

Supporting Information

New insights into 1,2,4-trioxolane stability and the crucial role of ozone in promoting polymer degradation

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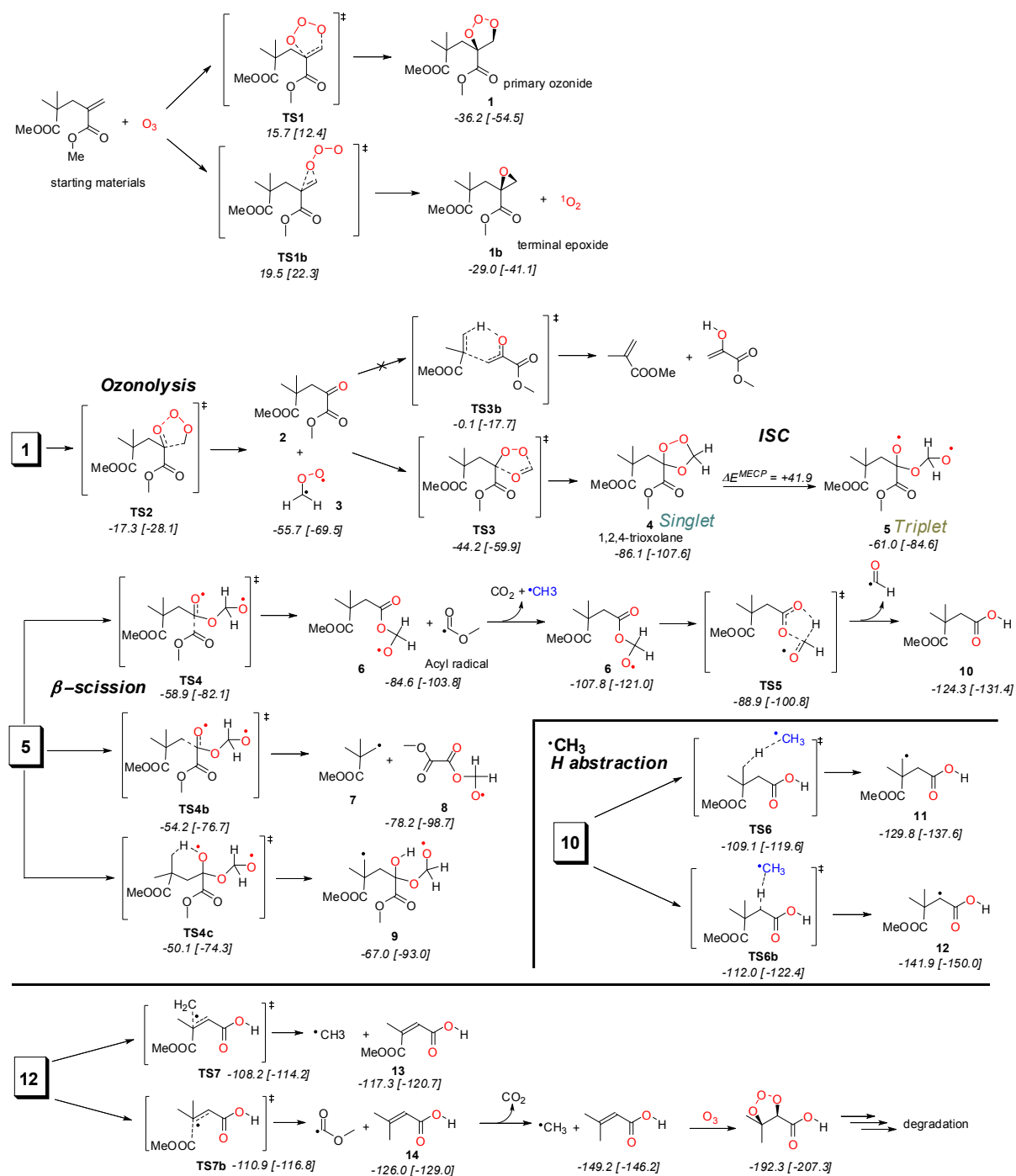
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Computational method

Quantum chemical calculations were carried out with Gaussian 09¹ and MOLPRO 2012². The minimum crossing point energy (MECP) was located with a FORTRAN script written by Harvey *et al* [see main text] evoking iterative calculations with Gaussian 09. Geometries of minimum and transition state electronic structures were optimised at Becke's three parameter³ and Lee-Yang-Parr's⁴ B3LYP density functional with Pople's⁵⁻⁷ basis set 6-31+G(d). Frequency calculations were carried out at that level to ensure convergence (all positive eigenvalues for minima and single negative for saddle points). Thermochemical corrections and zero point vibrational energies were determined at B3LYP/6-31+G(d) geometries and frequencies and combined with high level G3(MP2)-RAD composite method⁸ single point energy calculation to constitute free energy as we have previously demonstrated its accuracy in radical chemistry⁹. Minnesota meta hybrid functional M06-2X¹⁰ with Pople triple- ζ basis set 6-311++G(2d,2p) was also selected for comparison due to its reliability in radical thermochemistry¹¹. The differences between the G3(MP2)-RAD and the M06-2X calculations are reasonably systematic (see S-6). Mean absolute deviation for barrier height is 1.5 and ΔG_{rxn} 5.2 and importantly the conclusions are identical at both the M06-2X level of theory and the higher G3(MP2)-RAD level.

The MECP was found at the M06-2X/6-311+G(2d,2p) level of theory and the ΔE^{MECP} was calculated as the difference between the electronic energy of **4** optimised at the same level of theory and the MECP. The $\Delta E^{\text{MECP}} = 41.9$ kcal/mol is close to the activation barrier for 1,2,4-trioxolane O-O unimolecular bond homolysis process calculated by Ljubić and Sabljic using multireference methods (40.5 kcal/mol; see main text) but due to computational limitations we were unable to exercise CASSCF calculations on the critical structures with reasonable basis sets for quantitative comparison. Single-point calculations at M06-2X level also reveal large singlet-triplet energy gap for the singlet biradical **5** $\Delta E_{\text{S-T}} = 58.6$ kcal/mol. Thus **4** may undergo photochemical excitation to T_1 state and correspondingly follow the reaction channel to **5**. Expedient decomposition of **5** by β -scission forms more thermodynamically stable species relative to **4** in subsequent steps.

Solvation free energies were calculated on optimized geometries with Cramer and Truhlar's SMD polarizable continuum solvation model¹² at B3LYP/6-31+G(d) level of theory. The free energy of solvation ΔG_{solv} was taken from SMD calculation to combine with gas phase free energy constituting free energy of solution ΔG_{soln} with a correction term: $\Delta G_{\text{soln}} = \Delta G_{\text{gas}} + \Delta G_{\text{solv}} + \Delta nRT \ln(RT/P^\circ)$. Where $\Delta nRT \ln(RT/P^\circ)$ is the correction term that accounts for passage from 1 atm to 1 mol/L in solution.



Values are G3(MP2)-RAD Gibbs free condensed phase energies (kcal/mol) relative to starting materials. M06-2X free energies in parenthesis for comparison.

Molecule	Entropy(cal/mol K)	Tc	ZPVE	HLC	B3LYP/6-31G*	ROMP2/6-31G*	ROMP2/GTMP2Large	URCCSD(T)/6-31G*	G3(MP2)-RAD	M06-2X/6-311++G(2d,2p)	ΔG_{soliv}
Starting material	128.9996654	0.017161798	0.247274729	-0.37652	-691.6232065	-687.4539689	-687.6833562	-689.6240709	-690.0268027	-691.5438976	-12.47
O2 (triplet)	49.00934512	0.003305732	0.003664635	-0.056478	-150.3275769	-149.5928472	-149.6459279	-149.9611543	-150.0870168	-150.3147501	-4.67
O2 (singlet)	46.82607553	0.003305847	0.003639878	-0.056478	-150.2660519	-149.5282411	-149.5830399	-149.9116914	-150.0382598	-150.254833	-5.47
O3	56.89495698	0.003903866	0.007169492	-0.084717	-225.419503	-224.2515977	-224.3367525	-224.8755201	-225.0613375	-225.3873461	-8.27
TS1b	146.9342256	0.020390707	0.255753304	-0.461237	-917.0335475	-911.6472173	-911.9586743	-914.4860814	-915.0524093	-916.9101553	-23.68
1b	132.2578155	0.017755018	0.252215692	-0.404759	-766.8205198	-762.2842857	-762.5398931	-764.6424334	-765.0956374	-766.7460796	-17.46
TS1a	144.2809512	0.020236069	0.256327976	-0.461237	-917.044632	-911.6834935	-911.9935898	-914.5002768	-915.0635641	-916.9327426	-18.56
1	139.3052103	0.019270501	0.260579356	-0.461237	-917.1228198	-911.8313284	-912.1389112	-914.585371	-915.140496	-917.0391625	-22.24
TS2	141.4664675	0.019661703	0.257535174	-0.461237	-917.0916501	-911.7466683	-912.0548139	-914.5495653	-915.1089324	-916.992075	-25.01
2	129.7603967	0.017103675	0.223720015	-0.37652	-727.5440002	-723.293423	-723.536666	-725.4951495	-725.935711	-727.4687514	-16.21
3	59.59770554	0.00422849	0.030648143	-0.084717	-189.5912515	-188.5506644	-188.6241587	-189.0833905	-189.2350277	-189.5657003	-10.26
TS3b	126.2808556	0.01666475	0.216606932	-0.37652	-727.4606477	-723.1599034	-723.4096808	-725.3928986	-725.8458942	-727.3791098	-15.08
TS3	144.0416587	0.020233708	0.256991963	-0.461237	-917.1404128	-911.8485401	-912.1590414	-914.5928941	-915.1558111	-917.0456417	-20.54
4	138.3921367	0.019321615	0.261255913	-0.461237	-917.2013765	-911.9309216	-912.2390203	-914.6655604	-915.22004	-917.1250512	-22.15
5	146.3943117	0.020478385	0.255497353	-0.461237	-917.1688773	-911.9460924	-912.2514873	-914.6212571	-915.1814349	-917.0813254	-23.22
TS4	150.1404159	0.020616759	0.254186022	-0.461237	-917.1626187	-911.8995695	-912.2084504	-914.6108272	-915.1774429	-917.0737275	-23.62
6	126.790153	0.015864864	0.20472748	-0.35225	-688.779612	-684.8070438	-685.0384327	-686.844912	-687.2681703	-688.7070669	-20.8
Acyl radical	69.49467017	0.005508246	0.048384574	-0.107512	-228.4094557	-227.1493983	-227.2304659	-227.7849772	-227.9526666	-228.315957	-3.13
TS4b	149.9114006	0.02071415	0.253615159	-0.461237	-917.155975	-911.9008125	-912.209928	-914.6032318	-915.1704468	-917.0652487	-23.34
7	100.132457	0.011338564	0.156939288	-0.220468	-385.6708578	-383.2982049	-383.4274874	-384.51873	-384.7477549	-385.6139554	-7.67
8	103.0124044	0.010605142	0.093579584	-0.239294	-531.5035716	-528.6503444	-528.8344305	-530.0916386	-530.4597538	-531.4581142	-18.24
TS4c	144.8924713	0.019721196	0.25073266	-0.461237	-917.146721	-911.8828217	-912.1938651	-914.5921436	-915.1627784	-917.0588546	-24.01
9	147.1942639	0.02088326	0.253951362	-0.461237	-917.1631298	-911.9331087	-912.2460297	-914.6171811	-915.186406	-917.0887295	-26.04
CO2	51.12698375	0.003579775	0.011340392	-0.075304	-188.5903926	-187.630973	-187.7006549	-188.1212107	-188.2755563	-188.5801671	-2.04
•CH3	47.47241874	0.003802742	0.029346524	-0.032208	-39.83094312	-39.54485002	-39.5610275	-39.68012249	-39.71790301	-39.81299145	1.3
CH4	46.65810229	0.003807694	0.044172424	-0.037652	-40.52060686	-40.1949008	-40.21199574	-40.35591578	-40.3848402	-40.50020822	0.4
TS5	125.0262428	0.015574405	0.200402933	-0.35225	-688.7603237	-684.7299544	-684.965441	-686.8133728	-687.2445062	-688.6775217	-14.91
10	110.4747371	0.013462921	0.186612455	-0.301216	-574.9197892	-571.5500903	-571.7489772	-573.2912759	-573.643767	-574.8656678	-19.08
Fomyl radical	53.75645315	0.003810398	0.013074652	-0.051034	-113.8554882	-113.2345727	-113.275905	-113.5511588	-113.6521686	-113.8378498	-0.86
TS6	128.1881453	0.01639044	0.214549876	-0.333424	-614.7385884	-611.0487479	-611.2637201	-612.9521625	-613.330494	-614.6650088	-18.28
TS6b	126.4939293	0.016384765	0.214896705	-0.333424	-614.7457539	-611.0561967	-611.2713699	-612.9590236	-613.3364105	-614.6716812	-17.54
11	111.7357075	0.013439612	0.172395848	-0.295772	-574.240452	-570.89849	-571.0985792	-572.6190028	-572.9820911	-574.1854028	-18.42
12	111.5876912	0.013558713	0.173209522	-0.295772	-574.2622524	-570.9194482	-571.11742	-572.6398044	-572.9997722	-574.2046166	-19.42
TS7	117.1528442	0.014396458	0.168757189	-0.295772	-574.2112249	-570.8527992	-571.0538735	-572.5808737	-572.9502014	-574.1453047	-16.84
13	104.8009321	0.011852257	0.136217635	-0.263564	-534.3804574	-531.3274766	-531.5138733	-532.9008611	-533.2525212	-534.3298325	-16.44
TS7b	118.8347275	0.014222281	0.170502876	-0.295772	-574.2163682	-570.8486194	-571.0502419	-572.5844475	-572.9535506	-574.1491981	-17.46
14	88.02452199	0.008999048	0.121175433	-0.18826	-345.8179609	-343.7282598	-343.8505487	-344.8074804	-345.029657	-345.7728707	-13.25
15	96.97227533	0.010767092	0.134245858	-0.272977	-571.3194836	-568.1108792	-568.3112348	-569.7733226	-570.1476937	-571.2721033	-27.16

Summary for energies taken at different levels of theory. Tc = temperature correction; ZPVE = zero-point vibrational energy; HLC = high level correction.

	G3(MP2)-RAD	M06-2X
SM -> TS1	15.7	12.4
SM -> 1	-36.2	-54.5
SM -> TS1b	19.5	22.3
SM -> 1b	29	41.1
1 -> TS2	18.9	26.4
1 -> 2 + 3	-19.5	-15
2 + 3 -> TS3	11.5	9.6
2 + 3 -> 4	-30.4	-51.9
4 -> 5	25.1	22.4
5 -> TS4b	6.8	7.9
4 -> 7 + 8	7.9	8.9
5 -> TS4c	10.9	10.3
4 -> 9	19.1	14.6
5 -> TS4	2.1	2.5
4 -> 6 + Acyl rad	1.5	3.8
4 -> 6 + CO2 + CH3	-21.7	-13.4
6 -> TS5	18.9	20.1
6 -> 10	-16.5	-10.4
10 -> TS6	15.2	11.8
10 -> 11	-5.5	-6.2
10 -> TS6b	12.3	9
10 -> 12	-17.6	-18.6

Activation barrier heights and reaction free energy comparison between G3(MP2)-RAD and M06-2X.

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Cartesian coordinates & input information

Starting material

C -1.4149779467 -1.7282906376 1.5251644158
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O2 (triplet)

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O2 (singlet)

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O3

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TS1b

C -0.4481279065 1.8154443706 1.8885467571
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1b

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TS1a

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TS3b

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5

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9

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O 1.4014579177 -1.1855555608 1.2181547105
C 3.3419294319 -1.1735177887 -0.6641143567
H 3.8676641335 -1.8304584511 -1.3791000016
H 3.4915781657 -1.5879808172 0.3549180483
O 3.8941032584 0.0501287733 -0.6663389851

TS4b

C -1.0297653252 -1.2565329593 2.0383269368
H -0.3778154407 -2.068580159 2.376921322
H -0.5629111636 -0.3108986631 2.3159006304
C -1.2437830088 -1.3637331347 0.518794143
C -1.9743546808 -2.7076515944 0.1987488335
H -1.3999092025 -3.5449614468 0.609341985
H -2.103844442 -2.8572378308 -0.8762464298
H -2.9643336026 -2.7110642747 0.6704982673
H -0.0144766414 -1.168107782 -1.3255921757
C 1.4989695533 -0.0720794749 0.1372852986
C -2.1368352814 -0.2132051176 0.0229990031
C 0.0558154331 -1.4067684486 -0.266997019
C 0.6877288781 1.238260141 -0.0881635462
O 0.25165016 1.5933864172 -1.1606403564
O -2.5700431813 0.6839498253 0.7183419774
O -2.4031909298 -0.3251499693 -1.2923854303
O 0.5584844584 1.8940070069 1.0635458646
C -3.1583251425 0.7486912298 -1.8886912682
H -2.5815103131 1.6751269358 -1.8375623876
H -4.1140946662 0.8731521015 -1.3736413275
H -3.3120417311 0.4497897317 -2.9257382276
C -0.2035002859 3.1221081795 1.0179195932
H 0.205301514 3.789427997 0.2555626783
H -0.0971895487 3.5548040614 2.0124099476
H -1.2496912287 2.892729411 0.8048149728
H -1.9889377765 -1.3352827863 2.5595674391
H 0.66908226 -2.2791311306 -0.0456265511
O 2.2883712912 -0.2857030152 -0.997400214
O 1.8816993406 -0.4155021925 1.2714998713
C 3.5210496665 -0.9748614998 -0.7887558836
H 3.7373470766 -1.4830728203 -1.7456186847
H 3.4141325444 -1.7467231657 -0.0035926807
O 4.561282417 -0.1989065725 -0.4575365816

7

C 0.7333682917 1.5569397964 -1.0247049348
H 0.4720926205 2.6025613762 -1.2228684817
H 0.6368962889 0.9895532147 -1.9549589888
H 1.782491345 1.5250820917 -0.7070216994
C 0.1938063658 -0.4757924398 0.3542725369
O 0.5598218137 -0.9159692501 1.4251919242
O 0.0852178921 -1.2459199365 -0.7541629721
C -0.0522861083 1.7887629482 1.3390238923
H 0.9182162873 2.1782883473 1.6317260092
H -0.8440049457 1.7908142832 2.0822773299
C 0.430902608 -2.6348302226 -0.5954054512
H 1.4720826775 -2.7339390807 -0.2769418286
H 0.2835018733 -3.0833518361 -1.5784647425
H -0.2189722322 -3.1065716574 0.14651404

C -1.6705118053 1.0280766547 -0.4110006974
H -1.9652759766 2.0656496346 -0.6043061248
H -2.347999998 0.6202380592 0.3487826346
H -1.7965184448 0.4508545069 -1.3316608498

8

C 0.2974337699 0.1423075086 -0.4709235487
C -0.8429563671 0.3875423324 0.5329661879
O 1.1649033063 -0.7584332813 0.0249160042
C 2.3106769917 -1.0815037859 -0.8039940369
H 3.1117556349 -1.330551612 -0.0868117638
H 2.6128633229 -0.1869091886 -1.3789515878
O 2.120635999 -2.0920071776 -1.6472836741
O 0.4049608267 0.7215405287 -1.5255290498
O -0.6887080234 0.3928564138 1.732724671
O -1.9838627001 0.6247046552 -0.1153809487
C -3.1306487884 0.9157061109 0.7136052082
H -3.3266135828 0.0803232041 1.3903937901
H -3.956081777 1.0561712354 0.0168015803
H -2.9501557527 1.8240067362 1.2937859681

6

C -1.2783595814 -0.062863845 0.8706460759
C -2.7835831792 -0.4227119619 0.9129094187
H -2.9905204735 -1.0503255334 1.7876717046
H -3.093531556 -0.9648597331 0.0145602979
H -3.3953947031 0.482863955 0.9972725219
C -0.4751088952 -1.387154456 0.6964896104
H -0.7218992394 -1.8350602879 -0.2722575597
C 1.0286878867 -1.2422214649 0.7825094661
C -1.0481576916 0.8794430619 -0.3217514125
O -0.7029690645 2.0403243477 -0.2385458743
O -1.324565318 0.2740559841 -1.496913954
C -1.1293817676 1.068899401 -2.681377177
H -0.0830193041 1.3748642401 -2.7602272116
H -1.7672085231 1.9563066622 -2.6544130317
H -1.4041011771 0.4198108111 -3.5132446865
H -0.7691796605 -2.0848122775 1.4854645835
O 1.5119049715 -0.4341069972 -0.1978582597
O 1.735102704 -1.7734453543 1.6159393438
C 2.9413641053 -0.2033829336 -0.2234560447
H 3.3902793522 -0.6822652996 0.6715172849
H 3.0817789823 0.8893733446 -0.1395009335
O 3.5400953126 -0.6743204078 -1.3090974779
C -0.8793192424 0.6512679411 2.1721350948
H 0.1671458588 0.9712388221 2.1587058434
H -1.0235767091 -0.0214086214 3.0252463118
H -1.4900079277 1.545658943 2.3259819855

Acyl radical

C -0.7942230808 1.2471596542 3.1437497819
O -1.4484046945 0.770568833 4.0249534694
O 0.0105920696 2.2904179892 3.1374077061
C 0.1527804135 3.0130612181 4.4057206857
H 0.8492233051 3.8225640359 4.1927406686
H 0.5522234085 2.3376164901 5.1653014106
H -0.8209262613 3.4002405694 4.7135581276

CO2

O 0.2358337706 0.2830430313 0.
O -2.0327374069 0.8516569687 0.

CH3 radical

C -1.5108112784 0.7700967511 -0.0011083922
H -0.40148 0.77786 0.00778
H -1.8839551824 0.2306826656 0.8936268917
H -1.8696358988 0.2583663245 -0.9176955507

CH4

C -1.1067403912 0.2143466834 -0.0033576115
H -0.0131586963 0.2145922367 0.0048345765
H -1.4715532231 1.2452843648 0.0048393498
H -1.4778111518 -0.3107099986 0.8812949004
H -1.4644384936 -0.2917798695 -0.904399273

TS5

C -1.3743940577 -0.89128747 0.0587233562
C -2.6962513272 -1.3122853361 -0.6330904852
H -2.6949214525 -2.3933201427 -0.8172942358
H -2.8305227079 -0.7992573414 -1.5911084809
H -3.5549124243 -1.0807957815 0.0068447701
C -0.2090425647 -1.2274110129 -0.9022919611
H -0.3437216981 -0.7040013724 -1.8567329367
C 1.1828750307 -0.8535218233 -0.4182515599
C -1.4705464957 0.6169676989 0.3340709338
O -1.7444879827 1.1091739901 1.4083316432
O -1.294577681 1.3452477849 -0.7908449629
C -1.3653780114 2.7749484468 -0.6333577358
H -0.5898487467 3.112838666 0.0586426369
H -2.3472928315 3.0687223772 -0.2529850992
H -1.1979785231 3.1841913687 -1.6300980455
H -0.2102029004 -2.2995506671 -1.1236155278
O 1.3550862033 0.140154656 0.344645434
O 2.1599668848 -1.5626762675 -0.8439312441
C 3.3062529585 0.2038911996 0.5640183899
H 3.1853570702 -0.7586168017 -0.1822280706
H 3.275278008 -0.0724229224 1.6295783264
O 3.7939723271 1.2274336603 0.1399567407
C -1.2275585105 -1.6472790117 1.3899990013
H -0.3247600673 -1.3424176707 1.9274648857
H -1.1784302134 -2.7263813077 1.2008066387
H -2.0808232865 -1.4480689194 2.0438755885

10

C -0.718440773 -0.00576583340.8153109669
C -2.2235838349 -0.3707195669 0.8894018899
H -2.4102912763 -1.012307529 1.7591393577
H -2.5535461288 -0.9052873617 -0.0081757423
H -2.833116841 0.532690831 0.9988964109
C 0.0846431295 -1.3159495905 0.667234775
H -0.2942344904 -1.910451469 -0.172737272
C 1.570858296 -1.1442814894 0.4427857049
C -0.5470878067 0.9131988968 -0.4024950922

O -0.5685292175 2.1250909159 -0.3639632104
O -0.4567630519 0.2133970145 -1.5577446022
C -0.3135635009 0.9976633933 -2.7567967787

H 0.597032311 1.5998442435 -2.7038035282
H -1.1771032473 1.6552179411 -2.8879253994
H -0.2517889271 0.2738638051 -3.5701893622
H -0.0548355291 -1.933785259 1.5630249462
O 2.1509233899 -0.1094383576 0.1905329287
C -0.3133565132 0.7557704354 2.090262536
H 0.7373471094 1.0563227838 2.0594447061
H -0.4737623772 0.1179160927 2.9681772905
H -0.9161663496 1.6605414877 2.2046406809
O 2.2219753408 -2.3331760058 0.538874179
H 3.1657238782 -2.1580277984 0.3611089549

Formyl radical

C -1.01263 1.112 0.
O -0.68429 2.28668 0.
H -2.063 0.84276 0.

TS6

C -0.2143147576 -0.0141723926 -0.7565829304
C -0.6903650697 0.7018875317 -2.0477140717
H 0.1197287289 0.7244601844 -2.784841493
H -0.9980212604 1.732967562 -1.8419645383
H -1.5379905508 0.1682910459 -2.4906513536
C 0.975404499 0.7804779334 -0.1738594758
H 0.7044367376 1.8340519103 -0.0375568474
C 1.4926332984 0.2885661124 1.1596031474
C -1.4209882587 -0.0203551669 0.2030305984
O -2.23553709 -0.9150318095 0.2819131657
O -1.524959078 1.1367157161 0.896932212
C -2.6397627025 1.2269253886 1.8049234921
H -2.5571223549 2.2113160847 2.2669170061
H -2.573660368 0.4381583378 2.5585534119
H -3.5831045378 1.1318044825 1.2606767651
H 1.8078300458 0.7698013096 -0.8868991999
O 0.9702268551 -0.5337290303 1.8821141628
O 2.655902155 0.9077087475 1.4921535597
H 1.229478818 -1.4635273805 -1.9021310022
C 0.1732385796 -1.4556604024 -1.0731204243
H -0.591493414 -2.0013786648 -1.6285921682
H 0.518276651 -2.0270425365 -0.2098154431
H 2.9222446516 0.5665645008 2.3671389183
H 2.1922698556 -0.7988853244 -3.4938953486
C 2.307793214 -1.5767150976 -2.7373053816
H 2.2242816753 -2.5857875687 -3.1435574349
H 3.1860789976 -1.4399167934 -2.1042376765

TS6b

C 0.1212123416 0.9474783214 0.3177873737
C 0.0778386894 1.6729779061 1.6878685478
H 1.0955999512 1.9057761016 2.0209024922
H -0.4011950845 1.0549324795 2.4555494754
H -0.4751235008 2.6145611951 1.6047737543
C 0.8884286726 -0.3700176588 0.4827892649
H 0.6766701652 -0.8884928451 1.420558251
C 0.8754516807 -1.3265218269 -0.6554297879
C -1.3459416847 0.691324014 -0.079675855
O -2.0293876403 1.4532815198 -0.7292758919
O -1.8221981733 -0.4590448064 0.4491942995
C -3.1994205775 -0.7642285854 0.1564583725
H -3.3964593336 -1.7140243892 0.654578168

H -3.3429158835 -0.8554294486 -0.9231746401
H -3.8540585686 0.0205235451 0.5449083312

H 2.1407747437 -0.0865379221 0.6483677031
O 0.4817315646 -1.1096326998 -1.7874562328
O 1.4119354368 -2.5292960597 -0.3014717511
H 1.7811712584 2.1386502226 -0.4185433002
C 0.7661430085 1.8722157264 -0.7335281185
H 0.1820131615 2.7902692169 -0.8380492036
H 0.8148911014 1.3852327437 -1.7103043214
H 1.3938289474 -3.0903190996 -1.0994534672
H 3.5675482182 0.963975129 1.5888437295
C 3.5357726326 0.1302071397 0.8886594744
H 3.8507214272 -0.8267073617 1.3023394596
H 3.9304517558 0.3509104723 -0.1023741076

11

C 0.3558889234 0.9465312679 0.4480751827
C 0.013026065 1.8163030896 1.7025507145
H 0.9347793073 2.0873637671 2.228353181
H -0.6304531596 1.257595697 2.3912161717
H -0.499166134 2.7365577101 1.4052725367
C 1.083700035 -0.3366403342 0.941065649
H 0.5200245927 -0.8134160152 1.7445424921
C 1.3645124362 -1.4309774265 -0.0901815727
C -0.983935637 0.6276379291 -0.2423550097
O -1.4527170552 1.2656478181 -1.1626003174
O -1.6015529 -0.4192352939 0.3316413776
C -2.8818922852 -0.7906536236 -0.2231649715
H -3.2006484898 -1.6593416061 0.3522183572
H -2.7723090185 -1.0439602271 -1.2801632244
H -3.5918549119 0.0332600088 -0.115126089
H 2.0528830469 -0.0339034362 1.3627549731
O 1.3475496365 -2.6063861915 0.1877438557
O 1.6786443578 -1.0337055902 -1.3493352597
H 1.6653134955 -0.0535678513 -1.4180672008
C 1.2193067172 1.7520659405 -0.4786720571
H 2.231448248 1.996883369 -0.1645020069
H 0.7717703897 2.3199763187 -1.2872904022

12

C 2.0949707659 -3.5702345349 0.888502735
C 1.4229305034 -4.9079870705 1.2947969771
H 1.0792582912 -5.4375976914 0.3986323086
H 0.5611718552 -4.7382768816 1.9485120147
H 2.1368319595 -5.5531909283 1.817339725
C 1.0860772303 -2.701101372 0.1881465117
H 0.130693355 -3.1237415958 -0.1069519212
C 1.2602935981 -1.3124500937 -0.1822358313
O 3.7343933917 -3.0107500168 2.6178112895
O 1.6081624888 -2.2864735539 2.8467722262
C 1.9644141231 -1.672045181 4.1005608641
H 1.0475634035 -1.2071123115 4.4635646763
H 2.7443197091 -0.9225657009 3.9437858173
H 2.3220613489 -2.4269407568 4.8058725614
O 0.42209165979 -0.649468759 -0.7818309878
O 2.4602661272 -0.7786269974 0.1975601261
H 2.4610030564 0.1503036605 -0.0976392109
C 3.3036888124 -3.857687829 -0.036774301
H 2.9623412483 -4.3675166688 -0.944208096
H 4.0212443284 -4.4999773616 0.482502985

H 3.8137786858 -2.9339153877 -0.3194641613
C 2.6046291199 -2.917122968 2.1902836915

TS7

C -0.3591216098 1.1780759852 0.0984598712
C 0.3002578679 2.3794177504 -0.5546968688
H -0.4171977876 3.2104288126 -0.5907036839
H 0.6100424928 2.1664480587 -1.5831447292
H 1.1770745541 2.7099244603 0.008928719
C -1.4526594191 0.5356074657 -0.7554394645
H -1.0170737355 0.1532534122 -1.6871910772
C -2.2822515209 -0.5603164967 -0.0834961258
C 1.3087772036 -0.310660693 -0.3009967254
O 1.0317931736 -1.4758771029 -0.496432119
O 2.4850471813 0.1749712886 0.053513925
C 3.5676422507 -0.789332934 0.2462761134
H 4.428026513 -0.1914389376 0.5436599919
H 3.7604400444 -1.3176794962 -0.6897059656
H 3.2896244195 -1.4980906912 1.0294256931
H -2.1600227149 1.3250589917 -1.0336238836
O -3.4228614693 -0.3815867935 0.2819678513
O -1.687533213 -1.7583259646 0.0825642144
H -0.7538789513 -1.7508321378 -0.2278972559
C -0.340778304 1.0394553717 1.4641814599
H -0.9508898844 0.3036980923 1.98000692
H 0.342661909 1.628041558 2.0699711399

TS7b

C 0.1441199382 0.1433921458 -0.1772610746
C 0.7068223763 0.8407975528 -1.3970831396
H 0.9320543804 0.1291190851 -2.1924291297
H 1.6492877162 1.3375144602 -1.1290162785
H 0.0243701509 1.6028868078 -1.7691893671
C -1.5652996898 -1.0717422407 -1.3460780743
H -0.9443728361 -1.6652495321 -2.0100455536
C 0.7643785502 -1.1755461733 0.232136156
O 0.4357522638 -1.8333501317 1.2004120258
O 1.7586576813 -1.5456459303 -0.6041011157
C 2.4236018252 -2.7813427692 -0.2777639959
H 3.1860729929 -2.9086853196 -1.0465752997
H 1.7121640214 -3.6112339318 -0.2940825436
H 2.8786987146 -2.7158725361 0.7137875407
H -2.0556694743 -0.1980289317 -1.7613978634
C -0.5794013574 0.7426042588 0.8300144459
H -0.7515270662 0.168074811 1.7341258985
H -2.0375708871 -1.572847286 -0.5086478753
C -1.2197458922 2.0594916227 0.8755397455
O -1.1579445102 2.8013200517 -0.2695557276
H -1.6251325996 3.6350564345 -0.0738513414
O -1.7894572981 2.4850505531 1.868544567

13

C -0.8464005828 1.323205361 0.3183800369
C -1.1120471071 0.2663965488 -0.4786484068
H -1.0231708189 0.3767233052 -1.5530254149
C -1.5288374651 -1.0814449525 -0.0281439101
O -1.7047916032 -1.4783347728 1.1089511168
O -1.7091279071 -1.8955984369 -1.105384033
H -1.9811898296 -2.7663786062 -0.7594265008
C -0.9137953846 1.3662909873 1.817593395

H -1.6161398179 2.1459216967 2.136339643
H -1.2162010105 0.4068519284 2.232442239
H 0.0620518691 1.6556461817 2.2259359588
C -0.4331611338 2.6268473706 -0.3160077191
O -0.1781452962 3.6244865499 0.3318935038
O -0.3719886603 2.5863632011 -1.6629900676
C 0.0191152579 3.8119206854 -2.3108526182
H 1.0174738641 4.1123357151 -1.9823153909
H 0.0136194486 3.5865457743 -3.3773943103
H -0.6935617526 4.6074367529 -2.0781052414

14

C -0.901585396 1.2616335571 0.2403747727
C -0.5081277907 2.523688193 -0.4856062138

H -1.2522266434 3.3133894102 -0.3127132652
H -0.4103998421 2.3709747535 -1.5645352042
H 0.4471418481 2.9065924386 -0.10090142
C -1.0948246006 0.1232884595 -0.4623293056
H -0.9619711019 0.1381439776 -1.5405590195
C -1.4803405238 -1.1908249974 0.08018564
O -1.6979602363 -1.5060848512 1.2385587799
O -1.5807584073 -2.1081895988 -0.9277010383
H -1.836041895 -2.9514275065 -0.5093776989
C -1.0449025988 1.4024091197 1.7319821613
H -1.7882075037 2.1789916026 1.9609714708
H -1.3388644464 0.4721594463 2.2157323152
H -0.0948617321 1.7476384358 2.1637691856

15

H -0.2490123145 0.3919285458 0.3180219988
C -0.0698606434 0.1511926669 1.369482774
H 1.0104575134 0.0778695639 1.5297417208
H -0.454147313 0.9660397408 1.9917702508
C -0.7197626544 -1.1822662818 1.7454972442
C -0.3942752882 -1.6133016862 3.1720371766
H 0.6899485557 -1.6521325203 3.3189306635
H -0.8120979231 -2.602062864 3.385929132
H -0.81134294 -0.8904187037 3.8809072845
C -2.2760648858 -1.2575084267 1.4324927851
H -2.7960630635 -1.7709768534 2.2465826429
C -2.9329289111 0.1107031306 1.285309805
O -3.1224393461 0.4954803192 0.0121544769
H -3.5469339359 1.3747142424 0.0352885491
O -3.2453207255 0.7797148958 2.2491483298
O -0.237304595 -2.2309000619 0.8767747747
O -1.0419701018 -2.0621392424 -0.2885289558
O -2.3881294279 -2.0904884651 0.2885283473

MECP (singlet)

C -0.91028905 -1.27824995 2.00183549
H -0.35860151 -2.18663306 2.24614542
H -0.29125638 -0.41948784 2.24980453
C -1.28691202 -1.2918677 0.52244374
C -2.26083602 -2.44964332 0.23928026
H -1.80706782 -3.38749063 0.56015494
H -2.50010274 -2.51842133 -0.81999396
H -3.18852869 -2.3129197 0.79502933
C -0.0707058 -1.49895339 -0.39643748
H -0.3625439 -1.37571517 -1.43898319

C 1.15663944 -0.56620029 -0.21289084
C -1.99112281 0.01650869 0.1666074
C 0.71996536 0.92098705 -0.24418559
O 0.26588178 1.42655365 -1.23392543
O -2.13846162 0.94500344 0.91763117
O -2.43818077 0.01595598 -1.09243405
O 0.87583331 1.52303794 0.92059585
C -2.9940626 1.25309882 -1.54376874
H -2.2230921 2.02098618 -1.53082487
H -3.82349384 1.55033845 -0.90635605
H -3.33460286 1.07143941 -2.55742733
C 0.40551263 2.8752585 0.9748547
H 0.91011338 3.47566459 0.22114881
H 0.64752198 3.22448333 1.97267521
H -0.6692015 2.88964844 0.80943845
H -1.809752 -1.23809234 2.61491525
H 0.31198429 -2.51194982 -0.26415166
O 1.97929625 -0.80821061 -1.34300655
O 1.80908016 -0.91209736 0.9150832
C 3.3373656 -0.69197774 -0.97521127
H 3.84505965 -0.08684216 -1.74329959
H 3.80087971 -1.68737723 -0.94806876
O 3.50305626 -0.06477955 0.20498349

MECP (triplet)

C -0.91028905 -1.27824995 2.00183549
H -0.35860151 -2.18663306 2.24614542
H -0.29125638 -0.41948784 2.24980453
C -1.28691202 -1.2918677 0.52244374
C -2.26083602 -2.44964332 0.23928026
H -1.80706782 -3.38749063 0.56015494
H -2.50010274 -2.51842133 -0.81999396
H -3.18852869 -2.3129197 0.79502933
C -0.0707058 -1.49895339 -0.39643748
H -0.3625439 -1.37571517 -1.43898319
C 1.15663944 -0.56620029 -0.21289084
C -1.99112281 0.01650869 0.1666074
C 0.71996536 0.92098705 -0.24418559
O 0.26588178 1.42655365 -1.23392543
O -2.13846162 0.94500344 0.91763117
O -2.43818077 0.01595598 -1.09243405
O 0.87583331 1.52303794 0.92059585
C -2.9940626 1.25309882 -1.54376874
H -2.2230921 2.02098618 -1.53082487
H -3.82349384 1.55033845 -0.90635605
H -3.33460286 1.07143941 -2.55742733
C 0.40551263 2.8752585 0.9748547
H 0.91011338 3.47566459 0.22114881
H 0.64752198 3.22448333 1.97267521
H -0.6692015 2.88964844 0.80943845
H -1.809752 -1.23809234 2.61491525
H 0.31198429 -2.51194982 -0.26415166
O 1.97929625 -0.80821061 -1.34300655
O 1.80908016 -0.91209736 0.9150832
C 3.3373656 -0.69197774 -0.97521127
H 3.84505965 -0.08684216 -1.74329959
H 3.80087971 -1.68737723 -0.94806876
O 3.50305626 -0.06477955 0.20498349

4 [optimised at M06-2X/6-311++G(2d 2p) level of theory]

C -0.6760448812 1.1671170227 2.0305430459

H -0.2956000481 0.7166251804 2.9474304475
H 0.1545682398 1.6247953747 1.4986623055
C -1.3694436239 0.1013173335 1.1849897433
C -2.6089888864 -0.4296528802 1.9220205488
H -2.3116286164 -0.8100432393 2.8993614185
H -3.0893907188 -1.2302923723 1.3628416167
H -3.3341729704 0.3696776779 2.0753840796
C -0.4533638893 -1.1055418676 0.8941287834
H -0.941040214 -1.7723894187 0.18381155
C 0.9280523708 -0.8225161614 0.3246552533
C -1.8296178626 0.726709248 -0.1302593279
C 0.8614775473 0.0660832252 -0.9330453866
O 0.3137174015 -0.3103103292 -1.9335118662
O -1.5922625066 1.8552424877 -0.4746256911
O -2.5352454844 -0.1312361146 -0.8716180106
O 1.4105930396 1.2548934436 -0.7615766273
C -2.8809908509 0.3350379473 -2.1780146235
H -1.9720108165 0.5130002593 -2.7490948065
H -3.4610204564 1.2522978754 -2.1090230526
H -3.4668353438 -0.4584562703 -2.6289296638
C 1.2725570003 2.1500922696 -1.8716051967
H 1.721152934 1.7118201971 -2.7600357381
H 1.793836084 3.054948354 -1.5807564562
H 0.2171345035 2.3492757322 -2.0430485558
H -1.3830085306 1.9535914228 2.2906982713
H -0.2899182589 -1.6575923913 1.821109347
O 1.5444419985 -2.0469318747 -0.0360407185
O 1.766905535 -0.2890267773 1.3220468349
C 2.837044737 -2.0018688608 0.5261739702
H 3.5875716682 -2.301015202 -0.2018368684
H 2.8672435198 -2.6075067299 1.4338772992
O 3.0547872399 -0.644644602 0.8212882144