Supporting Information for

Primary Formation of Highly Oxidized Multifunctional Products in the OH-Initiated Oxidation of Isoprene. A Combined Theoretical and Experimental Study

Sainan Wang,[a,b] Matthieu Riva,[b,c] Chao Yan,[b] Mikael Ehn,[b] and Liming Wang[a,d*]*

[a] School of Chemistry & Chemical Engineering, South China University of Technology, Guangzhou 510640, China.

[b] Institute for Atmospheric and Earth System Research / Physics, Faculty of Science, University of Helsinki, P.O. Box 64, Helsinki 00014, Finland

[c] Now at Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, F-69626, Villeurbanne, France

[d] Guangdong Provincial Key Laboratory of Atmospheric Environment and Pollution Control, South China University of Technology, Guangzhou 510006, China.

AUTHOR INFORMATION

Corresponding Author

Liming Wang, Email: wanglm@scut.edu.cn
Mikael Ehn, Email: mikael.ehn@helsinki.fi

Contents of Supporting Information (8 Pages including this page)

Figure S1. Structures of main transition states involved in the proposed mechanisms.

Figure S2. Time profiles of selected species under low-NO conditions.

Figure S3. Mass spectra recorded from the reaction of OH radicals with isoprene with the presence of NO.

Figure S4. Branching ratios of bimolecular reactions of $ISOPO_2$ isomers with NO and the intramolecular H-shift in $ISOPO_2$ isomers in 1-OH and 4-OH system.

Figure S5. The yields of eight species as a function of the traditional sink rate with NO.

Figure S6. The yield of HOMs using forward and reverse rate constants for O_2 additions obtained from our calculations and the modeling of Teng et al.

Table S1. Geometries of nine conformers of 4-ZH-2OOH'-3OO at M06-2X/6-311++G(2df,2p) level.

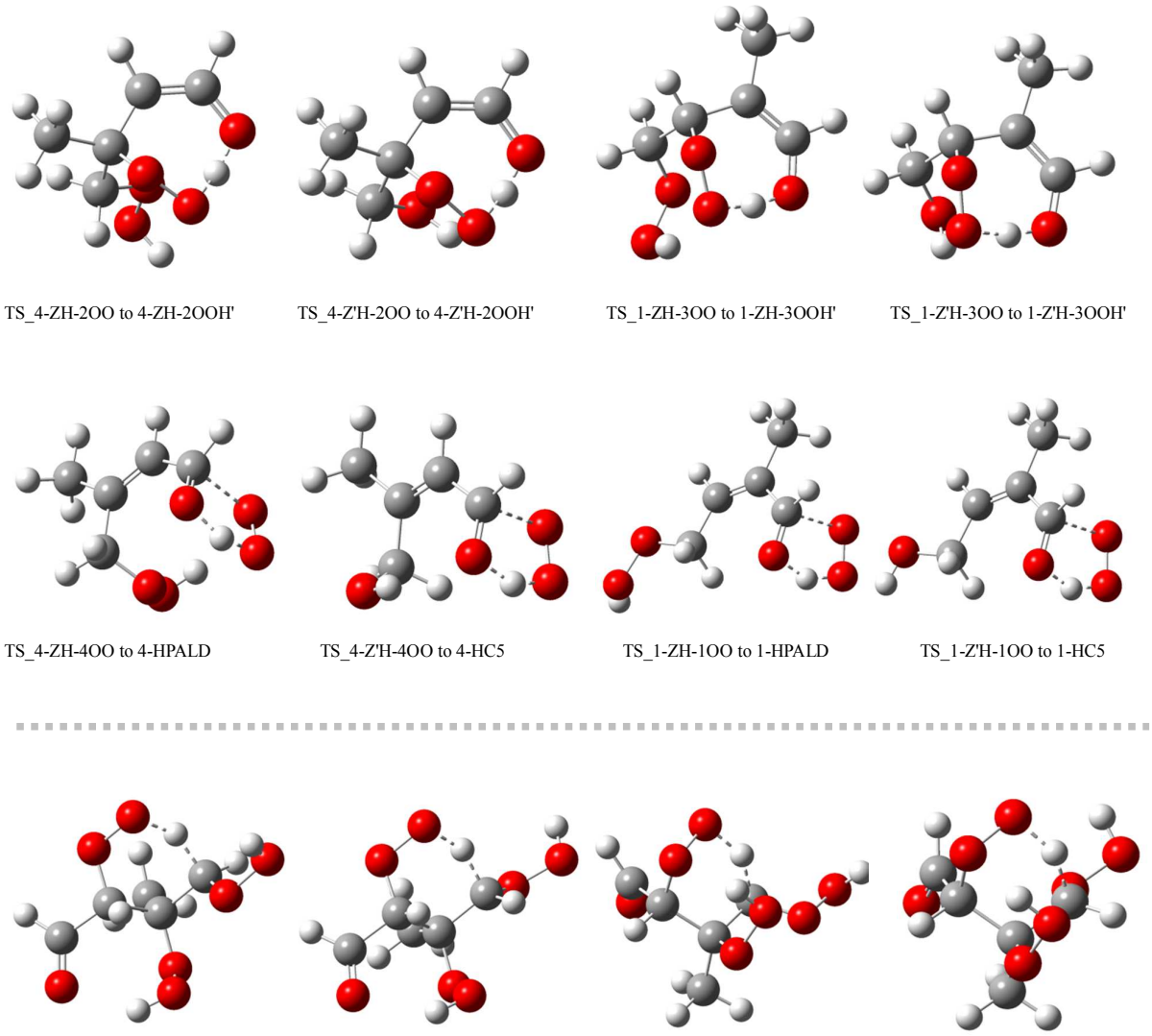

Figure S1. Structures of main transition states involved in the proposed mechanisms

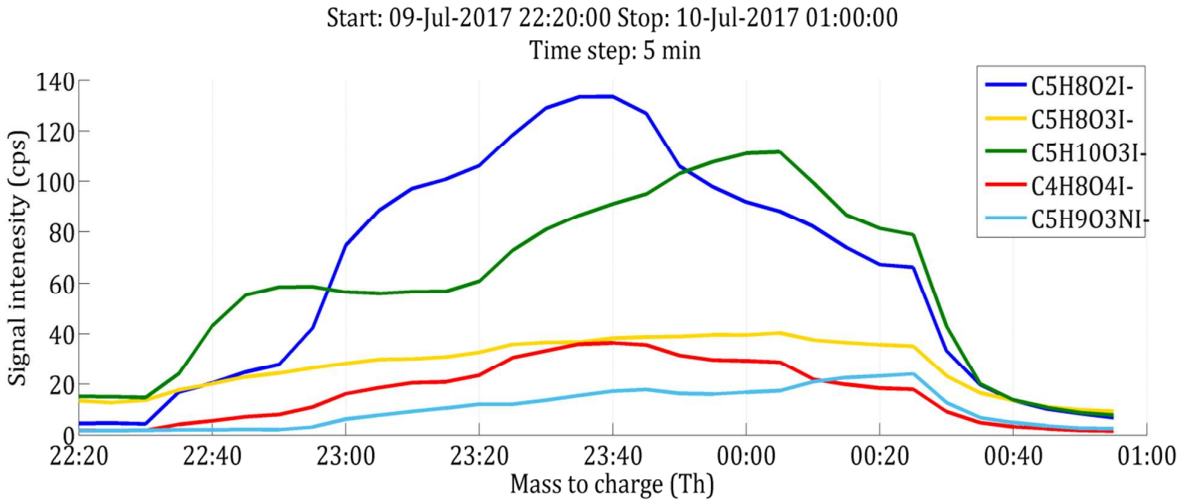

Figure S2. Time profiles of selected species under low-NO conditions. NO was produced by photolysis of NO_2 and only monitored at the beginning with the concentration of 125 ppt. NO_2 was increased by four times at 23:20 and then decreased by half at 23:46 (13 ppb to 65 ppb and then to 39 ppb). H_2O_2 was doubled at 23:21, and decreased to the initial concentration at 00:09 (0.72 ppm to 1.45 ppm and then to 0.72 ppm).

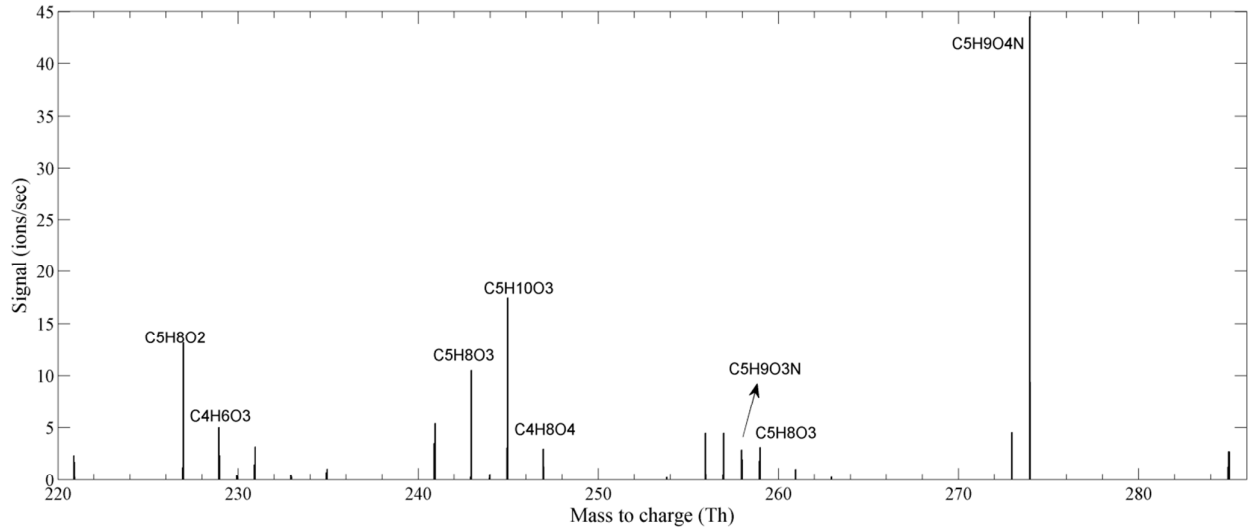

Figure S3. Mass spectra recorded from the reaction of OH radicals with isoprene with the presence of NO. Products are detected as adduct with iodide.

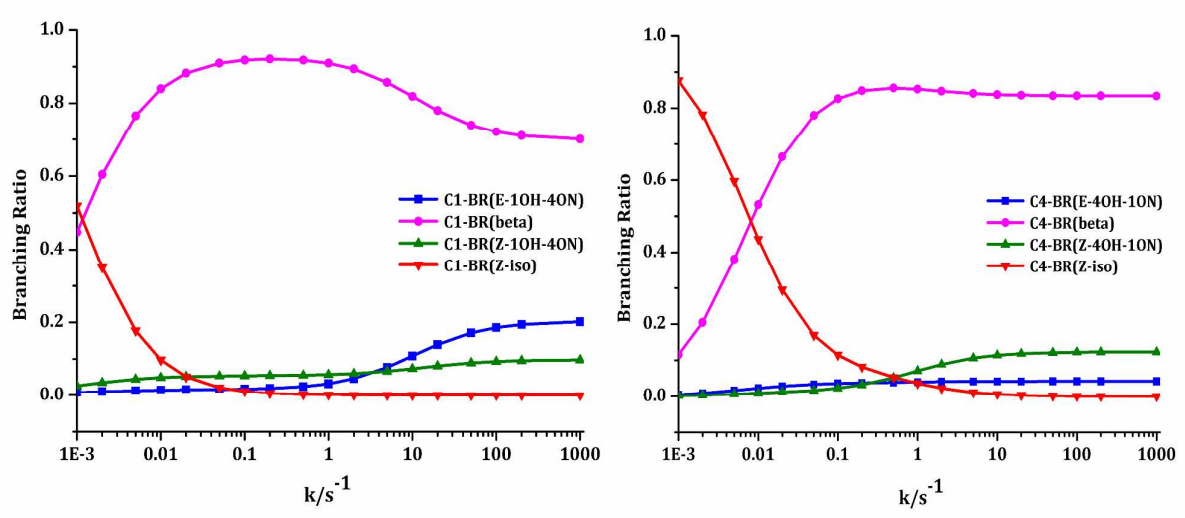

Figure S4. Branching ratios of bimolecular reactions of $ISOPO_2$ isomers with NO and the intramolecular H-shift in $ISOPO_2$ isomers in 1-OH and 4-OH system.

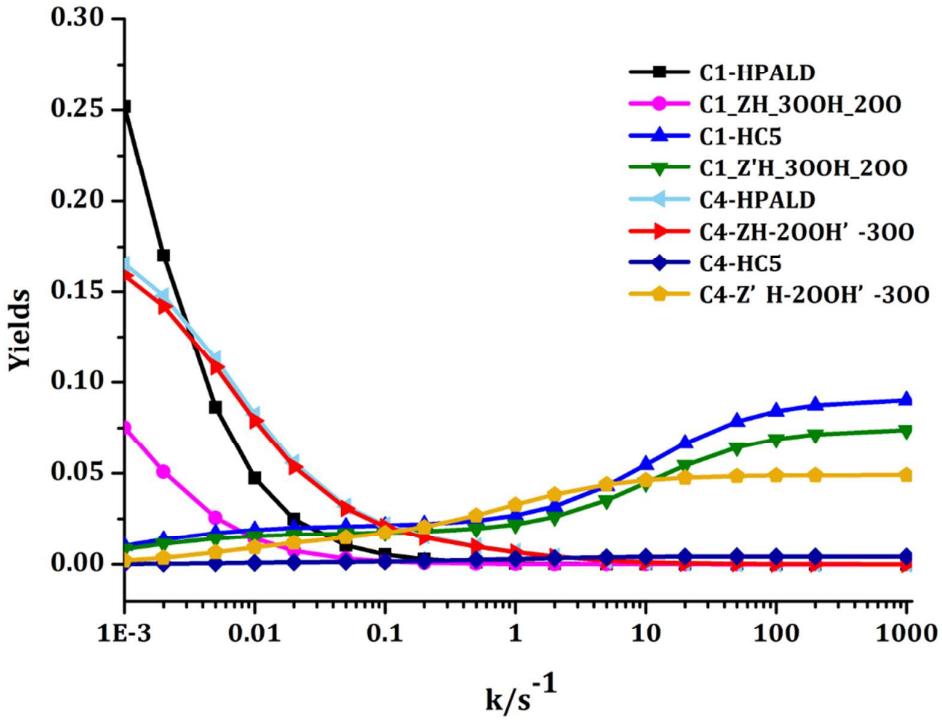

Figure S5. The yields of eight species as a function of the traditional sink rate with NO (The yields of C1-HPALD and C1_ZH_3OOH_2OO can be expressed as 0.63*[C1-BR(Z-iso)]*0.77 and 0.63*[C1-BR(Z-iso)]*0.23, respectively. The yields of C1-HC5 and C1_Z'H_3OOH_2OO can be expressed as 0.63*0.87*([C1-BR(E-1OH-4ON)]+[C1-BR(Z-1OH-4ON)])*0.55 and 0.63*0.87*([C1-BR(E-1OH-4ON)]+[C1-BR(Z-1OH-4ON)])*0.45, respectively. This is the case in modeling the yields of C4-type products. HOMs formed through unimolecular H-shifts in four peroxy radicals can be obtained by multiplying the corresponding yield by $k_{H\text{-}shift}/(k_{H\text{-}shift} +k)$.

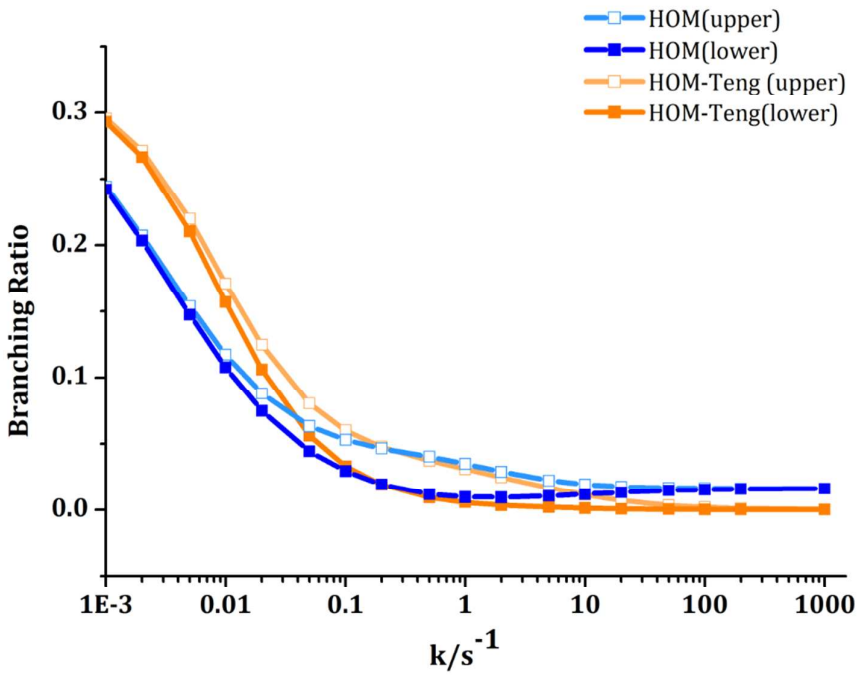

Figure S6. The yield of HOMs using forward and reverse rate constants for O_2 additions obtained from our calculations and the modeling of Teng et al.[1]

Table S1. Geometries of nine conformers of 4-ZH-2OOH'-3OO at M06-2X/6-311++G(2df,2p) level (Given as the Cartesian coordinates *x*, *y*, and *z* of atoms in Anstrong).

4-ZH-2OOH'-3OO_M1				4-ZH-2OOH'-3OO_M2			
C	-0.17926	-0.68688	0.409183	C	0.01213	-0.33555	0.27856
C	-0.89163	0.333676	-0.5068	C	-1.27286	0.027865	-0.50863
H	-0.77799	0.033528	-1.55187	H	-1.23491	-0.38418	-1.52155
C	1.130043	-1.12332	-0.24077	C	1.191344	-0.22593	-0.68499
H	0.910706	-1.84964	-1.02702	H	1.339631	0.801223	-1.01661
H	1.775618	-1.57606	0.513211	H	0.982553	-0.86062	-1.55326
O	1.748713	0.004865	-0.82632	O	2.339661	-0.6909	-0.01894
O	2.853047	-0.46965	-1.57239	O	3.426708	-0.46008	-0.89998
C	-0.51826	1.809027	-0.41005	C	-1.56844	1.51428	-0.61123
H	3.596065	-0.18465	-1.02687	H	3.766873	-1.35354	-1.0216
H	-1.16197	2.448011	-1.03794	H	-2.64272	1.765405	-0.61343
O	0.345593	2.2853	0.264939	O	-0.72563	2.358634	-0.71517
H	1.224135	1.218953	1.505236	H	0.60703	2.234327	0.811378
O	-0.00977	-0.17196	1.726162	O	0.112295	0.523697	1.419591
O	1.286251	0.349877	1.93615	O	1.088086	1.533123	1.272819
C	-1.05775	-1.92059	0.597766	C	-0.09779	-1.7432	0.852583
H	-1.90205	-1.67722	1.238467	H	-0.8874	-1.7797	1.599369
H	-1.4372	-2.28395	-0.35624	H	-0.32749	-2.46451	0.068273
H	-0.46913	-2.70008	1.078051	H	0.846776	-2.00071	1.322055
O	-2.31116	0.3548	-0.23847	O	-2.4432	-0.53087	0.111892
O	-2.99481	-0.34078	-1.09395	O	-2.80251	-1.65643	-0.42428
4-ZH-2OOH'-3OO_M3				4-ZH-2OOH'-3OO_M4			
C	0.060559	0.016009	0.638972	C	0.103751	0.42641	0.717373
C	-0.89042	-0.31961	-0.52752	C	-0.72212	-0.45353	-0.24671
H	-0.41313	-1.05108	-1.18781	H	-0.25992	-0.46556	-1.23322
C	1.475962	0.245393	0.099534	C	1.57349	0.007196	0.687578
H	2.123748	0.558123	0.918652	H	1.695638	-0.94267	1.21374
H	1.499932	1.0011	-0.68623	H	2.160295	0.782262	1.188614
O	1.89646	-1.00466	-0.41539	O	1.989857	-0.15173	-0.65004
O	3.242591	-0.84875	-0.82263	O	3.289181	-0.716	-0.60615
C	-1.37053	0.842222	-1.3792	C	-2.16394	-0.0021	-0.37431
H	3.167924	-0.86853	-1.78391	H	3.822698	0.004067	-0.96195
H	-2.28505	0.620534	-1.95543	H	-2.91838	-0.67181	0.073325
O	-0.82645	1.90654	-1.46455	O	-2.46912	1.014652	-0.9298
H	-0.10677	2.636476	0.224732	H	-0.69568	2.069341	-1.3372
O	-0.41975	1.159828	1.347355	O	-0.0719	1.789856	0.388271
O	0.307443	2.335119	1.046656	O	0.205823	2.004763	-0.98428
C	0.049393	-1.11613	1.658428	C	-0.41154	0.340456	2.148919
H	-0.90634	-1.12974	2.178163	H	-1.43498	0.709786	2.200881
H	0.204688	-2.07969	1.17736	H	-0.37842	-0.68434	2.510571
H	0.843068	-0.94292	2.382062	H	0.20619	0.966028	2.791507
O	-2.10496	-0.92497	-0.04746	O	-0.68526	-1.78858	0.277828
O	-2.10507	-2.21705	-0.1701	O	-1.318	-2.61267	-0.50126
4-ZH-2OOH'-3OO_M5				4-ZH-2OOH'-3OO_M6			
C	0.246933	0.171147	0.349279	C	-0.08962	-0.59459	0.460364
C	-1.0462	-0.35141	-0.32025	C	0.656403	0.557045	-0.25845

H	-1.00469	-0.21111	-1.40144	H	0.505154	0.502741	-1.33718
C	1.429969	-0.34405	-0.46571	C	-1.45848	-0.85065	-0.17147
H	1.479061	0.197468	-1.41208	H	-1.94083	-1.67158	0.364154
H	1.310111	-1.41512	-0.66063	H	-1.34419	-1.12261	-1.22259
O	2.599755	-0.1127	0.285028	O	-2.21617	0.332042	-0.04097
O	3.692594	-0.43584	-0.55669	O	-3.50986	0.040003	-0.5418
C	-2.30379	0.315092	0.212835	C	2.152672	0.566386	0.026935
H	4.05797	-1.21146	-0.11607	H	-3.56569	0.636777	-1.2969
H	-2.94545	-0.32095	0.845937	H	2.500575	1.387269	0.676894
O	-2.5871	1.451058	-0.03717	O	2.909426	-0.24551	-0.42298
H	-0.92699	2.334373	-0.87668	H	1.820875	-1.78244	-1.10877
O	0.218858	1.585079	0.380741	O	0.673084	-1.78243	0.356325
O	0.009215	2.083938	-0.92965	O	0.903019	-2.08389	-1.01154
C	0.320734	-0.23121	1.81528	C	-0.19685	-0.34154	1.955333
H	-0.58227	0.079075	2.340247	H	0.785295	-0.14635	2.385507
H	0.438658	-1.3087	1.908261	H	-0.85157	0.505037	2.145373
H	1.176949	0.257781	2.27258	H	-0.61246	-1.22798	2.430782
O	-1.12691	-1.76131	-0.05968	O	0.116919	1.804782	0.202434
O	-2.16756	-2.28008	-0.63868	O	0.663337	2.797409	-0.43066
	4-ZH-2OOH'-3OO_M7				4-ZH-2OOH'-3OO_M8		
C	0.30942	0.023099	0.902245	C	0.089227	-0.08298	0.579402
C	0.47589	1.032892	-0.2654	C	-1.35591	-0.18168	0.0336
H	1.192538	1.80095	0.03218	H	-2.0525	-0.01181	0.854802
C	-0.97537	-0.79202	0.766772	C	1.083764	-0.31807	-0.55258
H	-1.80537	-0.23871	1.209518	H	0.97668	0.44181	-1.32614
H	-0.85197	-1.7509	1.273621	H	0.903022	-1.30988	-0.98609
O	-1.24165	-0.9745	-0.61082	O	2.375195	-0.26075	0.001208
O	-2.56144	-1.47276	-0.72037	O	3.280796	-0.34466	-1.08628
C	-0.8317	1.679203	-0.6926	C	-1.66202	-1.49925	-0.6568
H	-2.40322	-2.37978	-1.0078	H	3.744241	-1.1664	-0.88878
H	-1.05365	1.619362	-1.77052	H	-1.72073	-1.44655	-1.75904
O	-1.555	2.228931	0.086371	O	-1.83481	-2.52037	-0.05991
H	1.917402	-1.63453	-0.63002	H	-0.26484	2.69637	0.251542
O	1.464028	-0.79978	0.990588	O	0.270686	1.178087	1.207835
O	1.361945	-1.90533	0.112552	O	0.558757	2.192265	0.262291
C	0.305895	0.782198	2.22142	C	0.268395	-1.07363	1.721661
H	1.294264	1.202726	2.401347	H	-0.45045	-0.86352	2.512206
H	-0.42915	1.58336	2.188373	H	0.118907	-2.09432	1.378352
H	0.066091	0.097666	3.033632	H	1.273631	-0.96409	2.119517
O	1.015934	0.394727	-1.43291	O	-1.59583	0.83396	-0.96109
O	2.312205	0.447169	-1.46605	O	-2.18839	1.877973	-0.47757
	4-ZH-2OOH'-3OO_M9						
C	0.206348	-0.25909	0.836167				
C	0.49223	0.912446	-0.13028				
H	1.354393	1.46882	0.240315				
C	-0.65322	-1.32764	0.162442				
H	-0.98218	-2.05769	0.90413				
H	-0.09886	-1.8276	-0.63129				
O	-1.76127	-0.63062	-0.37355				

O	-2.597	-1.56909	-1.01751	
C	-0.67006	1.881028	-0.32926	
H	-2.35063	-1.46086	-1.94452	
H	-1.16234	1.82202	-1.31316	
O	-0.9918	2.668868	0.508465	
H	2.7634	-0.81385	-0.03459	
O	1.424629	-0.83465	1.289979	
O	2.109713	-1.47526	0.227782	
C	-0.43587	0.244752	2.121033	
H	0.102438	1.101516	2.520823	
H	-1.46743	0.534713	1.939732	
H	-0.41067	-0.56497	2.847631	
O	0.8187	0.42806	-1.45223	
O	2.07394	0.548805	-1.74415	

Reference

1. Teng, A. P.; Crounse, J. D.; Wennberg, P. O. Isoprene Peroxy Radical Dynamics. *J. Am. Chem. Soc.* **2017,** *139*, 5367-5377.