Supporting Information

Computational Investigation of the Formation of Peroxide (ROOR) Accretion Products in the OH- and NO_3 – Initiated Oxidation of α-pinene

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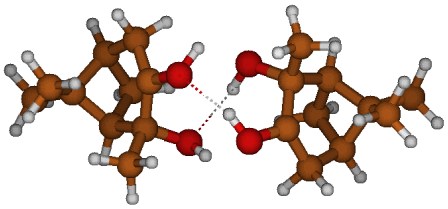
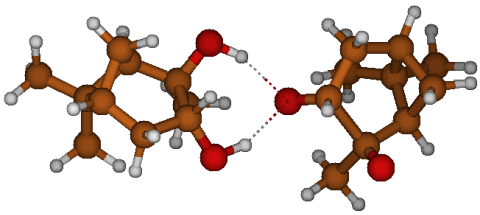
Contents

Section S1. Examples of unwanted reactions occurring in the configurational sampling at the XTB level.

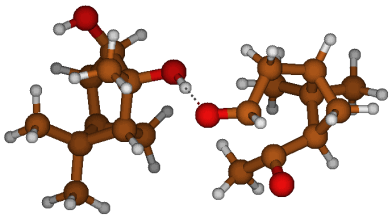
Figure S1. Figure of different unwanted reactions that happened during XTB optimizations. Color coding: brown=C, white=H, red=O.



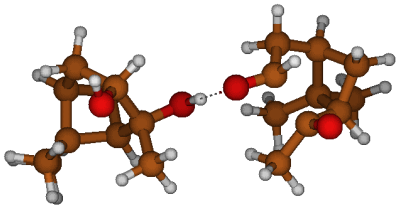
H-shifting to both RO



H-shifting to single RO



H-shift with β-scission



C-C Bond Scission

Section S2. SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for all (RO···OR') clusters (global minimum and one representative local minima conformer). See Section S4 for structures and relative energies of local minima.

Table S1: The SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for α-pinene, (*S*-alkoxy,*R*-hydroxy)$_2$ cluster (global minima).

Transition	SOCME	Energy Gap	k_{ISC} (s^{-1})
$T_1 \rightarrow S_1$	2.9	26.4	1.2×10^{10}
$T_1 \rightarrow S_2$	98.51	3146.3	2.0×10^{5}
$T_1 \rightarrow S_3$	101.41	5150.0	2.3×10^{0}
$T_1 \rightarrow S_4$	1.42	8376.0	5.0×10^{-12}
		Total rate	1.2×10^{10}

Table S2: The SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for α-pinene, (*S*-alkoxy,*R*-hydroxy)$_2$ cluster (local minima).

Transition	SOCME	Energy Gap	k_{ISC} (s^{-1})
$T_1 \rightarrow S_1$	0.2	25.9	5.7×10^{7}
$T_1 \rightarrow S_2$	104.23	3147.0	2.2×10^{5}
$T_1 \rightarrow S_3$	105.71	5149.6	2.6×10^{0}
$T_1 \rightarrow S_4$	0.45	8377.6	4.9×10^{-13}
		Total rate	5.7×10^{7}

Table S3: The SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for α-pinene, (*R*-alkoxy,*S*-hydroxy)$_2$ cluster (global minima).

Transition	SOCME	Energy Gap	k_{ISC} (s^{-1})
$T_1 \rightarrow S_1$	0.17	10.8	4.1×10^{7}
$T_1 \rightarrow S_2$	104.06	2378.0	1.7×10^{7}
$T_1 \rightarrow S_3$	103.98	3788.4	5.6×10^{3}
$T_1 \rightarrow S_4$	1.03	6168.7	7.4×10^{-7}
		Total rate	5.7×10^{7}

Table S4: The SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for α-pinene, (*R*-alkoxy,*S*-hydroxy)$_2$ cluster (local minima).

Transition	SOCME	Energy Gap	k_{ISC} (s^{-1})
$T_1 \rightarrow S_1$	0.03	15.3	1.3×10^{6}
$T_1 \rightarrow S_2$	102.5	3489.3	3.0×10^{4}
$T_1 \rightarrow S_3$	104.96	3500.4	3.0×10^{4}
$T_1 \rightarrow S_4$	0.77	6982.0	4.0×10^{-9}
		Total rate	1.4×10^{6}

Table S5: The SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for α-pinene, (*S*-alkoxy,*S*-hydroxy)$_2$ (global minima)

Transition	SOCME	Energy Gap	k_{ISC} (s^{-1})
$T_1 \rightarrow S_1$	2.5	21.4	9.0×10^{9}
$T_1 \rightarrow S_2$	88.85	1784.0	3.7×10^{8}
$T_1 \rightarrow S_3$	98.36	2237.5	3.4×10^{7}
$T_1 \rightarrow S_4$	1.83	3950.7	7.0×10^{-1}
		Total rate	9.4×10^{9}

Table S6: The SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for α-pinene, (*S*-alkoxy,*S*-hydroxy)$_2$ (local minima)

Transition	SOCME	Energy Gap	k_{ISC} (s^{-1})
$T_1 \rightarrow S_1$	0.3	20.9	1.3×10^{8}
$T_1 \rightarrow S_2$	104.29	1786.8	5.0×10^{8}
$T_1 \rightarrow S_3$	105.64	2238.8	4.0×10^{7}
$T_1 \rightarrow S_4$	3.03	3955.2	1.9×10^{0}
		Total rate	6.7×10^{8}

Table S7: The SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for α-pinene, (*R*-alkoxy,*R*-hydroxy)$_2$ cluster (global minima)

Transition	SOCME	Energy Gap	k_{ISC} (s^{-1})
$T_1 \rightarrow S_1$	3.06	15.0	1.5×10^{10}
$T_1 \rightarrow S_2$	67.86	1860.0	1.4×10^{8}
$T_1 \rightarrow S_3$	24.7	2707.2	1.5×10^{5}
$T_1 \rightarrow S_4$	69.54	4622.5	2.2×10^{1}
		Total rate	1.5×10^{10}

Table S8: The SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for α-pinene, (*R*-alkoxy,*R*-hydroxy)$_2$ cluster (local minima)

Transition	SOCME	Energy Gap	k_{ISC} (s^{-1})
$T_1 \rightarrow S_1$	0.44	14.0	2.9×10^{8}
$T_1 \rightarrow S_2$	105.42	1857.8	3.4×10^{8}
$T_1 \rightarrow S_3$	104.7	2719.7	2.5×10^{6}
$T_1 \rightarrow S_4$	2.84	4590.0	4.4×10^{-2}
		Total rate	6.3×10^{8}

Table S9: The SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for α-pinene, (*R*-alkoxy,*S*-nitroxy)$_2$ cluster (global minima).

Transition	SOCME	Energy Gap	k_{ISC} (s^{-1})
$T_1 \rightarrow S_1$	0.0	163.8	0
$T_1 \rightarrow S_2$	105.7	2800.4	1.1×10^{6}
$T_1 \rightarrow S_3$	105.4	3000.5	5.0×10^{5}
$T_1 \rightarrow S_4$	0.6	6350.0	3.4×10^{-9}
		Total rate	1.0×10^{6}

Table S10: The SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for α-pinene, (*R*-alkoxy,*S*-nitroxy)$_2$ cluster (local minima).

Transition	SOCME	Energy Gap	k_{ISC} (s^{-1})
$T_1 \rightarrow S_1$	3.81	78.4	1.6×10^{10}
$T_1 \rightarrow S_2$	69.47	2165.6	2.6×10^{7}
$T_1 \rightarrow S_3$	133.92	2411.1	2.4×10^{7}
$T_1 \rightarrow S_4$	3.47	4587.4	6.7×10^{-02}
		Total rate	1.6×10^{10}

Table S11: The SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for α-pinene, (*R*-alkoxy,*R*-nitroxy)$_2$ cluster (global minima).

Transition	SOCME	Energy Gap	k_{ISC} (s^{-1})
$T_1 \rightarrow S_1$	3.84	78.0	1.6×10^{10}
$T_1 \rightarrow S_2$	70.27	2161.1	2.6×10^{6}
$T_1 \rightarrow S_3$	133.49	2405.6	3.0×10^{7}
$T_1 \rightarrow S_4$	3.49	4575.0	3.7×10^{-2}
		Total rate	1.6×10^{10}

Table S12: The SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for α-pinene, (*R*-alkoxy,*R*-nitroxy)$_2$ cluster (local minima).

Transition	SOC	Energy Gap	k_{ISC} (s^{-1})
$T_1 \rightarrow S_1$	0.09	13.8	1.2×10^{7}
$T_1 \rightarrow S_2$	105.38	2730.3	2.4×10^{6}
$T_1 \rightarrow S_3$	105.83	2864.1	5.6×10^{5}
$T_1 \rightarrow S_4$	0.58	5576.3	1.1×10^{-6}
		Total rate	1.5×10^{7}

Table S13 The SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for α-pinene, (*S*-alkoxy,*S*-nitroxy)$_2$ cluster (global minima).

Transition	SOCME	Energy Gap	k_{ISC} (s^{-1})
$T_1 \rightarrow S_1$	0.17	-2072.0	4.6×10^{7}
$T_1 \rightarrow S_2$	85.15	1000.4	3.1×10^{10}
$T_1 \rightarrow S_3$	123.18	1200.3	2.0×10^{10}
$T_1 \rightarrow S_4$	1.23	4000.5	0.2×10^{-3}
		Total rate	5.7×10^{10}

Table S14: The SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for α-pinene, (*S*-alkoxy,*S*-nitroxy)$_2$ cluster (local minima).

Transition	SOC	Energy Gap	k_{ISC} (s^{-1})
$T_1 \rightarrow S_1$	0.09	2.0	1.3×10^{7}
$T_1 \rightarrow S_2$	19.44	3149.0	7.5×10^{3}
$T_1 \rightarrow S_3$	148.56	3173.7	3.8×10^{5}
$T_1 \rightarrow S_4$	0.34	6420.5	1.9×10^{-8}
		Total rate	1.3×10^{7}

Table S15: The SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for α-pinene, (*S*-alkoxy,*R*-nitroxy)$_2$ cluster (global minima).

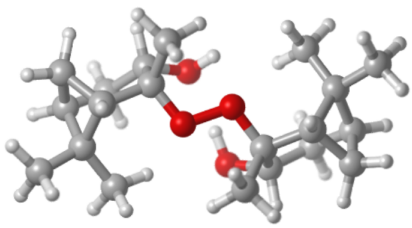
Transition	SOCME	Energy Gap	k_{ISC} (s^{-1})
$T_1 \rightarrow S_1$	0.4	2.0	2.1×10^{8}
$T_1 \rightarrow S_2$	81.0	3050.6	2.3×10^{5}
$T_1 \rightarrow S_3$	73.1	3832.6	2.2×10^{3}
$T_1 \rightarrow S_4$	1.1	6886.4	1.3×10^{-8}
		Total rate	2.1×10^{8}

Table S16: The SOCME (cm^{-1}), Energy Gap (cm^{-1}), and k_{ISC} (s^{-1}) computed for α-pinene, (*S*-alkoxy,*R*-nitroxy)$_2$ cluster (local minima).

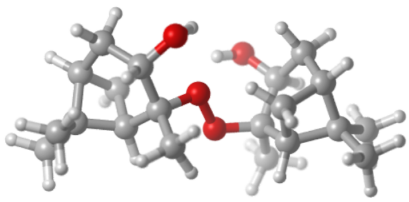
Transition	SOCME	Energy Gap	k_{ISC} (s^{-1})
$T_1 \rightarrow S_1$	0	5.1	0.0×10^{0}
$T_1 \rightarrow S_2$	105.47	3254.1	1.2×10^{5}
$T_1 \rightarrow S_3$	105.2	4016.5	1.6×10^{3}
$T_1 \rightarrow S_4$	0.31	7268.6	1.3×10^{-10}
		Total rate	1.2×10^{5}

Section S3. Results of optimization of the (RO···OR') complexes on the singlet surface ^{1}(RO···OR').

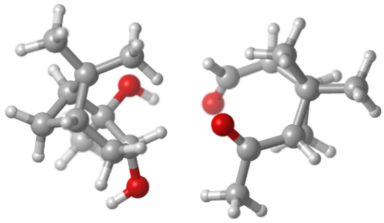
Figure S2. Results of optimization of the (RO···OR') complexes on the singlet surface ^{1}(RO···OR'). Color coding: gray=C, white=H, red=O, blue=N.



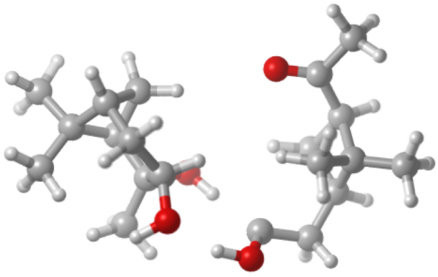
(*S*-alkoxy,*R*-hydroxy)$_2$



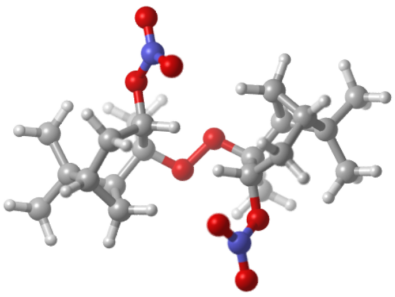
(*R*-alkoxy,*S*-hydroxy)$_2$



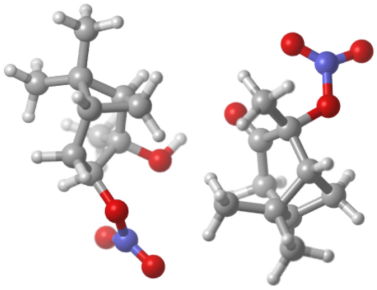
(*S*-alkoxy,*S*-hydroxy)$_2$



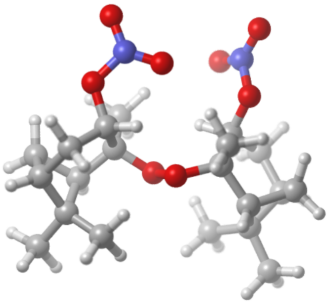
(*R*-alkoxy,*R*-hydroxy)$_2$



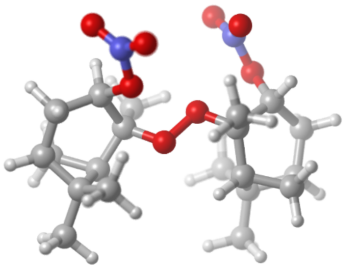
(R-alkoxy,*R*-nitroxy)$_2$



(*R*-alkoxy,*S*-nitroxy)$_2$



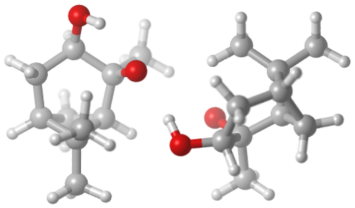
(*S*-alkoxy,*S*-nitroxy)$_2$



(*S*-alkoxy,*R*-nitroxy)$_2$

Section S4. Optimized structures of the representative local minima conformer used for calculating the ISC rates in section S2 (even-numbered tables).

Figure S3. Optimized structures and relative energies of the representative local minima conformers used to calculate the ISC rate in section S2. Color coding: gray=C, white=H, red=O, blue=N.



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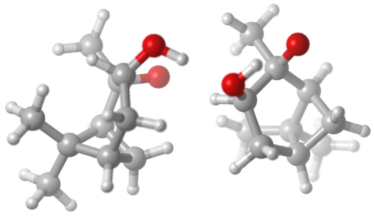
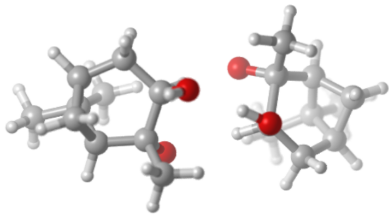
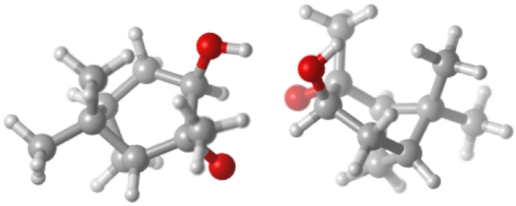
(*S*-alkoxy,*R*-hydroxy)$_2$
O-O distance = 3.45Å
[a]ΔE = 0.084 kcal/mol



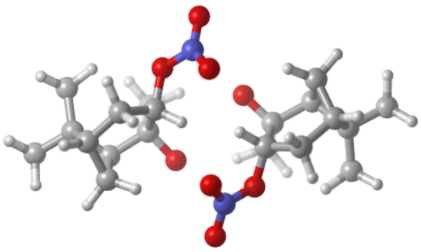
(*R*-alkoxy,*S*-hydroxy)$_2$
O-O distance = 4.87 Å
[a]ΔE = 1.862 kcal/mol



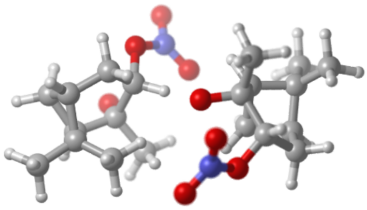
(*S*-alkoxy,*S*-hydroxy)$_2$
O-O distance = 3.6 Å
[a]ΔE = 1.021 kcal/ol



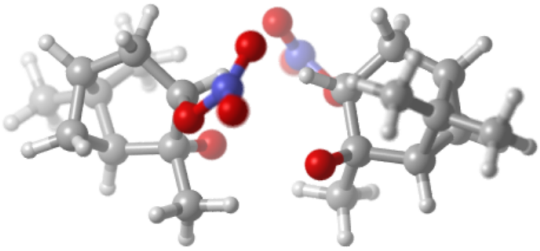
(*R*-alkoxy,*R*-hydroxy)$_2$
O-O distance = 3.5 Å
[a]ΔE = 0.013 kcal/mol



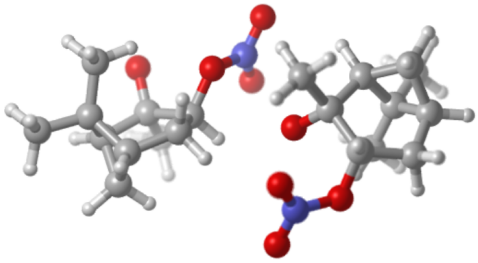
(R-alkoxy,*R*-nitroxy)$_2$
O-O distance = 3.2 Å
[a]ΔE= 0.0002 kcal/mol



(*R*-alkoxy,*S*-nitroxy)$_2$
O-O distance = 5.48 Å
[a]ΔE= 0.388 kcal/mol



(*S*-alkoxy,*S*-nitroxy)$_2$
O-O distance = 3.97 Å
[a]ΔE= 0.012 kcal/mol



(*S*-alkoxy,*R*-nitroxy)$_2$
O-O distance = 5.21 Å
[a]ΔE= 0.182 kcal/mol

[a]ΔE= Difference in electronic energies relative to the global minima conformer in kcal/mol, at the ωB97X-D/6-31++G** level.