Supporting Information for

Unimolecular Reactions Following Indoor and Outdoor Limonene Ozonolysis

Jing Chen,[†] Kristian H. Møller,[†] Paul O. Wennberg,[‡,¶] Henrik G. Kjaergaard*,[†]

[†]*Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100, Copenhagen Ø, Denmark*
[‡]*Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, United States*
[¶] *Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California 91125, United States*

Email: hgk@chem.ku.dk
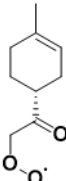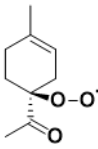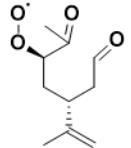Phone: +45-35320334   Fax: +45-35320322

Contents

Output files from all calculations including the B3LYP/6-31+G(d) and ωB97X-D/aug-cc-pVTZ xyz-geometries are available online at:

https://sid.erda.dk/public/archives/05c0c3962a7d8c3f01977adb0e694bd1/published-archive.html
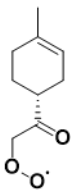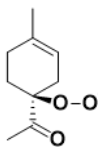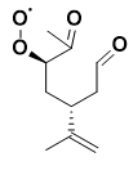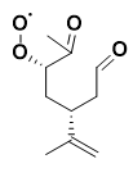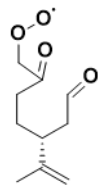
S1. Single-point energy cut-off test

Due to the large number of conformers for the ring-opened peroxy radicals (typically around 1000 to 4000 conformers for each reactant and TS), a B3LYP single point energy calculation was carried out for the conformers generated by Spartan and only the conformers within a certain energy cut-off were subsequently optimized at the B3LYP level. To find a suitable value for the cut-off, for 17 of the studied reactions, all conformers were optimized at the B3LYP level. For each reactant and transition state, the initial single-point energies and optimized energies were compared to find the single-point energy cut-off needed to retain all the relevant conformers. The data from these tests are given in Table S 1. The relevant conformers are defined as those within 2 kcal/mol in relative electronic energy following the B3LYP optimization. Based on the results in Table S 1, single-point cut-off values of 5 kcal/mol and 200 kcal/mol were chosen for reactants and TSs, respectively.

Table S 1. "Cut-off energy" is the single-point energy cut-off required to retain all relevant conformers. The highest necessary cut-off for any reactant and TS is highlighted in bold. Also the number of relevant conformers and the total number of conformers is given. For each peroxy radical, values for the reactant and all the studied transition states are given.

Radical	Type	Cut-off energy [kcal/mol]	# Relevant conf.	Total # conf.
L1	Reactant	**4.7**	29	40
	1,5-α-carbonyl	96.5	11	23
	1,6-allylic	0.9	2	22
	1,6-alkyl	18.5	3	18
	1,7-allylic	48.7	3	19
	8-cyclization	2.5	3	16
	1,9-allylic	39.2	3	11
L2	Reactant	1.4	4	15
	1,4-allylic	59.1	5	12
	1,4-alkyl	6.9	4	12
	1,5-double bond	0.0	1	34
	1,5-allylic	175.4	6	7
	1,5-α-carbonyl	163.1	9	11
	1,7-allylic	67.7	6	22
	5-cyclization	35.3	6	12
	6-cyclization	2.6	3	9
(R,R) - L3	Reactant	4.6	129	730
	1,6-allylic	90.4	109	398
	1,7-aldehydic	129.4	149	480
	7-cyclization	**198.2**	315	533

S2. Limonene ozonolysis peroxy radical rate coefficients and related data

Table S 2. The unimolecular reaction rate coefficients for the peroxy radicals L1-L5 calculated at the B3LYP/6-31+G(d), ωB97X-D/aug-cc-pVTZ and CCSD(T)-F12a/VDZ-F12 levels using MC-TST. [1] Only the reactions with a B3LYP level rate coefficient greater than 1×10^{-3} s^{-1} are calculated at the ωB97X-D and CCSD(T)-F12a levels.

Radical	Reaction type	k [s^{-1}]		
		B3LYP	ωB97X-D	CCSD(T)-F12a
L1	1,5- α-carbonyl	3.69×10^{-2}	6.81×10^{-2}	1.44×10^{-1}
	1,6-allylic	1.54×10^{1}	4.21	3.60
	1,6-alkyl	9.83×10^{-3}	4.47×10^{-3}	1.68×10^{-2}
	1,7-allylic	8.70	4.49	1.21
	1,7-double bond	5.95×10^{-15}	-	-
	1,9-allylic	3.87×10^{-6}	-	-
	7-cyclization	6.57×10^{1}	4.71	4.59
	8-cyclization	2.28×10^{-2}	3.31×10^{-3}	1.15×10^{-2}
L2	1,4-allylic	1.22×10^{-2}	2.12×10^{-3}	1.11×10^{-3}
	1,4-alkyl	1.35×10^{-8}	-	-
	1,5-double bond	2.78×10^{-19}	-	-
	1,5-allylic	1.11×10^{-1}	1.76×10^{-2}	4.55×10^{-2}
	1,5-α-carbonyl	4.90×10^{-6}	-	-
	1,7-allylic	2.97×10^{-12}	-	-
	5-cyclization	6.03×10^{-1}	2.26×10^{-3}	7.58×10^{-3}
	6-cyclization	3.17×10^{-3}	6.29×10^{-5}	2.10×10^{-3}
(R,R) - L3	1,5-α-carbonyl	3.56×10^{-6}	-	-
	1,5-allylic	5.58×10^{-1}	9.37×10^{-2}	2.68×10^{-1}
	1,6-α-carbonyl	4.66×10^{-1}	5.73×10^{-2}	7.20×10^{-2}
	1,7-aldehydic	4.25×10^{2}	2.53×10^{1}	4.16
	1,7-allylic	2.99	1.41	7.88×10^{-1}
	6-cyclization	1.38×10^{1}	4.04×10^{-1}	3.86
	7-cyclization	2.37×10^{1}	4.37×10^{-1}	6.61×10^{-1}
(R,S) - L3	1,5-α-carbonyl	2.84×10^{-6}	-	-
	1,5-allylic	2.24	1.65×10^{-1}	5.66×10^{-1}
	1,6-α-carbonyl	5.88×10^{-2}	1.22×10^{-2}	1.80×10^{-2}
	1,7-aldehydic	2.79×10^{2}	1.27×10^{1}	6.69
	1,7-allylic	2.46×10^{1}	3.66	4.35
	6-cyclization	6.27×10^{1}	4.05×10^{-1}	2.98
	7-cyclization	1.15×10^{2}	5.91×10^{-1}	3.23×10^{-1}
L4	1,5-α-carbonyl	4.37×10^{-4}	-	-
	1,7-allylic	6.44×10^{-1}	6.96×10^{-1}	6.63×10^{-1}
	1,8-α-carbonyl	5.13×10^{-3}	2.26×10^{-3}	1.54×10^{-3}
	1,9-aldehydic	2.09×10^{1}	9.13	4.50×10^{-1}
	1,9-allylic	1.65×10^{-1}	7.85×10^{-2}	3.02×10^{-2}
	8-cyclization	1.61×10^{-5}	-	-
	9-cyclization	1.32	5.72×10^{-2}	3.50×10^{-2}
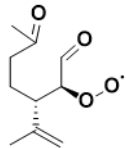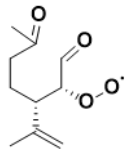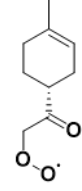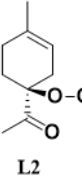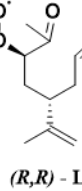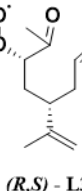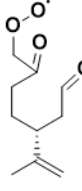
(S,S) - L5	1,4-allylic	3.48×10^{-5}	-	-
	1,4-aldehydic	1.50×10^{-1}	2.17×10^{-1}	0.60
	1,5-alkyl	3.31×10^{-4}	2.58×10^{-5}	3.48×10^{-4}
	1,6-allylic	1.58×10^{-1}	3.53×10^{-2}	3.28×10^{-2}
	1,6-α-carbonyl	1.98×10^{-2}	1.26×10^{-2}	1.18×10^{-2}
	1,8-α-carbonyl	1.01×10^{-6}	-	-
	5-cyclization	2.69×10^{3}	3.86×10^{1}	2.27×10^{2}
	6-cyclization	6.36×10^{2}	3.66	1.99×10^{1}
(R,S) - L5	1,4-allylic	1.36×10^{-5}	-	-
	1,4-aldehydic	4.63×10^{-1}	2.07×10^{-1}	4.91×10^{-1}
	1,5-alkyl	6.16×10^{-3}	1.50×10^{-3}	9.28×10^{-3}
	1,6-allylic	1.38×10^{-1}	3.78×10^{-2}	2.78×10^{-2}
	1,6-α-carbonyl	1.07×10^{-1}	4.87×10^{-2}	6.43×10^{-2}
	1,8-α-carbonyl	6.42×10^{-6}	-	-
	5-cyclization	4.86×10^{2}	1.56×10^{1}	4.47×10^{1}
	6-cyclization	5.38×10^{1}	8.97×10^{-1}	1.35

Table S 3. Calculated B3LYP level reaction rate coefficients (k), reaction energy barriers (E_a), tunneling factors (κ), imaginary frequencies (ṽ) and ratios of summed partition functions exponentially weighted by relative conformer energy (Q_{TS}/Q_R) for all seven peroxy radicals (L1-L5). A symmetric reaction barrier (E_{TS}-E_R = E_{TS}-E_P) was assumed when calculating the B3LYP level tunneling factors (see method section in main text).

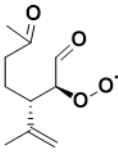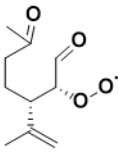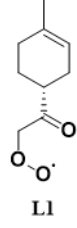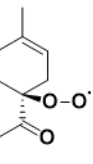| Radical	Reaction type	k [s^{-1}]	E_a [kcal/mol]	κ	ṽ [cm^{-1}]	Q_{TS}/Q_R
L1	1,5-α-carbonyl	3.7×10^{-2}	20.7	325.2	1842.2	0.0271
	1,6-allylic	1.5×10^{1}	16.1	140.9	1832.5	0.0113
	1,6-alkyl	9.8×10^{-3}	20.1	69.1	1636.4	0.0126
	1,7-allylic	8.7	16.2	65.9	1698.9	0.0154
	1,7-double bond	6.0×10^{-15}	38.4	1140.1	1731.0	0.0115
	1,9-allylic	3.9×10^{-6}	25.1	318.0	1758.7	0.0052
	7-cyclization	6.6×10^{1}	12.3	1.2	443.4	0.0090
	8-cyclization	2.3×10^{-2}	16.8	1.2	427.4	0.0060
L2	1,4-allylic	1.2×10^{-2}	23.4	1287.5	1951.3	0.2147
	1,4-alkyl	1.4×10^{-8}	34.0	37169.4	2051.4	0.5065
	1,5-double bond	2.8×10^{-19}	51.5	4194702.5	2139.9	0.5680
	1,5-allylic	1.1×10^{-1}	21.2	350.2	1841.1	0.1745
	1,5-α-carbonyl	4.9×10^{-6}	28.1	2504.7	1922.8	0.1308
	1,7-allylic	3.0×10^{-12}	36.7	6887.1	1881.7	0.0570
	5-cyclization	6.0×10^{-1}	17.0	1.3	526.4	0.2096
	6-cyclization	3.2×10^{-3}	19.7	1.3	489.6	0.1032
(R,R) - L3	1,5-α-carbonyl	3.6×10^{-6}	28.5	2626.8	1921.4	0.1593
	1,5-allylic	5.6×10^{-1}	18.3	39.2	1572.0	0.0620
	1,6-α-carbonyl	4.7×10^{-1}	19.1	220.9	1824.2	0.0359
	1,7-aldehydic	4.3×10^{2}	14.0	31.7	1606.6	0.0384
	1,7-allylic	3.0	17.2	88.8	1727.3	0.0221
	6-cyclization	1.4×10^{1}	13.2	1.2	443.6	0.0085
	7-cyclization	2.4×10^{1}	14.1	1.2	439.1	0.0642
(R,S) - L3	1,5-α-carbonyl	2.8×10^{-6}	28.0	2390.5	1920.2	0.0672
	1,5-allylic	2.2	17.9	91.6	1717.0	0.0547
	1,6-α-carbonyl	5.9×10^{-2}	19.1	214.4	1819.6	0.0048
	1,7-aldehydic	2.8×10^{2}	12.9	29.0	1612.2	0.0042
	1,7-allylic	2.5×10^{1}	14.8	72.6	1749.8	0.0039
	6-cyclization	6.3×10^{1}	12.0	1.2	461.7	0.0050
	7-cyclization	1.1×10^{2}	12.7	1.2	451.8	0.0285
L4	1,5-α-carbonyl	4.4×10^{-4}	24.4	1193.1	1981.9	0.0486
	1,7-allylic	6.4×10^{-1}	17.2	50.5	1633.0	0.0080
	1,8-α-carbonyl	5.1×10^{-3}	20.7	373.0	1859.5	0.0035
	1,9-aldehydic	2.1×10^{1}	14.4	42.4	1656.0	0.0029
	1,9-allylic	1.7×10^{-1}	19.0	299.3	1872.6	0.0070
	8-cyclization	1.6×10^{-5}	19.8	1.2	447.3	0.0007
	9-cyclization	1.3	13.7	1.3	486.9	0.0017
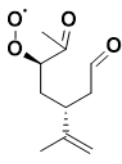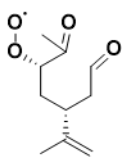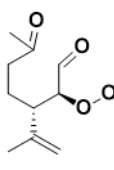
(S,S) - L5	1,4-allylic	3.5×10^{-5}	26.8	5440.6	2026.4	0.0491
	1,4-aldehydic	1.5×10^{-1}	20.7	1809.9	255.2	0.1383
	1,5-alkyl	3.3×10^{-4}	23.5	93.7	1634.5	0.0893
	1,6-allylic	1.6×10^{-1}	19.8	454.5	1910.9	0.0170
	1,6-α-carbonyl	2.0×10^{-2}	20.4	420.7	1833.9	0.0068
	1,8-α-carbonyl	1.0×10^{-6}	25.7	250.2	1723.3	0.0048
	5-cyclization	2.7×10^{3}	11.2	1.2	445.7	0.0577
	6-cyclization	6.4×10^{2}	11.8	1.3	500.5	0.0364
(R,S) - L5	1,4-allylic	1.4×10^{-5}	27.8	6059.5	2015.3	0.0863
	1,4-aldehydic	4.6×10^{-1}	20.9	306.8	1830.2	0.5001
	1,5-alkyl	6.2×10^{-3}	21.7	85.3	1644.3	0.0952
	1,6-allylic	1.4×10^{-1}	20.0	479.0	1910.7	0.0226
	1,6-α-carbonyl	1.1×10^{-1}	20.1	255.7	1822.0	0.0386
	1,8-α-carbonyl	6.4×10^{-6}	24.5	233.5	1733.3	0.0037
	5-cyclization	4.9×10^{2}	11.7	1.2	460.2	0.0221
	6-cyclization	5.4×10^{1}	13.5	1.3	510.5	0.0516

Table S 4. Calculated ωB97X-D level reaction rate coefficients (k, s⁻¹), reaction energy barriers (Eₐ, kcal/mol), tunneling factors (κ), imaginary frequencies (ṽ, cm⁻¹) and ratios of summed partition functions exponentially weighted by relative conformer energy (Q_TS/Q_R), as well as the calculated CCSD(T)-F12a level reaction rate coefficients (k, s⁻¹), reaction energy barriers (Eₐ, kcal/mol) and tunneling factors (κ). For four of the allylic H-shifts from the methyl group (indicated by a dash), the IRC end points at the CCSD(T)-F12a level had convergence issues and the ωB97X-D level tunneling factors were used instead.

Radical	type	ωB97X-D					CCSD(T)-F12a		
		k	E_a	κ	$\tilde{v}$	Q_{TS}/Q_R	k	E_a	κ
L1	1,5-α-carbonyl	6.8×10^{-2}	21.2	679.5	1993.7	0.0549	1.4×10^{-1}	20.8	718.2
	1,6-allylic	4.2	18.1	578.0	2003.3	0.0231	3.6	18.3	639.9
	1,6-alkyl	4.5×10^{-3}	20.4	26.4	1940.9	0.0257	1.7×10^{-2}	20.0	50.6
	1,7-allylic	4.5	17.1	79.4	1800.8	0.0308	1.2	18.0	106.6
	7-cyclization	4.7	14.5	1.3	519.9	0.0233	4.6	14.5	1.3
	8-cyclization	3.3×10^{-3}	18.6	1.3	522.5	0.0164	1.1×10^{-2}	17.8	1.3
L2	1,4-allylic	2.1×10^{-3}	26.0	16073.9	2167.2	0.2301	1.1×10^{-3}	26.6	25272.5
	1,5-allylic	1.8×10^{-2}	22.7	688.2	1979.0	0.1834	4.5×10^{-2}	22.2	801.4
	5-cyclization	2.3×10^{-3}	20.3	1.5	-633.6	0.1957	7.6×10^{-3}	19.8	1.5
	6-cyclization	6.3×10^{-5}	22.6	1.4	-585.6	0.2635	2.1×10^{-3}	20.5	1.4
(R,R) - L3	1,5-allylic	9.4×10^{-2}	19.1	52.6	1702.0	0.0300	2.7×10^{-1}	18.5	76.1
	1,6-α-carbonyl	5.7×10^{-2}	21.5	826.7	2065.9	0.0634	7.2×10^{-2}	21.6	1155.5
	1,7-aldehydic	2.5×10^{1}	15.3	22.2	1643.4	0.0326	4.2	16.6	30.5
	1,7-allylic	1.4	17.9	131.9	1906.4	0.0236	7.9×10^{-1}	18.3	-
	6-cyclization	4.0×10^{-1}	15.4	1.4	559.0	0.0092	3.9	14.1	1.4
	7-cyclization	4.4×10^{-1}	16.7	1.3	515.8	0.0903	6.6×10^{-1}	16.4	1.3
(R,S) - L3	1,5-allylic	1.7×10^{-1}	19.7	78.6	1727.3	0.0945	5.7×10^{-1}	19.0	78.3
	1,6-α-carbonyl	1.2×10^{-2}	21.1	245.9	2054.2	0.0249	1.8×10^{-2}	21.1	339.6
	1,7-aldehydic	1.3×10^{1}	15.6	28.5	1638.8	0.0201	6.7	15.7	36.4
	1,7-allylic	3.7	17.0	170.1	1935.5	0.0108	4.4	16.9	-
	6-cyclization	4.0×10^{-1}	15.7	1.4	579.3	0.0138	3.0	15.1	1.4
	7-cyclization	5.9×10^{-1}	16.2	1.4	542.7	0.0516	3.2×10^{-1}	16.5	1.4

 L4	1,7-allylic	7.0×10^{-1}	18.1	158.3	1851.8	0.0131	6.6×10^{-1}	18.2	175.0
	1,8-α-carbonyl	2.3×10^{-3}	21.3	481.9	2114.3	0.0032	1.5×10^{-3}	21.9	834.7
	1,9-aldehydic	9.1	14.9	35.5	1750.2	0.0033	4.5×10^{-1}	17.0	61.4
	1,9-allylic	7.9×10^{-2}	19.6	674.0	2086.8	0.0045	3.0×10^{-2}	20.2	674.0
	9-cyclization	5.7×10^{-2}	15.9	1.5	601.3	0.0029	3.5×10^{-2}	16.2	1.46
 (S,S) - L5	1,4-aldehydic	3.4×10^{-1}	20.5	158.7	1813.4	0.3323	0.6	20.0	209.4
	1,5-alkyl	2.6×10^{-5}	24.6	35.0	1815.7	0.1293	3.5×10^{-4}	11.7	42.4
	1,6-allylic	3.5×10^{-2}	21.1	596.0	2063.8	0.0263	3.3×10^{-2}	21.1	-
	1,6-α-carbonyl	1.3×10^{-2}	21.6	773.7	2052.7	0.0171	1.2×10^{-2}	21.8	1107.9
	5-cyclization	3.9×10^{1}	13.9	1.4	550.1	0.0683	2.3×10^{2}	12.8	1.4
	6-cyclization	3.7	15.1	1.4	578.9	0.0293	2.0×10^{1}	14.1	1.4
 (R,S) - L5	1,4-aldehydic	2.1×10^{-1}	20.6	133.4	1797.8	0.3112	4.9×10^{-1}	20.2	173.4
	1,5-alkyl	1.5×10^{-3}	21.8	25.9	1804.8	0.0937	9.3×10^{-3}	21.0	39.3
	1,6-allylic	7.0×10^{-2}	21.0	1105.4	2063.8	0.0254	2.8×10^{-2}	21.2	-
	1,6-α-carbonyl	4.9×10^{-2}	21.1	438.9	2039.4	0.0537	6.4×10^{-2}	21.1	608.3
	5-cyclization	1.6×10^{1}	13.9	1.4	587.5	0.0273	4.5×10^{1}	13.3	1.4
	6-cyclization	9.0×10^{-1}	16.3	1.4	570.6	0.0848	1.4	16.0	1.4

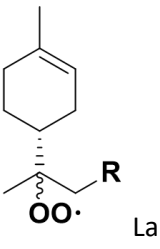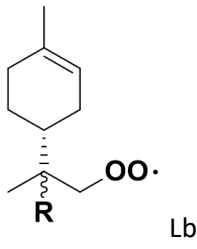## S3. Structure-activity-relationship results

Table S 5. Calculated H-shift reaction rate coefficients for the O_3 initiated peroxy radicals L1-L5 for limonene compared to the predictions from the available structure-activity-relationship (SAR)[2]. Reactions for L1 and L2 are shown in gray since the SAR does not include effect of rings but L1 and L2 have six-membered rings in their structures. The SAR is only available for the 1,4-1,7 H-shifts.

Radical	Reaction type	k [s^{-1}]		$k_{calc.}/k_{SAR}$
		Calculated	SAR[a]	
L1	1,5-α-carbonyl	1.4×10^{-1}	7.70×10^{-3}	18.80
	1,6-allylic	3.6	2.04	1.76
	1,6-alkyl	1.7×10^{-2}	8.84×10^{-4}	19.03
	1,7-allylic	1.2	8.22	0.15
L2	1,4-allylic	1.1×10^{-3}	2.55×10^{-5}	43.43
	1,5-allylic	4.5×10^{-2}	4.60×10^{-5}	988.08
(R,R)-L3	1,5-allylic	3.8×10^{-1}	1.87	0.21
	1,6-α-carbonyl	7.2×10^{-2}	7.83×10^{-3}	9.20
	1,7-aldehydic	4.2	1.71×10^{-1}	24.34
	1,7-allylic	7.9×10^{-1}	3.72×10^{-1}	2.12
(R,S)-L3	1,5-allylic	5.7×10^{-1}	1.87	0.30
	1,6-α-carbonyl	1.8×10^{-2}	7.83×10^{-3}	2.30
	1,7-aldehydic	6.7	1.71×10^{-1}	39.18
	1,7-allylic	4.4	3.72×10^{-1}	11.70
L4	1,7-allylic	6.6×10^{-1}	2.55×10^{-2}	26.01
	1,8-α-carbonyl	1.5×10^{-3}	-	-
	1,9-aldehydic	4.5×10^{-1}	-	-
	1,9-allylic	3.0×10^{-2}	-	-
(S,S)-L5	1,4-aldehydic	0.6	6.64×10^{-2}	1.1
	1,5-alkyl	3.5×10^{-4}	1.23×10^{-3}	0.28
	1,6-allylic	3.3×10^{-2}	1.55×10^{-2}	2.11
	1,6-α-carbonyl	1.2×10^{-2}	7.83×10^{-3}	1.51
(R,S)-L5	1,4-aldehydic	4.9×10^{-1}	6.64×10^{-2}	7.39
	1,5-alkyl	9.3×10^{-3}	1.23×10^{-3}	7.55
	1,6-allylic	2.8×10^{-2}	1.55×10^{-2}	1.81
	1,6-α-carbonyl	6.4×10^{-2}	7.83×10^{-3}	8.22

a.   Calculated using the SAR in ref. [2]

S4. Comparison of OH, NO₃ and Cl peroxy radicals

Table S 6. B3LYP reaction rate coefficients (k), energy barriers (E$_a$), tunneling factors (κ) and ratios of summed partition functions exponentially weighted by relative conformer energy (Q$_{TS}$/Q$_R$) of the OH, NO$_3$ and Cl initiated peroxy radicals (La and Lb). The functional group (R) can be either OH, NO$_3$ or Cl.

	Radical	La			Lb		
	Reaction type	6-Cyclization			1,6-allylic H-shift		
	Stereo	*(R,R)*	*(R,S)*	*(R,R)/(R,S)*	*(R,R)*	*(R,S)*	*(R,R)/(R,S)*
R = OH	k [s^{-1}]	1.9×10^1	3.4	5.59	3.3×10^2	1.0×10^3	0.33
	E$_a$ [kcal/mol]	13.9	15.4	0.90	14.2	13.2	1.08
	Q$_{TS}$/Q$_R$	3.2×10^{-2}	8.3×10^{-1}	0.04	2.4×10^{-2}	2.2×10^{-2}	1.09
	κ	1.2	1.3	0.92	55.1	32.9	1.67
R = NO₃	k [s^{-1}]	3.0×10^2	3.2×10^1	9.34	2.9×10^3	1.3×10^4	0.22
	E$_a$ [kcal/mol]	11.9	13.6	0.87	12.0	11.9	1.02
	Q$_{TS}$/Q$_R$	2.0×10^{-2}	3.8×10^{-2}	0.51	9.7×10^{-3}	3.2×10^{-2}	0.31
	κ	1.2	1.2	1.00	33.0	33.4	0.99
R = Cl	k [s^{-1}]	2.8×10^2	3.2×10^1	8.54	2.5×10^3	3.0×10^2	8.37
	E$_a$ [kcal/mol]	12.0	13.6	0.88	12.7	13.9	0.91
	Q$_{TS}$/Q$_R$	2.2×10^{-2}	3.6×10^{-2}	0.60	1.7×10^{-2}	1.6×10^{-2}	1.06
	κ	1.2	1.3	0.92	43.7	44.9	0.97
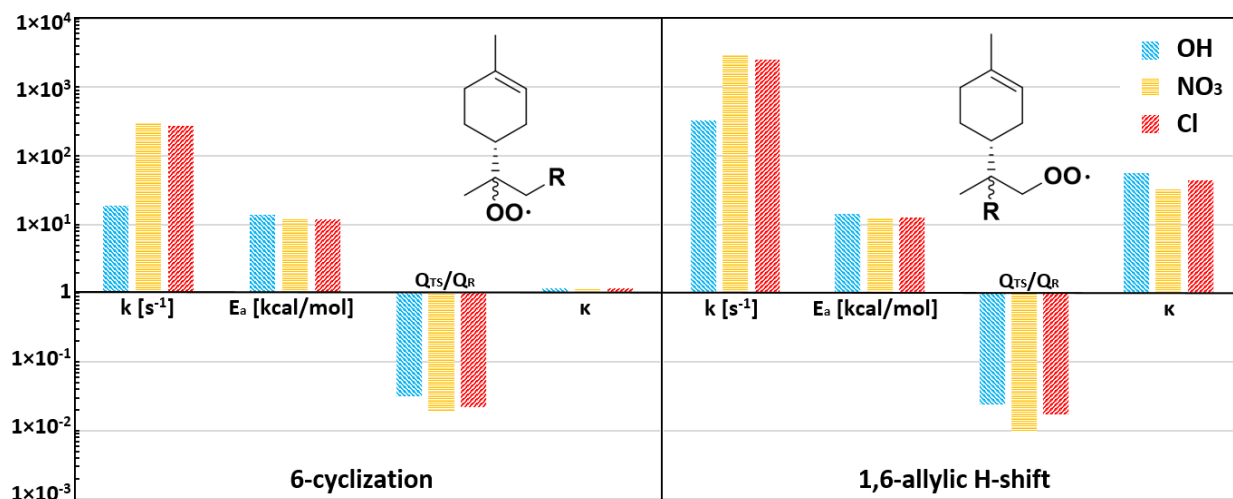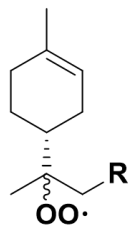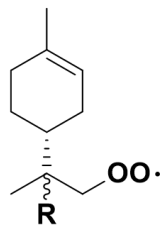
Figure S 1. Comparison of the unimolecular reaction rate coefficients (k), reaction energy barriers (E_a), ratios of summed partition functions exponentially weighted by relative conformer energy (Q_{TS}/Q_R) and tunneling factors (κ) between OH, NO_3 and Cl peroxy radical (La and Lb) calculated at the B3LYP level. The functional group R can be either OH, NO_3 or Cl. Only the results for the (R,R) stereoisomers are shown here. The corresponding values for the (R,S) stereoisomers can be found in Table S 6.

.

Table S 7. ωB97X-D reaction rate coefficients (k), energy barriers (E_a), tunneling factors (κ) and and ratios of summed partition functions exponentially weighted by relative conformer energy (Q_{TS}/Q_R) of the OH, NO$_3$ and Cl initiated peroxy radicals (La and Lb). The functional group (R) can be either OH, NO$_3$ or Cl.

	Radical	La			Lb		
	Reaction type	6-Cyclization			1,6 Allylic H-shift		
	Stereo	*(R,R)*	*(R,S)*	*(R,R)/(R,S)*	*(R,R)*	*(R,S)*	*(R,R)/(R,S)*
R = OH	k [s^{-1}]	7.9×10^{-1}	2.2×10^{-1}	3.59	6.3×10^{1}	1.3×10^{2}	0.48
	E_a [kcal/mol]	16.0	17.4	0.92	16.3	15.5	1.05
	Q_{TS}/Q_R	4.8×10^{-2}	1.5×10^{-1}	0.31	5.4×10^{-2}	4.7×10^{-2}	1.15
	κ	1.4	1.4	1.00	179.5	101.5	1.77
R = NO$_3$	k [s^{-1}]	9.9	1.5	6.60	2.8×10^{2}	1.2×10^{3}	0.24
	E_a [kcal/mol]	14.2	15.8	0.90	14.6	14.3	1.02
	Q_{TS}/Q_R	2.9×10^{-2}	6.2×10^{-2}	0.46	2.0×10^{-2}	4.0×10^{-2}	0.50
	κ	1.4	1.4	0.97	112.4	146.7	0.77
R = Cl	k [s^{-1}]	8.9	1.9	4.74	3.8×10^{2}	5.4×10^{1}	7.00
	E_a [kcal/mol]	14.4	15.6	0.92	14.7	15.8	0.93
	Q_{TS}/Q_R	3.7×10^{-2}	6.1×10^{-2}	0.60	2.0×10^{-2}	2.5×10^{-2}	0.79
	κ	1.4	1.4	1.00	180.3	137.8	1.31
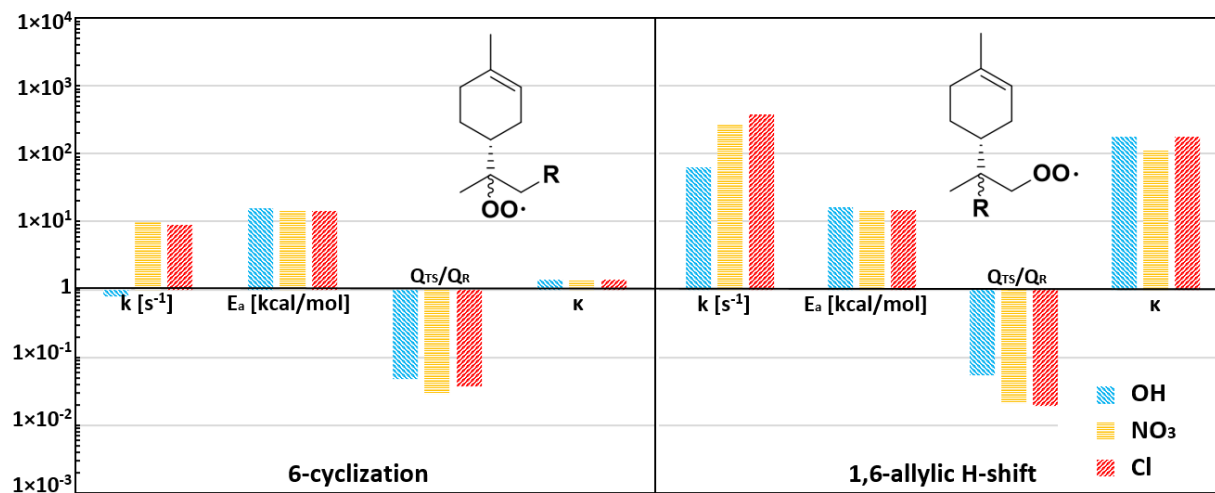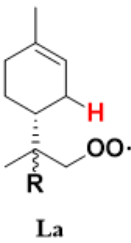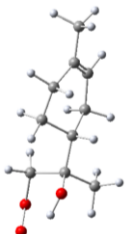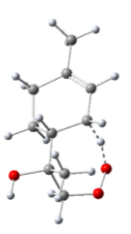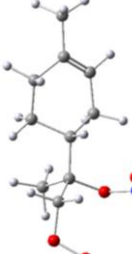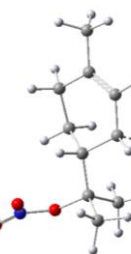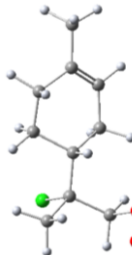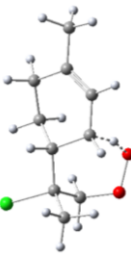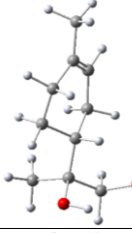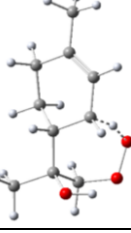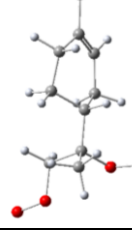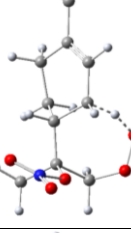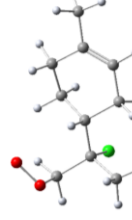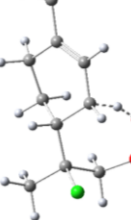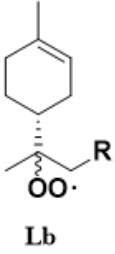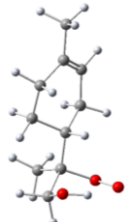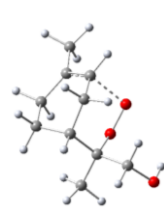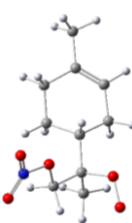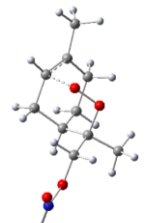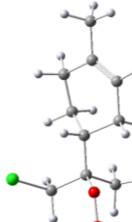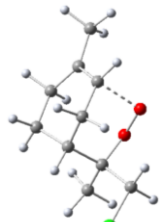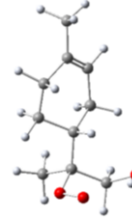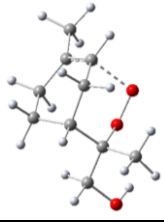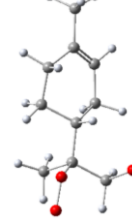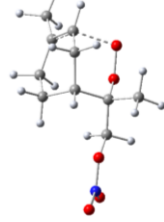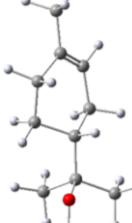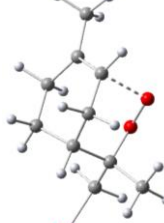
Figure S 2. Comparison of the unimolecular reaction rate coefficients (k), reaction energy barriers (E$_a$), ratios of summed partition functions exponentially weighted by relative conformer energy (Q$_{TS}$/Q$_R$) and tunneling factors (κ) between OH, NO$_3$ and Cl peroxy radical (La and Lb) calculated at the ωB97X-D level. The functional group R can be either OH, NO$_3$ or Cl. Only the result for the (R,R) stereoisomers are shown here. The corresponding values for the (R,S) stereoisomers can be found in Table S 7.

Table S 8. The lowest energy ωB97X-D conformers of reactant and TS for OH, NO₃ and Cl derived peroxy radicals La and Lb. White: hydrogen. Grey: carbon. Red: Oxygen. Blue: nitrogen. Green: chlorine. For the OH derived La and Lb reactant conformers, the hydroxy group is directed towards the peroxy group indicating the presence of a hydrogen bond.

Radical	Stereo	R	Reactant	TS
La	(R,R)	OH		
		NO₃		
		Cl		
	(R,S)	OH		
		NO₃		
		Cl		

Radical	Stereo	R	Reactant	TS
Lb	(R,R)	OH		
		NO₃		
		Cl		
	(R,S)	OH		
		NO₃		
		Cl		

S5. Proposed oxidation pathways in pristine environments

Table S 9. The product prediction rules in pristine environments, $k'_{bimolecular} \sim 3 \times 10^{-2}$ s^{-1}.

1	H-shifts can happen back and forward rapidly between a hydroperoxy and a peroxy group until terminated by other pathways. [3]
2	For the cyclization reactions, the 5-, 6- and 7-membered ring formation reactions are able to compete with the possible bimolecular reactions ($k_{5-cyc.} > k_{6-cyc.} > k_{7-cyc.} > k'_{bimolecular}$).[4]
3	For the H-shift reactions, the 1,4 to 1,9-aldehydic H-shifts are considered the most competitive pathways ($k_{alde.} > k'_{bimolecular}$). [2, 3]
4	When a hydrogen is abstracted from the aldehyde group, both the CO loss and the O_2 addition pathways are considered.
5	If both cyclization reactions and aldehydic H-shifts are possible, both possibilities are considered.
6	If no aldehydic H-shift nor cyclization reactions can happen, the 1,5 to 1,9-allylic H-shifts are considered. [4]
7	If none of above reactions can happen, 1,5 to 1,7-α-carbonyl H-shifts are considered, the α-carbonyl position with a hydroperoxy or endoperoxy group being preferred.[2, 3]
8	α-hydroperoxy H-shifts result in O-O bond scission to yield a carbonyl group and OH recycling. [2, 3]
9	α-endoperoxy H-shifts (abstracting a hydrogen from a carbon connected to an endocyclic peroxy group) also leads to peroxy bond scission, forming a carbonyl group and an alkoxy radical (RO). [5]
10	α-hydroxy and α-hydroperoxy H-shifts are considered next. [3]
11	When a radical center is formed on an α-hydroxy carbon in the β-position of a hydroperoxy group, an epoxide can form along with OH loss.[5, 6]
12	Three possible reaction channels for alkoxy radicals (RO) are considered: the isomerization channel, the decomposition channel and the reaction with O_2.[7-9]
13	When a hydroperoxy H-shift happens between a hydroperoxy and a hydroperoxy acid group, the formation of the hydroperoxy acid is strongly preferred.[10]

Figure S 3 . Proposed product formation pathways for L1 in pristine environments. The part in the solid box is the CCSD(T)-F12a level calculation form this work. The closed-shell final products are shown in green with their chemical formulas.
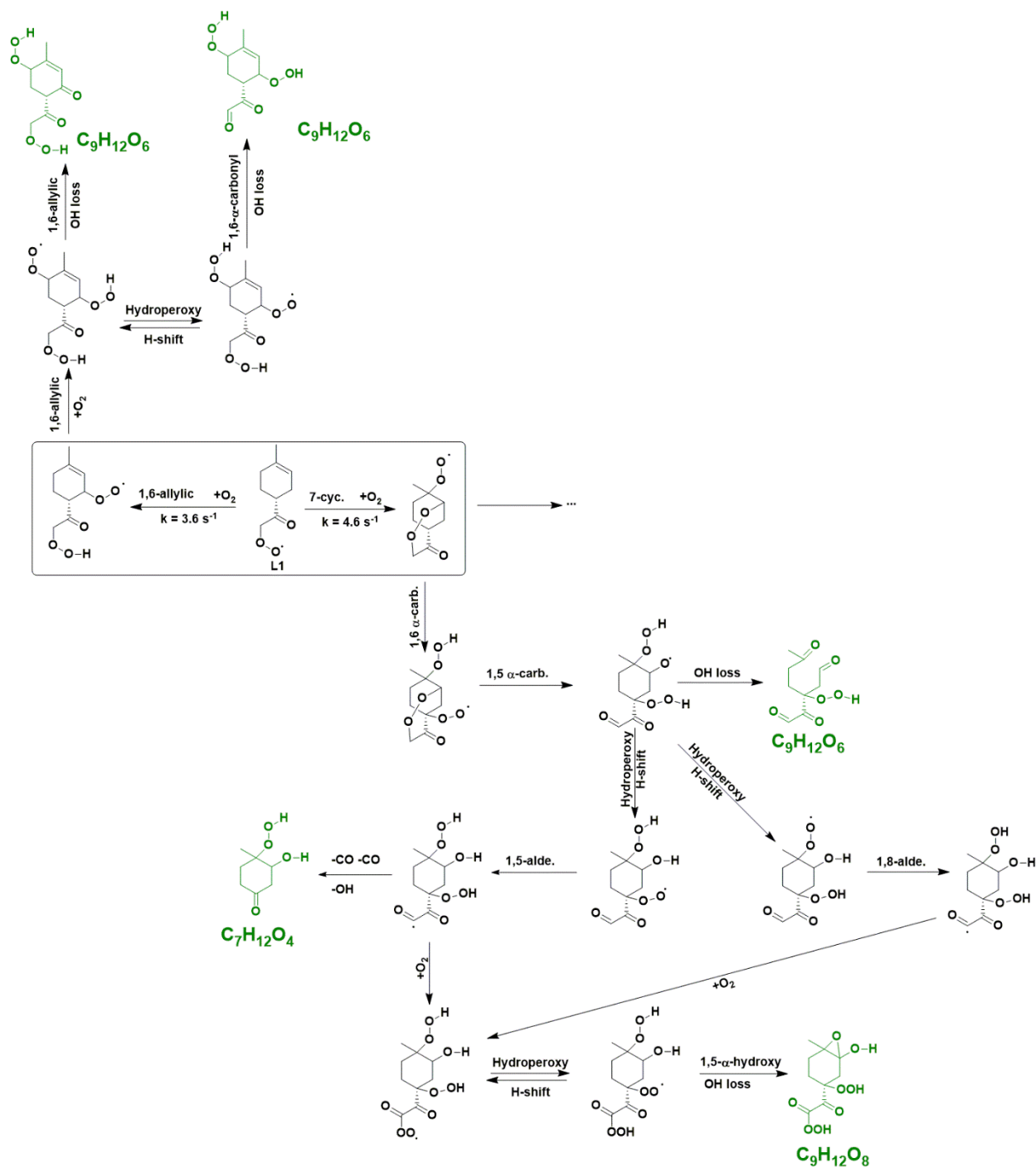
Figure S 4. Proposed product formation pathways for L2 in pristine environments. The part in the solid box is the CCSD(T)-F12a level calculation form this work. The closed-shell final products are shown in green with their chemical formulas.
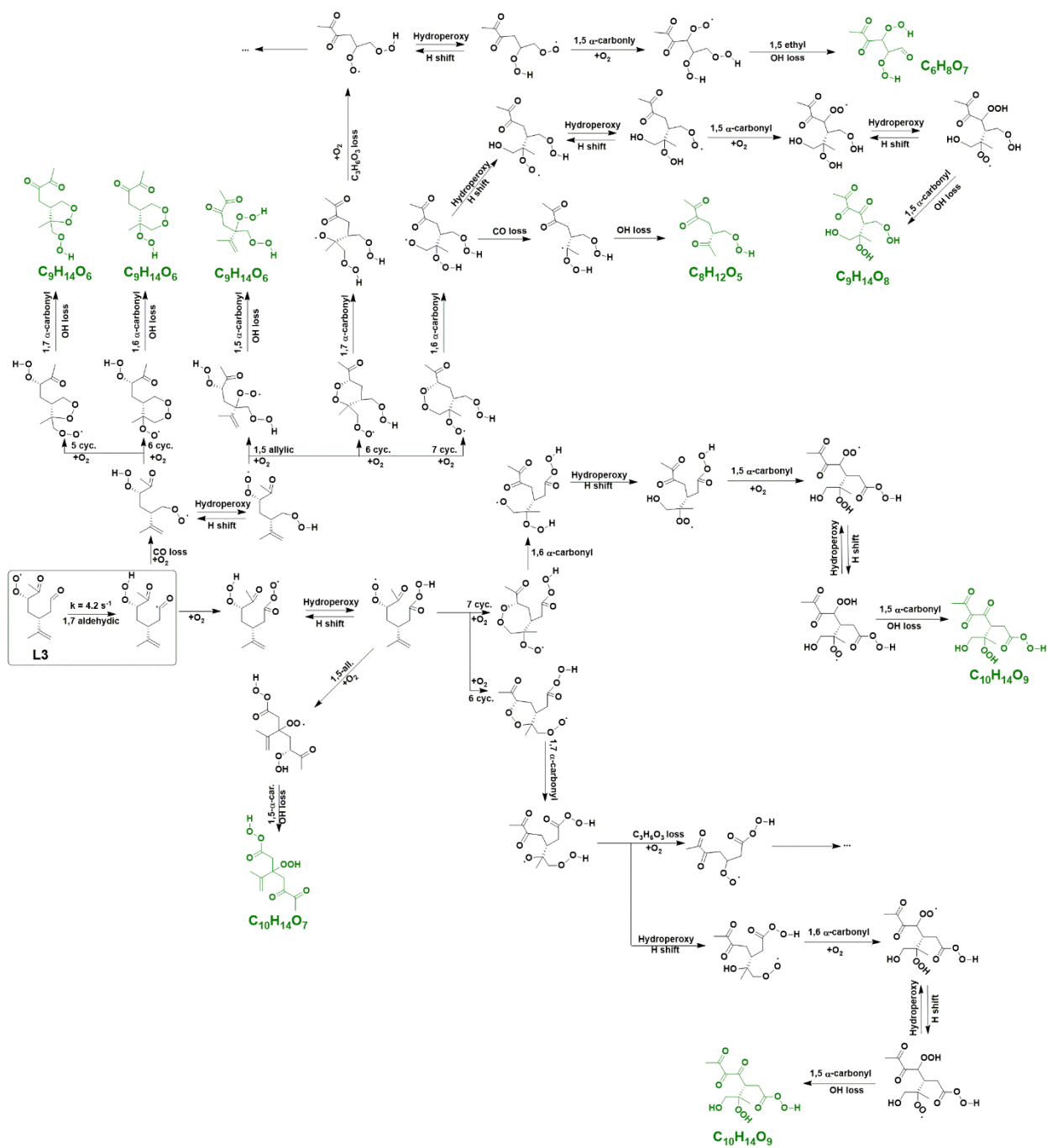
Figure S 5. Proposed product formation pathways for (R,R)-L3 in pristine environments. The part in the solid box is the CCSD(T)-F12a level calculation form this work. The closed-shell final products are shown in green with their chemical formulas.

Figure S 6. Proposed product formation pathways for L4 in pristine environments. The part in the solid box is the CCSD(T)-F12a level calculation form this work. The closed-shell final products are shown in green with their chemical formulas.
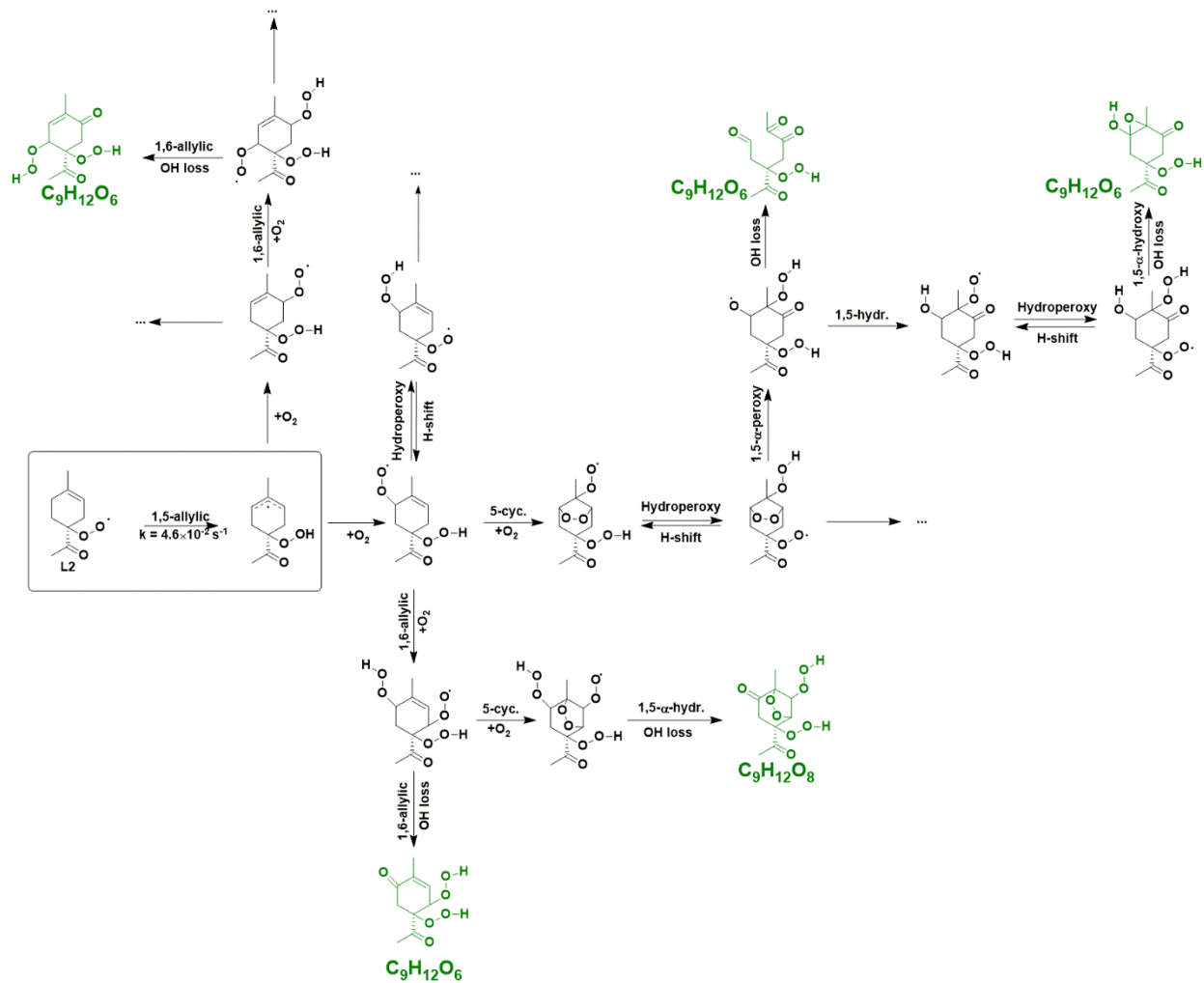
Figure S 7. Proposed product formation pathways for (R,R)-L5 in pristine environments. The part in the solid box is the CCSD(T)-F12a level calculation form this work. The closed-shell final products are shown in green with their chemical formulas.
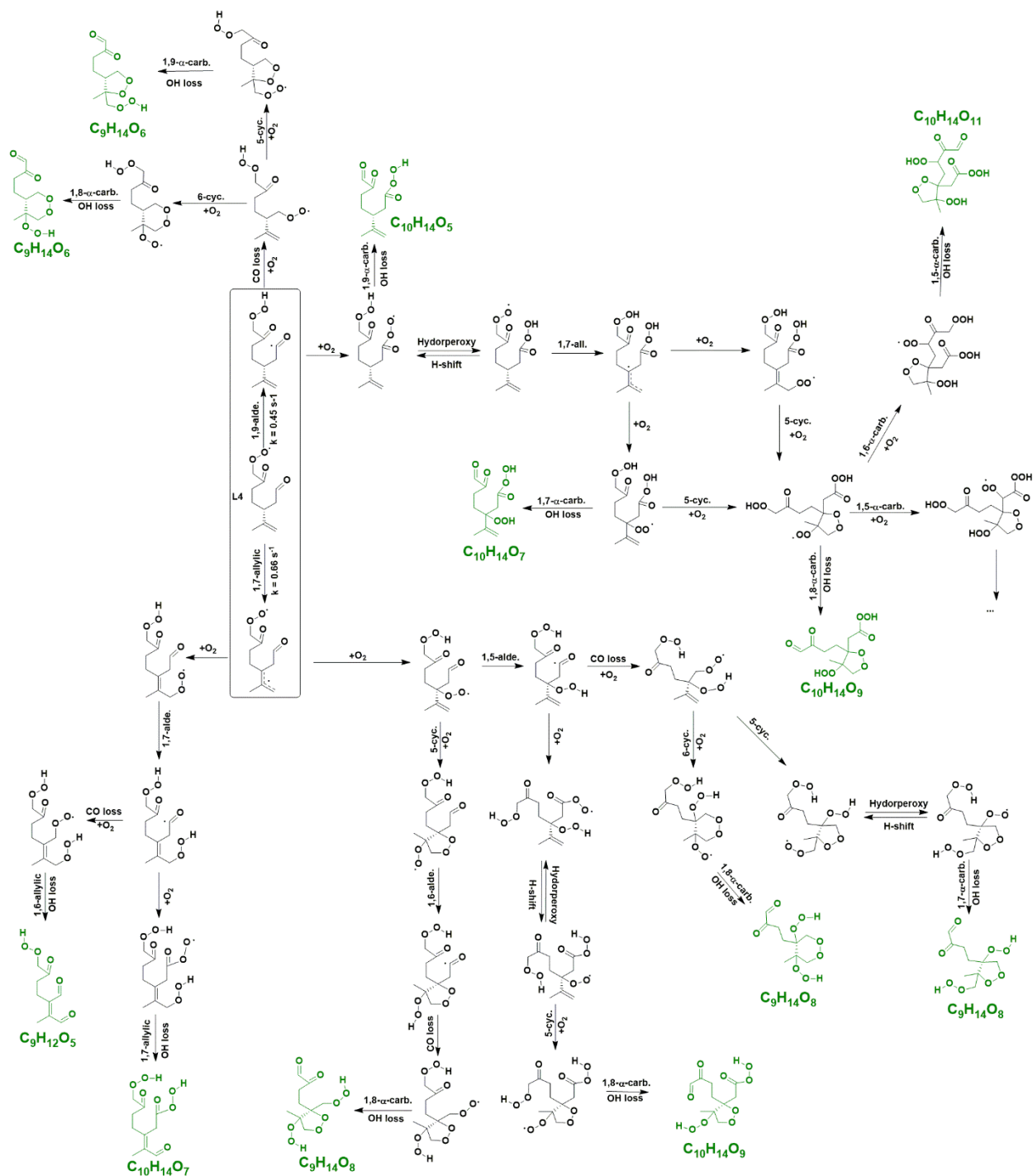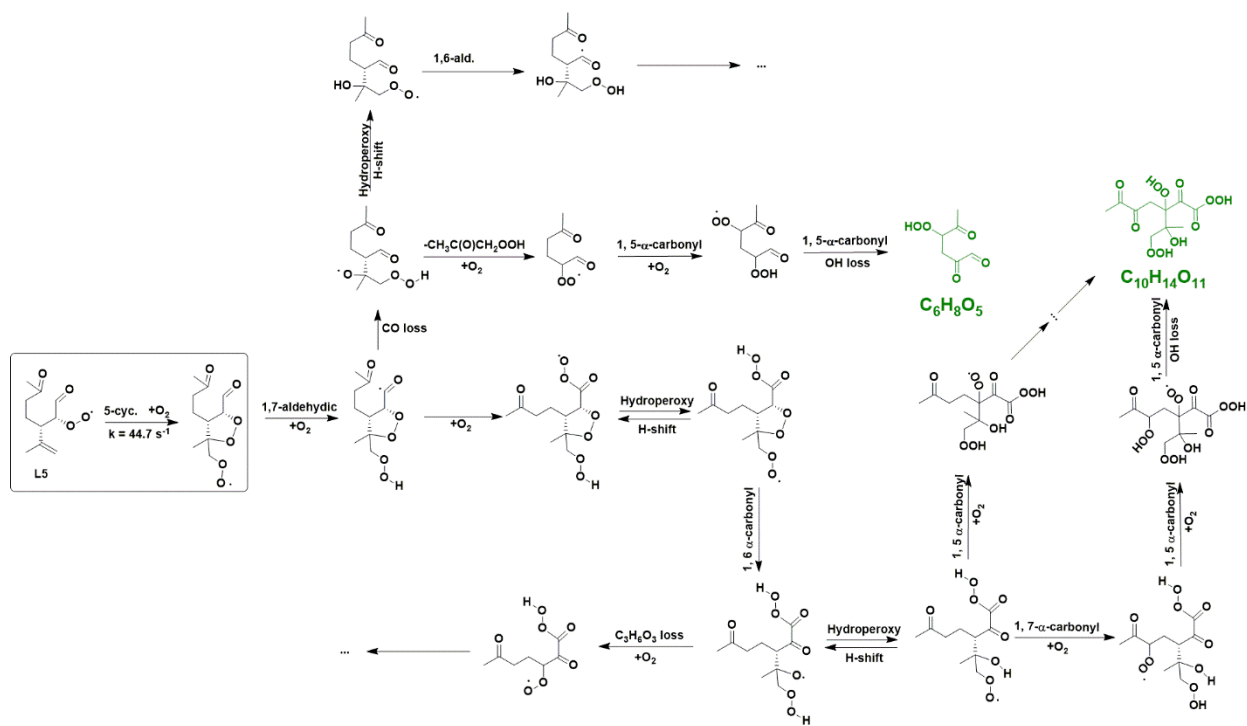
S6. Proposed oxidation pathways in polluted environments

Table S 10. The product prediction rules under polluted conditions ($k'_{bimolecular} \sim 1\ s^{-1}$)

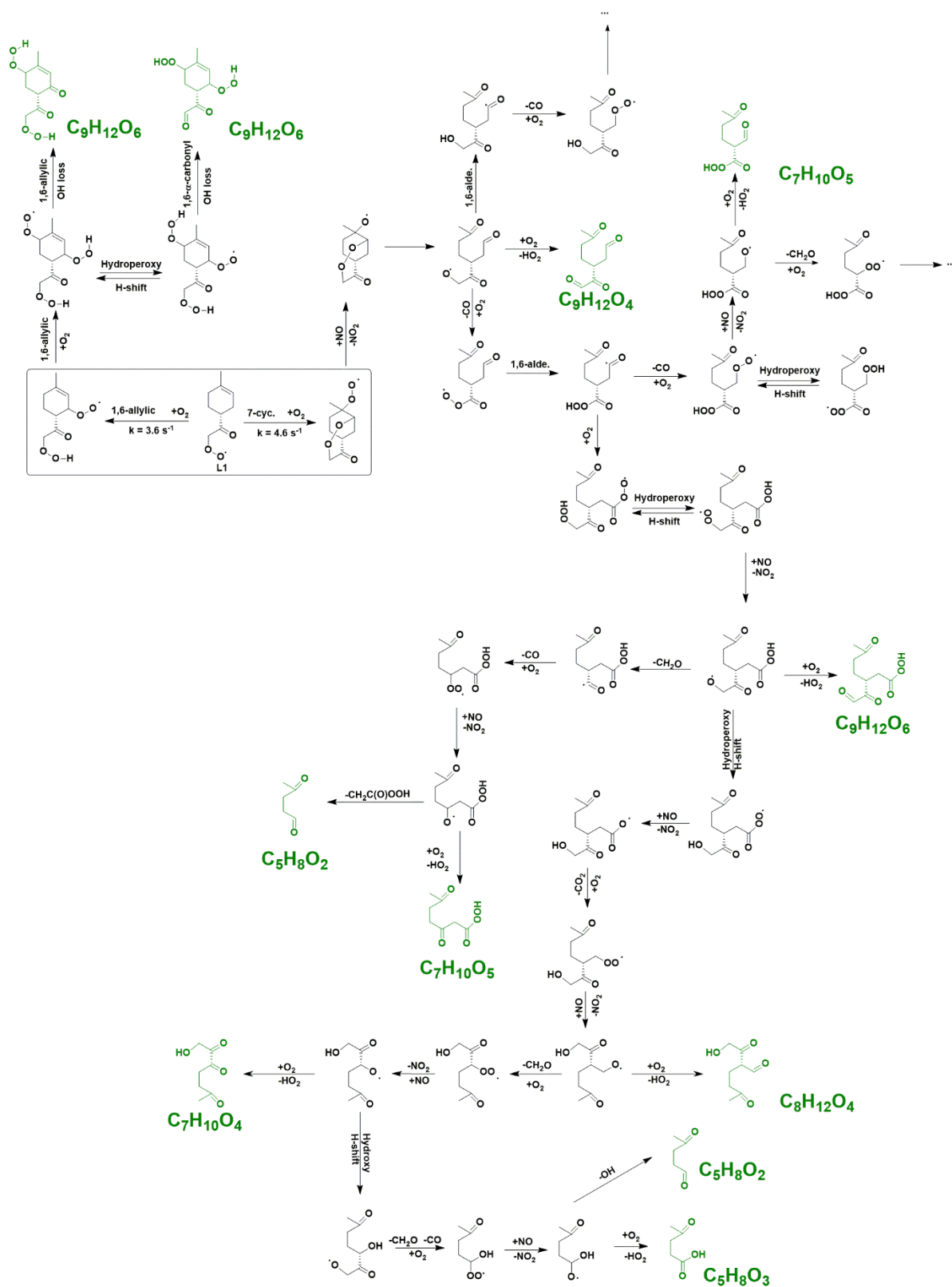|	
1	The following reactions are considered competitive: [4, 11-13] • The hydroperoxy H-shifts between a hydroperoxy and a peroxy group ($k_{hydrop.}$) [3] • The 5, 6 and 7-cyclization reaction ($k_{5\text{-cyc.}} > k_{6\text{-cyc.}} > k_{7\text{-cyc.}}$) [13] • The 1,4 to 1,9-aldehydic (alde.) H-shifts ($k_{6\text{-alde.}} \approx k_{7\text{-alde.}} > k_{4\text{-alde.}} \approx k_{9\text{-alde.}}$)[3, 11] • The 1,6 and 1,7-allylic (all.) H-shift ($k_{6\text{-all.}} \approx k_{7\text{-all.}}$) [11, 14] • The listed reactions are considered in the order: $k_{hydrop.} > k_{cyc.} \approx k_{alde.} > k_{all.}$
2	Among the reactions listed in (1), the 7-cyclization, 1,9 and 1,4-aldehydic H-shifts, 1,6 and 1,7-allylic H-shifts are considered to have rates comparable to the competing bimolecular reactions. ($k_{7\text{-cyc.}} \approx k_{4\text{-alde.}} \approx k_{9\text{-alde.}} \approx k_{6\text{-all.}} \approx k_{7\text{-all.}} \approx k_{bimolecular}$)[11, 14]
3	When more than one reaction with similar rate coefficients can happen ($k_1 \approx k_2$), all possibilities are considered.
4	When a hydrogen is abstracted from an aldehyde group, both the CO loss and the O_2 addition pathways are considered.
5	α-hydroperoxy H-shifts result in O-O bond scission to yield a carbonyl group and OH recycling. [3]
6	α-endoperoxy H-shifts also lead to O-O bond scission to yield a carbonyl group and an alkoxy radical (RO). [15]
7	Three possible reaction channels for alkoxy radical (RO) are considered: the isomerization channel, the decomposition channel and the reaction with O_2. [7-9]
8	When a hydroperoxy H-shift happens between a hydroperoxy and a hydroperoxy acid group, the formation of the hydroperoxy acid is strongly preferred.[10]

Figure S 8. Proposed product formation pathways for L1 in polluted environments. The part in the solid box is the CCSD(T)-F12a level calculation form this work. The closed-shell final products are shown in green with the chemical formulas.

Figure S 9. Proposed product formation pathways for (R,R)-L3 in polluted environments. The part in the solid box is the CCSD(T)-F12a level calculation form this work. The closed-shell final products are shown in green with the chemical formulas.

Figure S 10. Proposed product formation pathways for (S,S)-L5 in polluted environments. The part in the solid box is the CCSD(T)-F12a level calculation form this work. The closed-shell final products are shown in green with the chemical formulas.
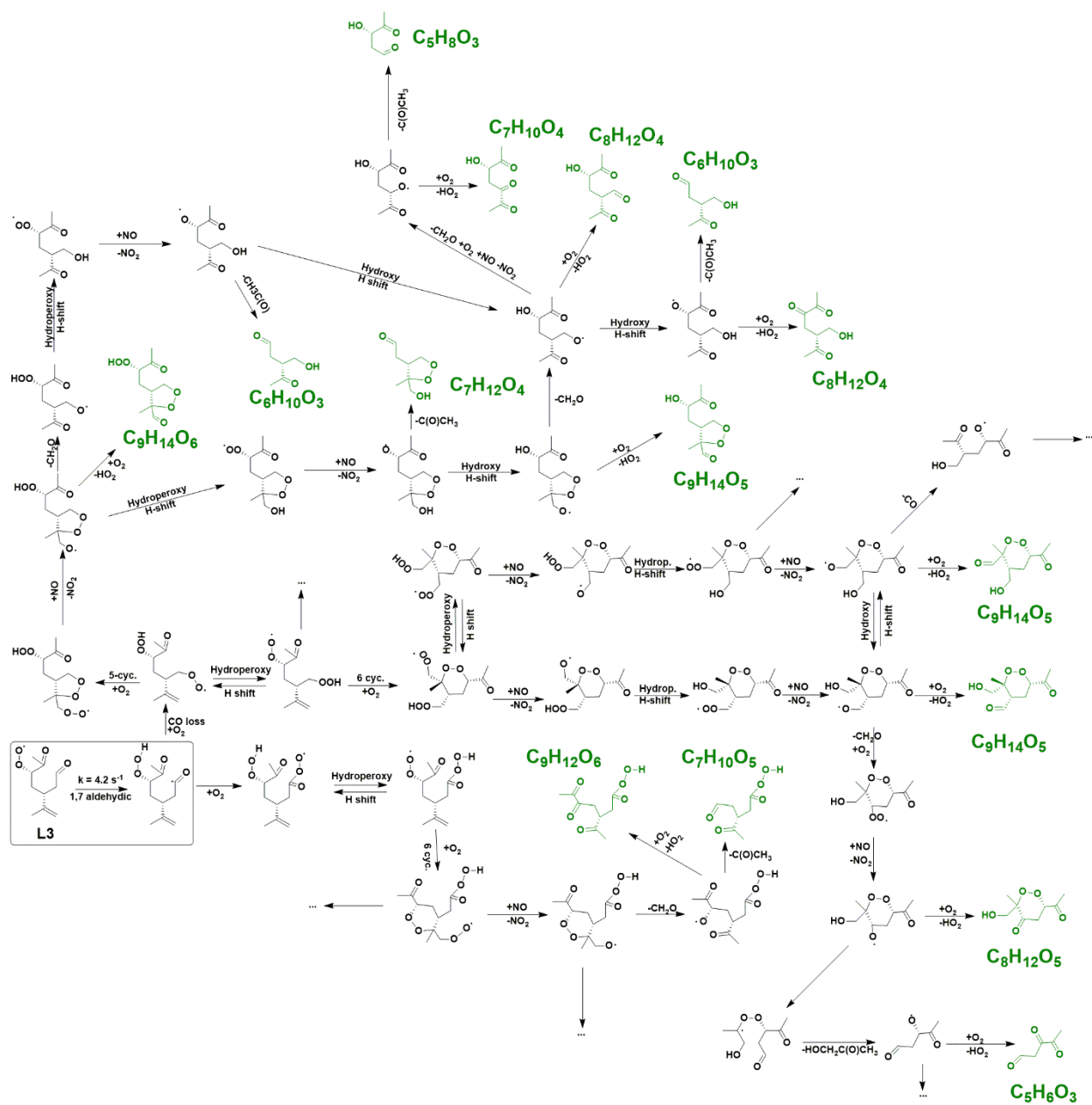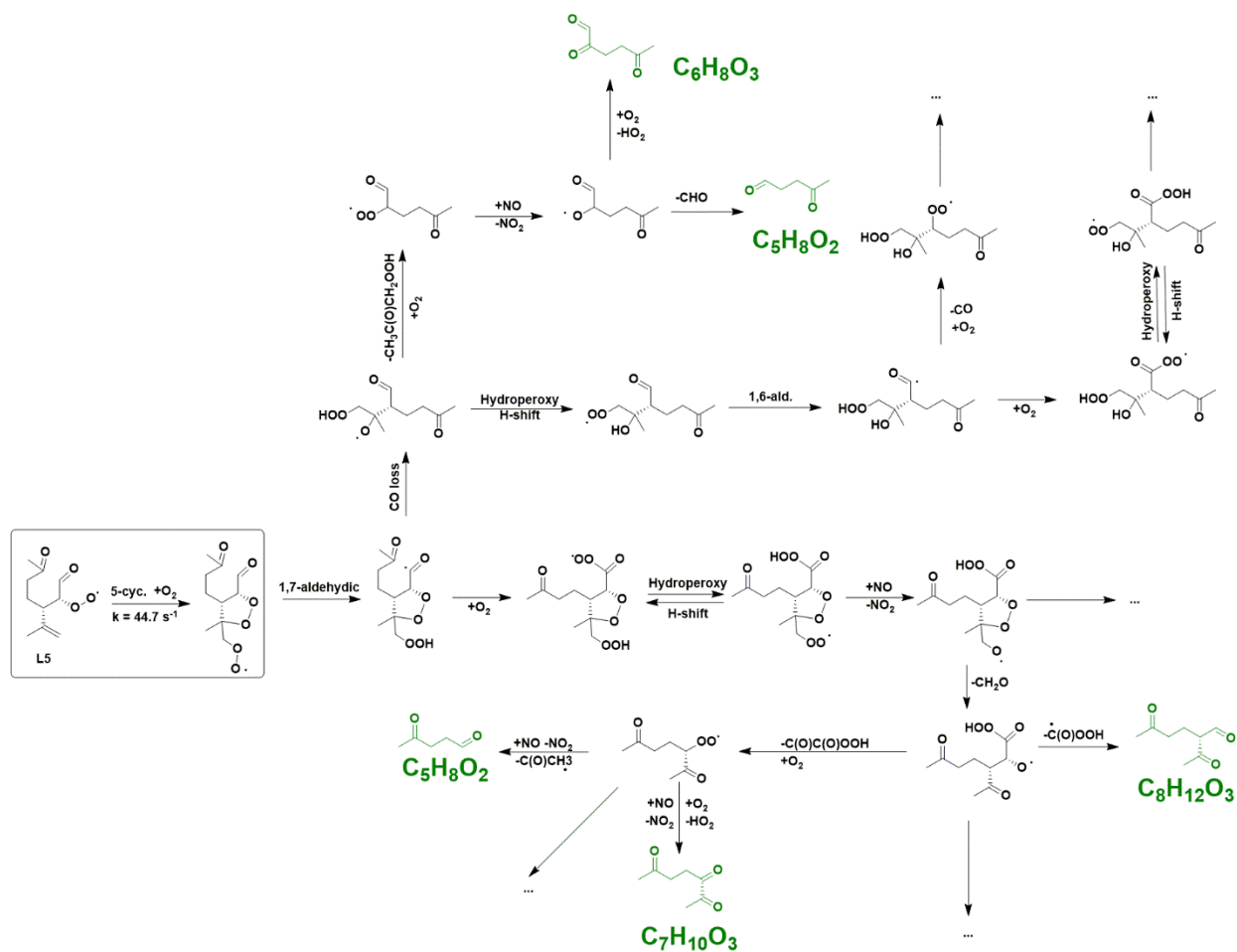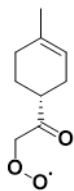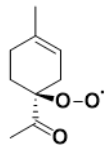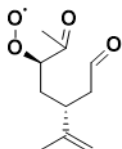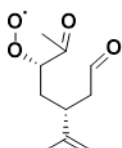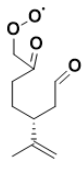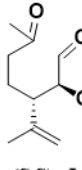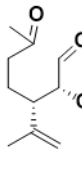
S7. Temperature dependence of the calculated reaction rate coefficients

Table S 11. The temperature dependency of the CCSD(T)-F12a level calculated unimolecular reaction rate coefficients. Two different types of fitting methods are provided.

Radical	Fitting	$k = A exp(-B/T)\, exp(C/T^3)$			$k = A exp(-Ea/RT)$		
		A	B	C	A [s^{-1}]	Ea/R [K]	Ea [kcal/mol]
L1	1,5-α-carbonyl	7.10E+11	1.05E+04	1.55E+08	1.50E+06	4803.27	9.55
	1,6-allylic	2.14E+11	9.08E+03	1.49E+08	7.08E+05	3621.08	7.20
	1,6-alkyl	4.42E+11	9.97E+03	6.86E+07	1.34E+09	7462.85	14.83
	1,7-allylic	1.95E+11	8.91E+03	1.08E+08	2.08E+07	4954.77	9.85
	7-cyclization	7.31E+10	7.06E+03	4.95E+06	4.81E+10	6879.50	13.67
	8-cyclization	4.37E+10	8.69E+03	4.97E+06	2.872E+10	8511.39	16.91
L2	1,4-allylic	3.77E+12	1.34E+04	2.46E+08	3.66E+03	4457.62	8.86
	1,5-allylic	2.46E+12	1.12E+04	1.61E+08	3.07E+06	5360.27	10.65
	5-cyclization	2.20E+12	1.00E+04	7.78E+06	1.14E+12	9732.87	19.34
	6-cyclization	1.64E+12	1.03E+04	6.47E+06	9.51E+11	10061.23	19.99
(R,R) - L3	1,5-allylic	5.75E-04	6.81E+03	9.07E+07	2.73E-07	3497.53	6.95
	1,6-α-carbonyl	7.33E-04	8.08E+03	1.61E+08	8.87E-10	2180.55	4.33
	1,7-aldehydic	3.53E-04	5.66E+03	7.41E+07	6.82E-07	2956.20	5.87
	1,7-allylic	1.96E-04	6.32E+03	1.04E+08	3.06E-08	2526.24	5.02
	6-cyclization	4.45E-05	4.30E+03	5.77E+06	2.73E-05	4086.88	8.12
	7-cyclization	5.46E-04	5.56E+03	4.86E+06	3.62E-04	5383.66	10.70
(R,S) - L3	1,5-allylic	3.14E+11	9.11E+03	1.05E+08	4.40E+07	5267.81	10.47
	1,6-α-carbonyl	1.03E+11	9.99E+03	1.21E+08	3.89E+06	5576.37	11.08
	1,7-aldehydic	1.55E+10	7.25E+03	8.55E+07	1.14E+07	4131.25	8.21
	1,7-allylic	2.99E+10	7.86E+03	1.10E+08	2.74E+06	3834.42	7.62
	6-cyclization	2.97E+10	6.80E+03	6.28E+06	1.75E+10	6568.498	13.05
	7-cyclization	9.86E+10	7.81E+03	5.45E+06	6.22E+10	7609.33	15.12
	1,7-allylic	3.52E+10	8.65E+03	1.21E+08	1.27E+06	4217.46	8.38

L4	1,8-α-carbonyl	1.86E+10	1.05E+04	1.46E+08	8.02E+04	5181.53	10.30
	1,9-aldehydic	6.70E+09	7.94E+03	9.21E+07	2.83E+06	4573.79	9.09
	1,9-allylic	2.87E+10	9.72E+03	1.40E+08	2.12E+05	4605.46	9.15
	9-cyclization	3.53E+09	7.55E+03	6.87E+06	1.98E+09	7297.01	14.50
(S,S) - L5	1,4-aldehydic	1.48E+12	9.72E+03	1.36E+08	1.59E+07	4770.84	9.48
	1,5-alkyl	1.41E+12	1.12E+04	7.05E+07	3.67E+09	8629.63	17.15
	1,6-allylic	1.92E+11	1.00E+04	1.37E+08	1.75E+06	4988.00	9.91
	1,6-α-carbonyl	6.62E+10	1.03E+04	1.62E+08	7.69E+04	4356.80	8.66
	5-cyclization	1.67E+11	5.84E+03	5.56E+06	1.04E+11	5639.51	11.21
	6-cyclization	9.33E+10	6.41E+03	6.27E+06	5.50E+10	6178.00	12.28
(R,S) - L5	1,4-aldehydic	4.23E+12	1.01E+04	1.30E+08	7.26E+07	5382.09	10.70
	1,5-alkyl	1.05E+12	1.02E+04	6.92E+07	3.03E+09	7688.00	15.28
	1,6-allylic	2.37E+11	1.02E+04	1.37E+08	2.16E+06	5195.88	10.33
	1,6-α-carbonyl	6.26E+11	1.03E+04	1.43E+08	3.58E+06	5093.84	10.12
	5-cyclization	7.15E+10	6.18E+03	6.46E+06	4.14E+10	5943.67	11.81
	6-cyclization	3.14E+11	7.66E+03	6.09E+06	1.88E+11	7440.05	14.78

References

1.   Møller, K. H.; Otkjær, R. V.; Hyttinen, N.; Kurten, T.; Kjaergaard, H. G., Cost-Effective Implementation of Multiconformer Transition State Theory for Peroxy Radical Hydrogen Shift Reactions. *J. Phys. Chem. A* **2016,** *120*, 10072-10087.

2.   Vereecken, L.; Nozière, B., H Migration in Peroxy Radicals under Atmospheric Conditions. *Atmos. Chem. Phys.* **2020,** *20*, 7429-7458.

3.   Møller, K. H.[†], Bates K. H.[‡], and Kjaergaard H. G.[†], The Importance of Peroxy Radical Hydrogen-Shift Reactions in Atmospheric Isoprene Oxidation. *J. Phys. Chem. A* **2019,** *123*, 920–932.

4.   Møller, K. H.; Otkjær, R. V.; Chen, J.; Kjaergaard, H. G., Double Bonds Are Key to Fast Unimolecular Reactivity in First-Generation Monoterpene Hydroxy Peroxy Radicals. *J. Phys. Chem. A* **2020,** *124*, 2885-2896.

5.   Wang, L.; Wu, R.; Xu, C., Atmospheric Oxidation Mechanism of Benzene. Fates of Alkoxy Radical Intermediates and Revised Mechanism. *J. Phys. Chem. A* **2013,** *117*, 14163-8.

6.   Møller, K. H.; Kurtén, T.; Bates, K. H.; Thornton, J. A.; Kjaergaard, H. G., Thermalized Epoxide Formation in the Atmosphere. *J. Phys. Chem. A* **2019,** *123*, 10620-10630.

7.   Atkinson, R., Atmospheric Reactions of Alkoxy and Hydroxyalkoxy Radicals. *Int. J. Chem. Kinet.* **1997,** *29*, 99–111.

8.   Vereecken, L.; Peeters, J., A Structure-Activity Relationship for the Rate Coefficient of H-Migration in Substituted Alkoxy Radicals. *Phys. Chem. Chem. Phys.* **2010,** *12*, 12608-20.

9.   Peeters J., Fantechi G., Vereecken, L., A Generalized Structure-Activity Relationship for the Decomposition of (Substituted) Alkoxy Radicals. *J. Atmos. Chem.* **2004,** *48*, 59–80.

10.   Knap, H. C.; Jorgensen, S., Rapid Hydrogen Shift Reactions in Acyl Peroxy Radicals. *J. Phys. Chem. A* **2017,** *121*, 1470-1479.

11.   Vereecken, L.; Nozière, B., H migration in peroxy radicals under atmospheric conditions. *Atmos. Chem. Phys.* **2020,** *20*, 7429-7458.

12.   Xu, L.; Møller, K. H.; Crounse, J. D.; Otkjær, R. V.; Kjaergaard, H. G.; Wennberg, P. O., Unimolecular Reactions of Peroxy Radicals Formed in the Oxidation of α-Pinene and β-Pinene by Hydroxyl Radicals. *J. Phys. Chem. A* **2019,** *123*, 1661-1674.

13.   Peeters J., Vereecken, L.., Nontraditional (Per)oxy Ring-Closure Paths in the Atmospheric Oxidation of Isoprene and Monoterpenes. *J. Phys. Chem. A* **2004,** *108*, 5197-5204.

14.   Møller, K. H.; Otkjær, R. V.; Chen, J.; Kjaergaard, H. G., Double Bonds Are Key to Fast Unimolecular Reactivity in First-Generation Monoterpene Hydroxy Peroxy Radicals. *J. Phys. Chem. A* **2020,** *124*, 2885-2896.

15.   Wang, L.; Wu, R.; Xu, C., Atmospheric oxidation mechanism of benzene. Fates of alkoxy radical intermediates and revised mechanism. *J. Phys. Chem. A* **2013,** *117*, 14163-8.