Supporting Information for The Impact of Unimolecular Reactions on Acyl Peroxy Radical Initiated Isoprene Oxidation

Ida Karppinen, Dominika Pasik, Emelda Ahongshangbam, and Nanna Myllys

Other calculated unimolecular reaction rate coefficients

Table S1 presents the rest of the calculated unimolecular reaction rates for the acyl peroxy radicals studied. These reactions are also illustrated in Figure S1. For acr-APR, cyc3-APR and cyc4-APR 1,4 H-shifts, the reaction product decomposed similarly to ace-APR 1,4 H-shift. This decomposition led to the formation of a hydroperoxy radical and a ketene corresponding to the reacting APR structure.

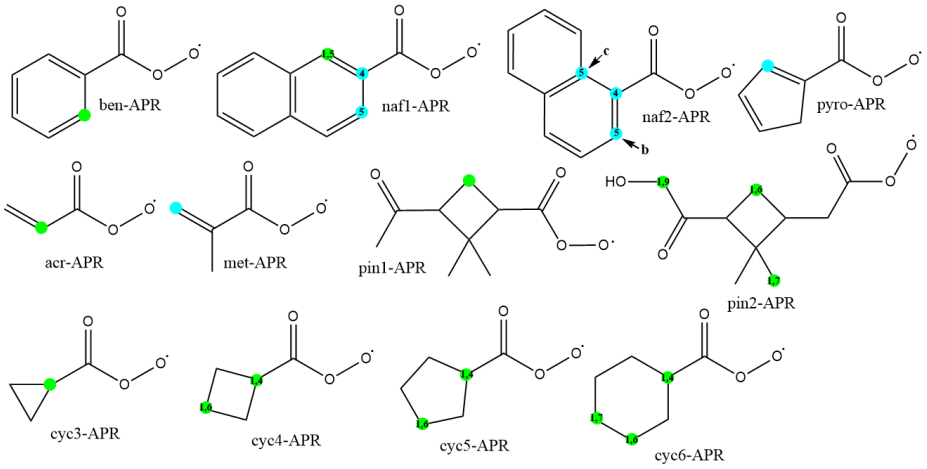

Figure S1: APR structures and studied unimolecular reactions corresponding to the results in Table S1. Reactions are marked with dots, green for H-shifts and blue for endoperoxide ring formations. For clarification, the prefixes for structures with multiple calculated rates are also marked.

Table S1: Calculated energy barrier heights (ΔE^{TS} in kcal/mol), Eckart tunneling coefficients (κ_{t}) for H-shifts and unimolecular MC-TST reaction rate coefficients (k_{uni} in s^{-1}) at 298 K of other unimolecular reactions for the studied APRs.

Radical	Reaction	ΔE^{TS}	κ_{t}	k_{uni}
Acr-APR	1,4 H-shift[a]	42.34	2	1.75×10^{-18}
Met-APR	5-endoperoxide	21.58	-	2.71×10^{-4}
Ben-APR	1,5 H-shift	29.76	9	2.58×10^{-9}
Pyro-APR	5-endoperoxide	23.18	-	9.30×10^{-6}
Cyc6-APR	1,4 H-shift	22.86	42	4.79×10^{-3}
	1,6 H-shift	24.51	32	6.19×10^{-5}
	1,7 H-shift	27.12	32	4.36×10^{-7}
Cyc5-APR	1,4 H-shift	22.87	40	1.73×10^{-3}
	1,6 H-shift	22.22	91	1.81×10^{-3}
Cyc4-APR	1,4 H-shift[a]	38.23	3	9.63×10^{-15}
	1,6 H-shift	27.48	238	1.24×10^{-6}
Cyc3-APR	1,4 H-shift[a]	39.72	2	1.81×10^{-16}
Pin1-APR	1,5 H-shift	24.42	26	5.52×10^{-5}
Pin2-APR	1,6 H-shift	22.88	66	9.26×10^{-4}
	1,7 H-shift	22.79	163	1.35×10^{-3}
	1,9 H-shift	24.96	101	6.03×10^{-6}
Naf1-APR	1,5 H-shift	29.57	7	1.67×10^{-9}
	4-endoperoxide	23.59	-	6.81×10^{-6}
	5-endoperoxide	22.55	-	1.73×10^{-5}
Naf2-APR	4-endoperoxide	19.64	-	5.59×10^{-3}
	5-endoperoxide[b]	19.94	-	1.53×10^{-3}
	5-endoperoxide[c]	28.89	-	3.03×10^{-10}

[a] Reaction product decomposes. [b&c] See Figure S1.

Comparison of ωB97X-D and M06-2X functionals for calculating rates for reactions between isoprene and APRs

Table S2 presents the calculated bimolecular reaction rate coefficients for the reactions of isoprene with ace-, pro- and ben-APR with two different functionals, ωB97X-D and M06-2X, using MC-TST. Also, the LC-TST rates calculated using the ωB97X-D functional are included.

Table S2: Calculated energy barrier heights (ΔE^{TS} in kcal/mol) and bimolecular reaction rate coefficients (k_{bi} in $\mathrm{cm^3 s^{-1}}$) at 298 K for ace-APR R4, pro-APR and ben-APR R1 reactions with isoprene calculated at the DLPNO-CCSD(T)/aug-cc-pVTZ//ωB97X-D/6-31+G* (LC-TST and MC-TST) and DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/6-31+G* level (MC-TST).

Radical	Reaction	Functional	Theory	ΔE^{TS}	k_{bi}
Ace-APR	R4	ωB97X-D	MC-TST	2.8	1.1×10^{-17}
		ωB97X-D	LC-TST		1.3×10^{-17}
		M06-2X	MC-TST	2.8	6.0×10^{-18}
Pro-APR	R1	ωB97X-D	MC-TST	1.3	1.3×10^{-16}
		ωB97X-D	LC-TST		8.5×10^{-17}
		M06-2X	MC-TST	1.4	2.8×10^{-17}
Ben-APR	R1	ωB97X-D	MC-TST	0.1	1.6×10^{-15}
		ωB97X-D	LC-TST		9.1×10^{-16}
		M06-2X	MC-TST	0.3	4.9×10^{-16}

PES graphs for reactions R1 and R4 between isoprene and OH

The PES graphs for the reactions R1 and R4 between isoprene and OH calculated with two different functionals, ωB97X-D and M06-2X, are presented in Figures S2 and S3.

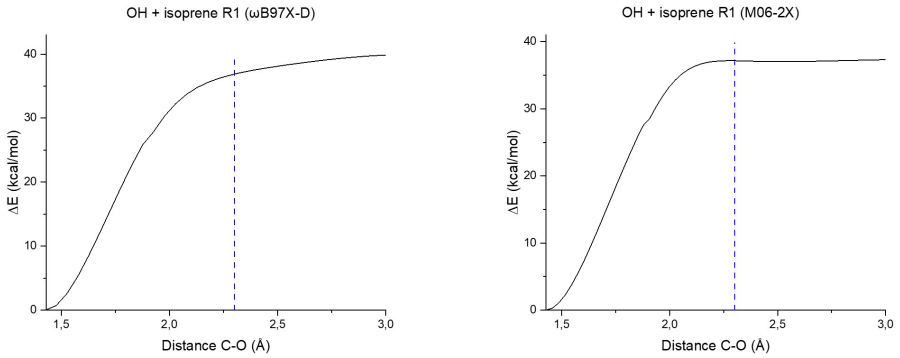

Figure S2: PES graphs for reaction R1 between isoprene and OH calculated with ωB97X-D and M06-2X functionals. Energies are relative to the equilibrium structure. Blue dashed line shows C−O bond distance for TS structure optimized at the M06-2X/6-31+G* level.

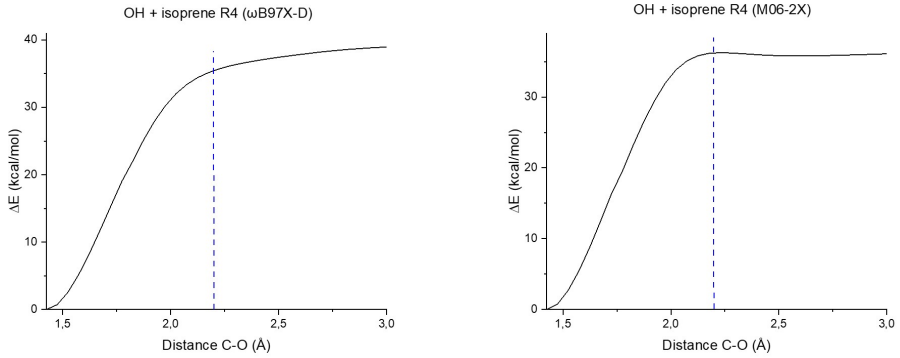

Figure S3: PES graphs for reaction R4 between isoprene and OH calculated with ωB97X-D and M06-2X functionals. Energies are relative to the equilibrium structure. Blue dashed line shows C−O bond distance for TS structure optimized at the M06-2X/6-31+G* level.

Energy diagrams for ace-APR and OH reactions R1 with isoprene

Energy diagrams are presented in Figure S4. Energies for reactants, complex, TS and product were calculated at the DLPNO-CCSD(T)/aug-cc-pVTZ//ωB97X-D/6-31+G* level for ace-APR and DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/6-31+G* level for OH.

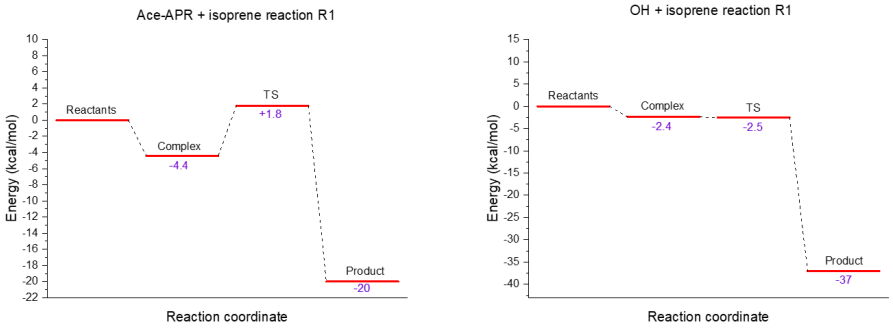

Figure S4: Energy diagrams for ace-APR and OH reactions R1 with isoprene calculated at the DLPNO-CCSD(T)/aug-cc-pVTZ//ωB97X-D/6-31+G* and DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/6-31+G* level, respectively.