56835700
H	1.14009600	1.74079700	-2.17562800
H	2.26155100	2.32488900	-0.95612000
C	3.64711300	0.77224200	0.85922100
H	2.96089500	1.38830600	1.43819000
H	4.34470000	0.29361400	1.54536400
H	4.20702300	1.41617100	0.17960300
C	-0.58947500	0.89511100	-0.00354400
O	0.72637300	0.58911900	0.32155600
C	-1.18991600	0.15382400	-1.19147200
H	-0.60801600	0.32486500	-2.09907100
C	-1.42448300	0.71444000	1.21825100
H	-1.10166600	1.20895100	2.12652300
C	-2.49621600	-0.07957900	1.15691100
C	-1.57116900	-1.31899800	-0.81946300
C	-2.84217000	-0.66990900	-0.18816100
H	-3.76038200	-1.26008000	-0.16279800
C	-3.35517100	-0.40625400	2.32867400
H	-4.39178900	-0.11491900	2.13887200
H	-3.35955900	-1.48516100	2.50853000
H	-3.01418600	0.09402200	3.23431500
C	-2.69984400	0.46824600	-1.21950300
O	2.45746900	-1.36123100	0.91338700
O	1.99529200	-0.87515900	2.16996800
H	1.17853500	-0.41964600	1.90750000
C	-1.89645300	-2.12318100	-2.07343500
H	-0.97514100	-2.38427900	-2.59977300
H	-2.39298800	-3.05702900	-1.80023200
H	-2.54165900	-1.59587500	-2.77481800
C	-0.67496500	-2.16463100	0.06593800
H	-1.19322600	-3.09256100	0.32236200
H	0.24612000	-2.44005400	-0.45025800
H	-0.39225600	-1.67023700	0.99197100
H	-3.14640300	0.24108500	-2.18441700
H	-3.00865300	1.46039500	-0.89529800
O	-0.51735900	2.34154900	-0.39275900
O	-1.51848400	3.05698400	0.02755500
H	2.82857100	1.23845600	-2.24156100
H	3.31734400	-1.84279200	-1.38218300
H	4.22312500	-0.34450800	-1.65769300

Energy (Hartree): -962.3776
ZPE (Hartree): 0.372663
Rotational constants (GHz): 0.5196242/0.2697343/0.2519635

R3

Cartesian Coordinates (Å):

C	4.24030400	1.17396900	-0.03996400
H	5.20691400	0.72480400	-0.26463300
C	3.18671000	0.08040200	0.03390200
C	1.80166300	0.70288200	0.27346000
H	1.65807600	1.44832600	-0.51552200
C	1.61580600	1.32109200	1.64544300
H	0.60157200	1.70406300	1.75471400
H	1.78178500	0.57596000	2.42370900
C	3.55543500	-0.97631200	1.05871000
H	2.74575800	-1.68795300	1.21013500
H	4.43153800	-1.52264300	0.71092200
H	3.79382000	-0.50380800	2.01234300
C	-0.45103200	0.00379100	-0.17446600
O	0.83970000	-0.33881400	0.07850600
C	-1.40618800	-1.14175300	-0.24479200
H	-0.90679600	-2.09895500	-0.08464200
C	-0.96048400	1.26979300	-0.40330200
H	-0.34496900	2.16060000	-0.38841100
C	-2.33420700	1.36928400	-0.61479000
C	-2.68300100	-0.81307000	0.60229900
C	-3.08573000	0.07119400	-0.63015600
H	-4.15171000	0.20396300	-0.82854100
C	-3.04381300	2.65469100	-0.84557700
H	-3.55097500	2.66718500	-1.81754600
H	-3.82160800	2.82756900	-0.09280600
H	-2.35769600	3.50236400	-0.81763900
C	-2.28417100	-0.92738800	-1.50130900
O	3.20776300	-0.45176900	-1.29940200
O	2.67863400	-1.77340700	-1.33990300
H	1.73185400	-1.60390500	-1.22432900
C	-3.58886300	-2.02546400	0.76705200
H	-3.15330800	-2.72769900	1.48262400
H	-4.56095600	-1.71705600	1.16038800
H	-3.76541200	-2.56678300	-0.16131100
C	-2.51231700	-0.15004600	1.95440900
H	-3.48513800	0.15175300	2.35105100
H	-2.07011000	-0.85143100	2.66680500
H	-1.87737100	0.73300400	1.90525000
H	-2.85329500	-1.81263100	-1.77373300
H	-1.78803900	-0.52052800	-2.38221700
H	2.30642200	2.15035500	1.79839600
H	4.00229500	1.88772800	-0.83014600
H	4.31790200	1.70924900	0.90602100

Energy (Hartree): -812.0187
ZPE (Hartree): 0.363639
Rotational constants (GHz): 0.7579494/0.2444378/0.2288002

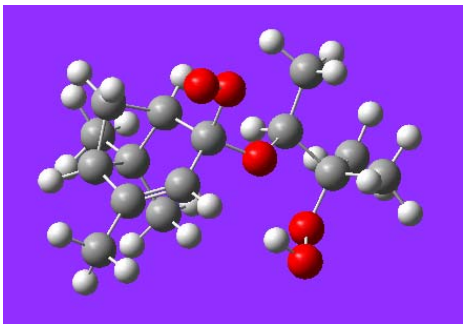
O_2

Cartesian Coordinates (Å):

O	4.24030400	1.17396900	-0.03996400
O	5.20691400	0.72480400	-0.26463300

Energy (Hartree): -150.3304
ZPE (Hartree): 0.003778
Rotational constants (GHz): 0.0000000/42.8795570/2.8795570

Level: MPW1B95/6-311++G(3df,3pd)// MPW1B95/6-31+G(d,p)



H abstraction, scheme 3 (R5→DHP)

Ground state

Cartesian Coordinates (Å):

C	-5.98194600	0.74499600	0.19192600	C	3.70367800	2.46886600	-0.81933000
C	-5.03268400	0.56519600	-1.05215000				
C	-7.16559700	1.67689200	-0.11142500	H	3.51059900	1.90482000	-1.73293600
C	-5.37678900	1.16648900	1.53244300				
C	-6.33843800	-0.77554800	-0.05241300				
C	-3.70834400	-0.11044100	-0.64824500	H	4.77933700	2.57551000	-0.67874200
C	-5.23940000	-1.67804700	0.49594600				
C	-6.01546800	-0.52845900	-1.55799200				
C	-5.62378700	-2.86947800	1.32607700	C	4.21643600	3.94656200	1.58444400
C	-3.97916200	-1.35072000	0.17650400				
H	-4.86392600	1.44542700	-1.68433600				
H	-7.91924100	1.61030100	0.68231100	H	4.25955500	5.03902300	1.65326200
H	-7.66424600	1.45429100	-1.05783000				
H	-6.82771400	2.71943400	-0.15533200				
H	-6.13911000	1.14162800	2.32110400	H	4.26193500	3.55158700	2.60553800
H	-5.00447000	2.19685000	1.47583300				
H	-4.55244000	0.52461100	1.84541400				
H	-7.34273200	-1.11452900	0.22506100	H	5.11513900	3.61321100	1.06093300
H	-3.12883700	-0.37678500	-1.54266700				
H	-3.07494000	0.58551400	-0.07820100				
H	-5.58734400	-1.37145000	-2.10734900	C	1.74765000	4.04578900	1.75792800
H	-6.85517400	-0.12001100	-2.12347400				
H	-4.74718300	-3.45000500	1.62841600				
H	-6.30227300	-3.53659600	0.77736200	H	1.77099200	3.60162200	2.75821300
H	-6.15951600	-2.56404800	2.23530200				
H	-3.12789100	-1.94760100	0.49408600				
O	-0.40179100	0.88633500	1.10868700	H	1.85253700	5.13094100	1.87616300
O	0.83559900	1.29427700	1.32783600				
O	1.62080600	0.18443900	-0.58647300				
C	2.31047100	-0.92444600	0.05903600	H	0.76619600	3.84497600	1.33095200
H	2.39318100	-0.68359700	1.12096800				
C	1.40146500	-2.21663800	-0.04576800	C	3.73512400	-1.07858200	-0.55498100
O	0.50933900	-2.12010700	-1.18096400				
O	-0.67028800	-1.34170900	-0.86315000				
H	-0.28611500	-0.44589000	-0.82589100	H	3.76227400	-0.49416700	-1.47964400
C	1.61150400	1.43822900	0.03706100				
C	0.91005900	2.40628600	-0.87843300				
C	2.97605900	1.99332600	0.47430100	H	4.47168400	-0.63328100	0.12434900
C	1.51858200	3.55472000	-1.21054900				
H	-0.07939000	2.13586400	-1.23130700				
C	2.90433900	3.51234700	0.90767000	C	2.25600500	-3.44157600	-0.43841000
H	3.48907900	1.30588900	1.15245800				
C	2.90905700	3.79601200	-0.64503900				
H	3.35185000	4.73313600	-0.99633500	H	1.63246700	-4.33959700	-0.39047500
C	0.90354500	4.59305500	-2.10123400				
H	0.82443300	5.55449700	-1.57800800				
H	1.52952600	4.76995800	-2.98504000				
H	-0.09410700	4.30102400	-2.43865000				

Energy (Hartree): -1547.7398853
ZPE (Hartree): 0.721328
Rotational constants (GHz): 0.1333217/0.0701135/0.0514983

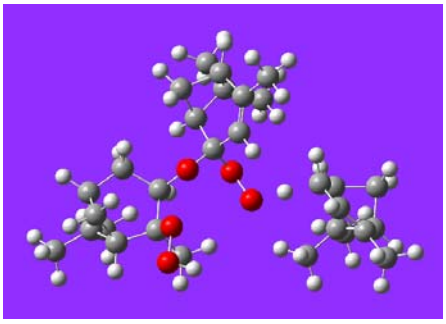
Transition state

Cartesian Coordinates (Å):

C	4.27180700	-1.63027900	-1.36276800	C	-1.62567700	3.50269800	0.30516500
C	4.12163500	-0.13001300	-0.89182200				
C	4.75856000	-1.72671800	-2.81751500				
C	3.10421600	-2.60352400	-1.19133300	H	-2.13549600	3.11325500	1.18733500
C	5.46385100	-1.67885900	-0.32585200				
C	3.39704900	-0.03759300	0.44648400				
C	4.92638200	-1.82151400	1.08671900	H	-2.28654700	4.19070900	-0.22362000
C	5.65718200	-0.15128800	-0.59169200				
C	5.53699200	-2.83337000	2.00738500				
C	3.93008400	-0.96921700	1.44322000	C	-0.29759800	4.51656300	-2.02240100
H	3.73984000	0.59292700	-1.61902000				
H	5.08457700	-2.74869100	-3.04273500	H	0.36337200	5.39048900	-2.04613500
H	5.58917800	-1.05670400	-3.05052100				
H	3.93808900	-1.48588700	-3.50300900				
H	3.41705300	-3.61437100	-1.48063300	H	-0.24091400	4.03558900	-3.00568600
H	2.26791200	-2.31451300	-1.83511400				
H	2.72752700	-2.64616500	-0.16979900				
H	6.29721100	-2.35948500	-0.52996300	H	-1.31947800	4.87890700	-1.89153400
H	3.23917100	0.98279900	0.81294400				
H	2.13661300	-0.31844100	0.24028800				
H	6.00898000	0.45185000	0.24910000	C	1.59347500	3.11953900	-1.24841100
H	6.26809200	0.06149700	-1.46983600				
H	5.08579800	-2.80471700	3.00307000				
H	6.61805100	-2.67222700	2.11299200	H	1.63223300	2.58414100	-2.20299400
H	5.41569800	-3.84854100	1.60579200				
H	3.52708400	-0.96830700	2.45364900				
O	0.92186900	-0.59116100	0.07744800	H	2.22516800	4.01162100	-1.34256100
O	0.32742800	0.47286000	-0.62772300				
O	-1.52268200	0.53638400	0.82230200				
C	-2.43589300	-0.14897200	-0.04979900	H	2.02550800	2.47272500	-0.48776000
H	-1.95958100	-0.23682100	-1.02816800				
C	-2.63734600	-1.63551200	0.45180500				
O	-2.30975000	-1.57835400	1.86381000	C	-3.76004000	0.65927000	-0.19336800
O	-2.55582600	-2.89380800	2.44677800				
H	-1.63995000	-3.16087100	2.62448500				
C	-0.47274300	1.29447200	0.25760100	H	-3.81338800	1.36212400	0.64413100
C	0.31699300	1.83745000	1.42786800				
C	-0.95944400	2.45897700	-0.63795600				
C	0.47260900	3.16216200	1.56521800	H	-3.71335100	1.26079400	-1.10926400
H	0.70234900	1.11417700	2.13774800				
C	0.15676900	3.53529400	-0.92720300				
H	-1.52027600	2.07898900	-1.49697200	C	-4.11755000	-2.06213300	0.29780700
C	-0.18526900	4.05545400	0.52262500				
H	-0.04756600	5.12134600	0.73259300	H	-4.21388500	-3.12980400	0.51279600
C	1.23164000	3.80176600	2.69166100				
H	2.06715400	4.40373200	2.31071800				
H	0.58845900	4.48722600	3.25842100				
H	1.63236400	3.05758000	3.38535600				

Energy (Hartree): -1547.7103502
ZPE (Hartree): 0.715197
Rotational constants (GHz): 0.1491418/0.0762260/0.0618824
Imaginary frequency (*i* cm^{-1}): 1679.80

Level: UB3LYP/6-311++G(df,pd)//6-31G(d,p) 5d



1,5-OH shift, scheme 3 (R3→R4)

Ground state (olefin part)

Cartesian Coordinates (Å):

C	3.35661400	0.44311100	-0.67033100
H	4.17001400	1.16868100	-0.77272000
C	2.12443800	1.13592800	-0.05296800
C	0.95057600	0.10707100	0.16455200
H	0.78499300	0.06833100	1.24505800
C	1.21586400	-1.33627400	-0.37674500
H	1.05189100	-2.06701800	0.42328000
H	0.46496400	-1.54150500	-1.14722500
C	1.73237700	2.36987300	-0.87406600
H	0.94254900	2.92991700	-0.37389400
H	2.61228100	3.01174300	-0.97840800
H	1.37045000	2.09441000	-1.86587700
C	-1.45831100	0.25119200	0.03548300
O	-0.24093700	0.64884400	-0.43130800
C	-2.62987300	0.96404400	-0.58573700
H	-2.30949800	1.69831600	-1.33044400
C	-1.73602600	-0.68788600	1.02485900
H	-0.95703200	-1.25360000	1.52633800
C	3.72471700	-0.95323100	-0.03842200
C	2.61257700	-1.52099000	-0.98334000
H	2.74313300	-2.54129100	-1.36417900
C	2.88299700	-0.33131800	-1.93749700
H	2.02413000	0.06695900	-2.48476400
H	3.69310400	-0.50953100	-2.64565500
C	5.13545300	-1.38811700	-0.47611500
H	5.31904800	-1.25066600	-1.54484300
H	5.89589900	-0.81434900	0.06678500
H	5.29344100	-2.44876600	-0.24714600
C	3.61049200	-1.20483400	1.46984300
H	3.81659100	-2.26137000	1.68413100
H	4.34454000	-0.60368300	2.01692200
H	2.62957200	-0.96747600	1.88322800
C	-3.08685500	-0.91960500	1.33212500
C	-3.75826300	-0.07673300	-0.97962600
C	-4.08391500	-0.06969400	0.57607200
H	-5.11987300	-0.26375100	0.87607100
C	-3.54993000	-1.92132200	2.34403800
H	-4.13161400	-1.44927600	3.15093700
H	-4.20992800	-2.68035300	1.89688400
H	-2.70704100	-2.44600500	2.80635300
C	-3.56450600	1.40712000	0.58707700
O	2.63263800	1.58053600	1.23172600
O	1.59552200	2.35588300	1.91539300
H	1.57878400	1.89442100	2.76903600
C	-4.87343600	0.56447900	-1.82003100
H	-4.52191200	0.74229300	-2.84396000
H	-5.73529000	-0.11135600	-1.88236400
H	-5.23141500	1.51825800	-1.42548100
C	-3.35758700	-1.39291900	-1.64793700
H	-4.22706200	-2.05769600	-1.72476600
H	-2.99682500	-1.20707100	-2.66738900
H	-2.57580800	-1.92316800	-1.10246900
H	-4.31890600	2.13235000	0.28083600
H	-3.07539100	1.75077500	1.50182800

Energy (Hartree): -1006.567228
ZPE (Hartree): 0.47447
Rotational constants (GHz): 0.5679896/0.1686243/0.1648720

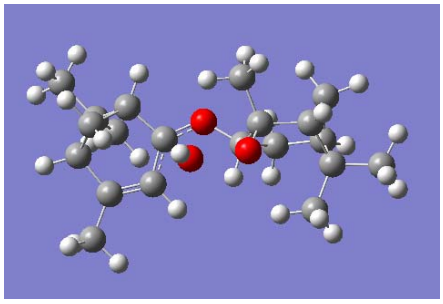
Transition state

Cartesian Coordinates (Å):

C	-3.42696100	-0.50481100	0.60985100
H	-4.07137300	-0.51363500	1.49430800
C	-1.95144900	-0.30343500	1.06870700
C	-1.05295400	-0.08235300	-0.22334300
H	-0.84700000	0.98137500	-0.22527800
C	-1.67016100	-0.52070100	-1.57213500
H	-1.39718600	0.21367300	-2.34008500
H	-1.22363100	-1.47549700	-1.87388200
C	-1.49337400	-1.49573000	1.93328200
H	-0.55930600	-1.22784200	2.42834800
H	-2.25301200	-1.67923100	2.70030700
H	-1.33606100	-2.41656400	1.36591400
C	1.36891400	-0.13344200	0.07111700
O	0.21872200	-0.76856900	-0.05153500
C	2.51469100	-0.98318500	0.54143800
H	2.17200700	-1.96851800	0.86508500
C	1.67921000	1.19097800	-0.32419600
H	0.91440300	1.88622600	-0.64404400
C	-3.88091300	0.39820700	-0.59690800
C	-3.19640300	-0.69451100	-1.49379000
H	-3.62100100	-0.87216800	-2.48898800
C	-3.48872000	-1.71677300	-0.36807600
H	-2.76104400	-2.52047400	-0.23251000
H	-4.48331700	-2.16068900	-0.42530200
C	-5.41492900	0.36931900	-0.75035700
H	-5.83941700	-0.63683300	-0.71272500
H	-5.88399800	0.95755800	0.04701000
H	-5.70743200	0.81690700	-1.70809200
C	-3.45342500	1.86643800	-0.71246900
H	-3.73594800	2.25553300	-1.69965800
H	-3.96961300	2.46817100	0.04327100
H	-2.38920500	2.03880500	-0.56719800
C	3.00996800	1.54742600	-0.30825800
C	3.71261100	-0.89231400	-0.49729100
C	3.98749200	0.50864000	0.19237300
H	5.01903900	0.87447500	0.20712600
C	3.50442900	2.90064100	-0.70814200
H	3.97881600	3.41173000	0.14277400
H	4.27330200	2.82853100	-1.48978800
H	2.69547500	3.53765000	-1.07639600
C	3.37793100	-0.09932100	1.49717500
O	-1.94212300	0.86209900	1.82843600
O	-0.15763500	1.18567100	1.94125600
H	-0.23455100	1.69123300	2.76527100
C	4.81321500	-1.92004000	-0.19580400
H	4.48174400	-2.92411300	-0.48585900
H	5.71138700	-1.68881100	-0.78090400
H	5.10409300	-1.95838200	0.85594300
C	3.40603800	-0.95252700	-1.99503900
H	4.31450900	-0.74742500	-2.57414200
H	3.06367200	-1.95772100	-2.26822200
H	2.64114900	-0.23986400	-2.30742800
H	4.09156000	-0.68197900	2.07924500
H	2.82897700	0.57924100	2.15183900

Energy (Hartree): -1006.544809
ZPE (Hartree): 0.471868
Rotational constants (GHz): 1.4672946/0.6609302/0.5612627
Imaginary frequency (*i* cm^{-1}): 454.04

Level: UB3LYP/6-311++G(df,pd)//6-31G(d,p) 5d



C-O cleavage, scheme 3 (R6→PA)

Ground state (olefin part)

Cartesian Coordinates (Å):

C	-4.441059	-0.398776	0.175306
H	-4.770477	0.644545	0.211455
H	-4.369684	-0.759733	1.207638
H	-5.217350	-0.984288	-0.326662
C	-3.095958	-0.528010	-0.550132
H	-2.827192	-1.598006	-0.631108
H	-3.189345	-0.175376	-1.586576
C	-2.010994	0.240826	0.124332
H	-1.914053	0.280821	1.205417
C	0.365350	0.660442	0.080062
C	1.353501	1.096289	-0.983592
H	1.094182	1.962729	-1.587617
C	2.486587	0.405035	-1.135012
H	3.233169	0.686568	-1.873270
C	0.880193	-0.598688	0.803876
H	0.158129	-0.912552	1.562092
O	0.176563	1.649481	1.070234
H	-0.102120	2.461946	0.623659
O	-0.864950	0.401606	-0.618775
C	1.389609	-1.635562	-0.233792
H	1.528752	-2.618459	0.226566
H	0.838709	-1.734737	-1.172162
C	2.712498	-0.804137	-0.251053
H	3.657960	-1.312960	-0.453509
C	2.365763	-0.400147	1.217263
H	2.679554	-1.162369	1.937245
H	2.673927	0.589541	1.561619

Energy (Hartree): -540.601593263
ZPE (Hartree): 0.231787
Rotational constants (GHz): 1.98548/0.53881/0.51483

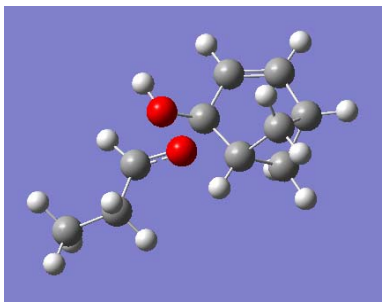
Transition state

Cartesian Coordinates (Å):

C	-4.408519	-0.412379	-0.051060
H	-4.704042	-0.458566	-1.104563
H	-4.738638	0.556033	0.342373
H	-4.956701	-1.191326	0.487669
C	-2.893298	-0.585627	0.109013
C	-2.637507	-0.597863	1.181204
H	-2.567582	-1.556544	-0.288023
C	-2.103203	0.493472	-0.580140
H	-2.582131	1.476960	-0.712375
C	0.403712	0.517683	0.363063
C	1.342375	1.453489	-0.263743
H	1.045661	2.489640	-0.410777
C	2.528266	0.962727	-0.674383
H	3.258137	1.582512	-1.187527
C	0.937817	-0.888432	0.504651
H	0.206106	-1.534397	0.994653
O	-0.304766	0.931618	1.457075
H	-0.502181	1.874471	1.364053
O	-0.877250	0.338561	-0.945621
C	1.575638	-1.333018	-0.842009
H	1.784330	-2.407167	-0.839809
H	1.060772	-1.045338	-1.759072
C	2.822777	-0.496685	-0.403522
H	3.814675	-0.802878	-0.743967
C	2.396528	-0.820663	1.065510
H	2.741472	-1.809651	1.381656
H	2.621193	-0.080718	1.838591

Energy (Hartree): -540.58351391
ZPE (Hartree): 0.229117
Rotational constants (GHz): 2.0708962/0.5340141/0.5156912
Imaginary frequency (i cm^{-1}): -516.09

Level: UB3LYP/6-311++G(df,pd)//6-31G(d,p) 5d



Fate of R3, scheme 3

It is not immediately clear what the fate of the R3 radical exactly is, since it can either (i) add O_2 or (ii) undergo an intramolecular 1,5-OH shift (see Scheme 3 in the paper). Although the O_2 addition is faster than the 1,5-OH shift, the main reaction flux will still proceed through R4. A thorough analysis of the competing fates of the R3 radical is given in the following table.

reaction	E_b	A	$k_{(1)}$
R3→R4	12.4 kcal mol^{-1} UB3LYP/6-311++G(df,pd)//UB3LYP/6-31G(d,p) on the full R3 radical	6×10^{11} s^{-1} Literature value, with 2 hindered rotations (L. Zhu, J. W. Bozzelli, L. M. Kardos, J. Phys. Chem. A, 2007, 111, 6361)	2.1×10^{4} s^{-1}
R3→R5	1 kcal mol^{-1} Literature value (Supp.inf. of Peeters et al, PCCP, 2009, 11, 5935)	2×10^{9} M^{-1} s^{-1}	1.8×10^{7} s^{-1} (at 1 bar O_2)
R5→R3	15.8 kcal mol^{-1} MPW1B9576-311++G(3df,3pd)//MPW1B95/6-31+G(d,p) ground state BDE calculation on the R5 model peroxyl-(1,2,2-trimethyl-2-hydroperoxylethoxy)-verbenyl, including E_b of the forward R3→R5 reaction (microscopic reversibility). Calculation procedure calibrated with the experimental value of oxygen addition to allyl (17.1 kcal mol^{-1}, Supp.inf. of Peeters et al, PCCP, 2009, 11, 5935), using a isodesmic correction term of +0.7 kcal mol^{-1}.	1×10^{14} s^{-1} (Supp.inf. of Peeters et al, PCCP, 2009, 11, 5935)	3.1×10^{4} s^{-1}
R5→DHP	14.7 kcal mol^{-1} UB3LYP/6-311++G(df,pd)//UB3LYP/6-31G(d,p) on the full R5 radical	3.25×10^{8} M^{-1} s^{-1} (I. Hermans, J. Peeters, P. A. Jacobs, J. Org. Chem., 2007, 72, 3057)	2.8 s^{-1}

The quintessence: O_2 addition to R3 is actually fast and reversible. A dynamic equilibrium between the two radicals R3 and R5 is established (equilibrium constant being determined by the R3→R5 and R5→R3 rate constants); both R3 and R5 can further react. The reaction R3→R4 is, however, approximately 10^4 times faster than the competitive reaction R5→DHP. The selectivity of the proposed pathway (i.e. R3→R4), relative to the side-reaction leading to dihydroperoxide (R3→R5→DHP), can be calculated by the ratio of the corresponding pseudo-first-order $k_{(1)}$ values in the table above:

$$S_{(R3\rightarrow R4)} = \frac{k_{(R3\rightarrow R4)} \times k_{(R5\rightarrow R3)}}{k_{(R5\rightarrow DHP)} \times k_{(R3\rightarrow R5)}} = \frac{13}{1}$$

In view of the experimental agreement with the proposed reaction model and an anticipated error of 1 to 2 kcal mol^{-1} on the E_b's, it seems reasonable indeed to neglect the reaction R5→DHP.