Supplemental Information for:

Interactions of peroxy radicals from monoterpene and isoprene oxidation simulated in the radical Volatility Basis Set

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Table 1: Kinetic parameters for α-pinene and isoprene autoxidation and association reactions.

E_a	7300 K
A_{ap_1}	7.2×10^9 s^{-1}
A_{ap_2}	2×10^9 s^{-1}
A_{ap_3}	8×10^8 s^{-1}
A_{ip_1}	8×10^8 s^{-1}
A_{ip_2}	4×10^8 s^{-1}
A_{ip_3}	1.8×10^8 s^{-1}
$k_{\mathrm{apOx_0RO_2}}$	5×10^{-12} cm^3 s^{-1}
$k_{\mathrm{apOx_1RO_2}}$	10^{-11} cm^3 s^{-1}
$k_{\mathrm{apOx_2RO_2}}$	5×10^{-11} cm^3 s^{-1}
$k_{\mathrm{apOx_3RO_2}}$	10^{-10} cm^3 s^{-1}
$k_{\mathrm{ipOx_0RO_2}}$	5×10^{-12} cm^3 s^{-1}
$k_{\mathrm{ipOx_1RO_2}}$	10^{-11} cm^3 s^{-1}
$k_{\mathrm{ipOx_2RO_2}}$	5×10^{-11} cm^3 s^{-1}
$k_{\mathrm{ipOx_3RO_2}}$	10^{-10} cm^3 s^{-1}

Table 2: Isoprene reactions and rate coefficients

#	Reaction	Rate coefficient*
1	$\mathrm{ip + O_3 \longrightarrow 0.25\,ipOx_0RO_2 + 0.75\,ipRO_2}$	9.6×10^{-18}
2	$\mathrm{ip + OH \longrightarrow 0.5\,ipRO_2 + 0.5\,ipOx_0RO_2}$	10^{-10}
3	$\mathrm{ipOx_0RO_2 \longrightarrow ipOx_1RO_2}$	$A_{\mathrm{ip_1}} \exp\left(-\mathrm{E}_a/T\right)$
4	$\mathrm{HO_2 + ipOx_0RO_2 \longrightarrow ipOx_0ROOH}$	10^{-11}
5	$\mathrm{2\,ipOx_0RO_2 \longrightarrow \gamma ipOx_0Ox_0ROOR + 2\,\alpha ipOx_0RO}$	$\mathrm{k_{ipOx_0RO_2}}$
6	$\mathrm{ipOx_0RO_2 \longrightarrow ipOx_0RO}$	6×10^{-8}
7	$\mathrm{ipOx_1RO_2 \longrightarrow ipOx_2RO_2}$	$A_{\mathrm{ip_2}} \exp\left(-\mathrm{E}_a/T\right)$
8	$\mathrm{HO_2 + ipOx_1RO_2 \longrightarrow ipOx_1ROOH}$	10^{-11}
9	$\mathrm{ipOx_1RO_2 + ipOx_0RO_2 \longrightarrow \gamma ipOx_1Ox_0ROOR + \alpha(ipOx_0RO + ipOx_1RO)}$	$2\sqrt{\mathrm{k_{ipOx_0RO_2}\,k_{ipOx_1RO_2}}}$
10	$\mathrm{2\,ipOx_1RO_2 \longrightarrow \gamma ipOx_1ipOx_1ROOR + 2\,\alpha ipOx_1RO}$	$\mathrm{k_{ipOx_1RO_2}}$
11	$\mathrm{ipOx_1RO_2 \longrightarrow ipOx_1RO}$	6×10^{-8}
12	$\mathrm{ipOx_2RO_2 \longrightarrow ipOx_3RO_2}$	$A_{\mathrm{ip_3}} \exp\left(-\mathrm{E}_a/T\right)$
13	$\mathrm{HO_2 + ipOx_2RO_2 \longrightarrow ipOx_2ROOH}$	10^{-11}
14	$\mathrm{ipOx_2RO_2 + ipOx_0RO_2 \longrightarrow \gamma ipOx_2Ox_0ROOR + \alpha(ipOx_0RO + ipOx_2RO)}$	$2\sqrt{\mathrm{k_{ipOx_2RO_2}\,k_{ipOx_0RO_2}}}$
15	$\mathrm{ipOx_1RO_2 + ipOx_2RO_2 \longrightarrow \gamma ipOx_2ipOx_1ROOR + \alpha(ipOx_2RO + ipOx_1RO)}$	$\sqrt{\mathrm{k_{ipOx_1RO_2}\,k_{ipOx_2RO_2}}}$
16	$\mathrm{2\,ipOx_2RO_2 \longrightarrow \gamma ipOx_2ipOx_2ROOR + 2\,\alpha ipOx_2RO}$	$\mathrm{k_{ipOx_2RO_2}}$
17	$\mathrm{ipOx_2RO_2 \longrightarrow ipOx_2RO}$	6×10^{-8}
18	$\mathrm{HO_2 + ipOx_3RO_2 \longrightarrow ipOx_3ROOH}$	10^{-11}
19	$\mathrm{ipOx_3RO_2 + ipOx_0RO_2 \longrightarrow \gamma ipOx_3ROOR + \alpha(ipOx_0RO + ipOx_3RO)}$	$2\sqrt{\mathrm{k_{ipOx_3RO_2}\,k_{ipOx_0RO_2}}}$
20	$\mathrm{ipOx_1RO_2 + ipOx_3RO_2 \longrightarrow \gamma ipOx_3ipOx_1ROOR + \alpha(ipOx_3RO + ipOx_1RO)}$	$2\sqrt{\mathrm{k_{ipOx_1RO_2}\,k_{ipOx_3RO_2}}}$
21	$\mathrm{ipOx_2RO_2 + ipOx_3RO_2 \longrightarrow \gamma ipOx_3ipOx_2ROOR + \alpha(ipOx_3RO + ipOx_2RO)}$	$2\sqrt{\mathrm{k_{ipOx_2RO_2}\,k_{ipOx_3RO_2}}}$
22	$\mathrm{2\,ipOx_3RO_2 \longrightarrow \gamma ipOx_3ipOx_3ROOR + 2\,\alpha ipOx_3RO}$	$\mathrm{k_{ipOx_3RO_2}}$
23	$\mathrm{ipOx_3RO_2 \longrightarrow ipOx_3RO}$	6×10^{-8}

* First-order coefficients have units s^{-1}; second-order coefficients have units $cm^3\ s^{-1}$.

γ and α represent the branching between dimer formation and alkoxy radical formation, respectively, as discussed in section 2.1.

Table 3: Isoprene and α-pinene cross reactions and rate coefficients

#	Reaction	Rate coefficient*
24	$apOx_0RO_2 + ipOx_0RO_2 \longrightarrow \gamma apOx_0ipOx_0ROOR + \alpha(apRO + ipOx_0RO)$	$2\sqrt{k_{apOx_0RO_2}\,k_{ipOx_0RO_2}}$
25	$apOx_0RO_2 + ipOx_1RO_2 \longrightarrow \gamma apOx_0ipOx_1ROOR + \alpha(apRO + ipOx_1RO)$	$2\sqrt{k_{apOx_0RO_2}\,k_{ipOx_1RO_2}}$
26	$apOx_0RO_2 + ipOx_2RO_2 \longrightarrow \gamma apOx_0ipOx_1ROOR + \alpha(apRO + ipOx_2RO)$	$2\sqrt{k_{apOx_0RO_2}\,k_{ipOx_2RO_2}}$
27	$apOx_0RO_2 + ipOx_3RO_2 \longrightarrow \gamma apOx_0ipOx_3ROOR + \alpha(apRO + ipOx_3RO)$	$2\sqrt{k_{apOx_0RO_2}\,k_{ipOx_3RO_2}}$
28	$apOx_1RO_2 + ipOx_0RO_2 \longrightarrow \gamma apOx_1ipOx_0ROOR + \alpha(apOx_1RO + ipOx_0RO)$	$2\sqrt{k_{apOx_1RO_2}\,k_{ipOx_0RO_2}}$
29	$apOx_1RO_2 + ipOx_1RO_2 \longrightarrow \gamma apOx_1ipOx_1ROOR + \alpha(apOx_1RO + ipOx_1RO)$	$2\sqrt{k_{apOx_1RO_2}\,k_{ipOx_1RO_2}}$
30	$apOx_1RO_2 + ipOx_2RO_2 \longrightarrow \gamma apOx_1ipOx_1ROOR + \alpha(apOx_1RO + ipOx_2RO)$	$2\sqrt{k_{apOx_1RO_2}\,k_{ipOx_2RO_2}}$
31	$apOx_1RO_2 + ipOx_3RO_2 \longrightarrow \gamma apOx_1ipOx_3ROOR + \alpha(apOx_1RO + ipOx_3RO)$	$2\sqrt{k_{apOx_1RO_2}\,k_{ipOx_3RO_2}}$
32	$apOx_2RO_2 + ipOx_0RO_2 \longrightarrow \gamma apOx_2ipOx_0ROOR + \alpha(apOx_2RO + ipOx_0RO)$	$2\sqrt{k_{apOx_2RO_2}\,k_{ipOx_0RO_2}}$
33	$apOx_2RO_2 + ipOx_1RO_2 \longrightarrow \gamma apOx_2ipOx_1ROOR + \alpha(apOx_2RO + ipOx_1RO)$	$2\sqrt{k_{apOx_2RO_2}\,k_{ipOx_1RO_2}}$
34	$apOx_2RO_2 + ipOx_2RO_2 \longrightarrow \gamma apOx_2ipOx_1ROOR + \alpha(apOx_2RO + ipOx_2RO)$	$2\sqrt{k_{apOx_2RO_2}\,k_{ipOx_2RO_2}}$
35	$apOx_2RO_2 + ipOx_3RO_2 \longrightarrow \gamma apOx_2ipOx_3ROOR + \alpha(apOx_2RO + ipOx_3RO)$	$2\sqrt{k_{apOx_2RO_2}\,k_{ipOx_3RO_2}}$
36	$apOx_3RO_2 + ipOx_0RO_2 \longrightarrow \gamma apOx_3ipOx_0ROOR + \alpha(apOx_3RO + ipOx_0RO)$	$2\sqrt{k_{apOx_3RO_2}\,k_{ipOx_0RO_2}}$
37	$apOx_3RO_2 + ipOx_1RO_2 \longrightarrow \gamma apOx_3ipOx_1ROOR + \alpha(apOx_3RO + ipOx_1RO)$	$2\sqrt{k_{apOx_3RO_2}\,k_{ipOx_1RO_2}}$
38	$apOx_3RO_2 + ipOx_2RO_2 \longrightarrow \gamma apOx_3ipOx_1ROOR + \alpha(apOx_3RO + ipOx_2RO)$	$2\sqrt{k_{apOx_3RO_2}\,k_{ipOx_2RO_2}}$
39	$apOx_3RO_2 + ipOx_3RO_2 \longrightarrow \gamma apOx_3ipOx_3ROOR + \alpha(apOx_3RO + ipOx_3RO)$	$2\sqrt{k_{apOx_3RO_2}\,k_{ipOx_3RO_2}}$

* First-order coefficients have units s^{-1}; second-order coefficients have units $cm^3\ s^{-1}$.
γ and α represent the branching between dimer formation and alkoxy radical formation, respectively, as discussed in section 2.1.

Table 4: Inorganic photochemical reactions and rate coefficients used in this work

#	Reaction	Rate coefficient*
40	$O_2 + h\nu \longrightarrow 2\,O(^3P)$	$j = 6.0 \times 10^{-34}$
41	$O_3 + h\nu \longrightarrow O_2 + O(^3P)$	$j = 10^{-6}$
42	$O_3 + h\nu \longrightarrow O(^1D) + O_2$	$j = 1.2 \times 10^{-7}$
43	$O_2 + O(^3P) \longrightarrow O_3$	$k_0 = 6.0 \times 10^{-34}(T/300)^{-2.4}$, $k_\infty = 3.0 \times 10^{-12}$
44	$H_2O + O(^1D) \longrightarrow 2\,OH$	2.2×10^{-10}
45	$HO_2 + O_3 \longrightarrow 2\,O_2 + OH$	$1.1 \times 10^{-14} \exp(-490/T)$
46	$O(^3P) + OH \longrightarrow O_2 + H$	$2.2\,10^{-11} \exp(-120/T)$
47	$O(^3P) + HO_2 \longrightarrow OH + O_2$	$3 \times 10^{-11} \exp(-200/T)$
48	$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$	$3.0 \times 10^{-13} \times \exp(460/T)$
50	$O_3 + OH \longrightarrow HO_2 + O_2$	$1.7 \times 10^{-12} \exp(-940/T)$

* First-order coefficients have units s^{-1}; second-order coefficients have units $cm^3\ s^{-1}$.

Table 5: α-Pinene (ap) chemical reactions and rate coefficients used in this work.

#	Reaction	Rate coefficient*
51	$\mathrm{ap + O_3 \longrightarrow 0.25\,apOx_0RO_2 + 0.75\,apRO_2 + 0.8\,OH}$	8×10^{-17}
52	$\mathrm{ap + OH \longrightarrow 0.25\,apOx_0RO_2 + 0.75\,apRO_2}$	5.4×10^{-11}
53	$\mathrm{apOx_0RO_2 \longrightarrow apOx_1RO_2}$	$A_{\mathrm{ap_1}} \exp\left(-\mathrm{E}_a/T\right)$
54	$\mathrm{HO_2 + apOx_0RO_2 \longrightarrow ROOH}$	10^{-11}
55	$\mathrm{2\,apOx_0RO_2 \longrightarrow \gamma apOx_0Ox_0ROOR + 2\,\alpha apOx_0RO}$	$\mathrm{k_{apOx_0RO_2}}$
56	$\mathrm{apOx_0RO_2 \longrightarrow apOx_0RO}$	6×10^{-8}
57	$\mathrm{apOx_1RO_2 \longrightarrow apOx_2RO_2}$	$A_{\mathrm{ap_2}} \exp\left(-\mathrm{E}_a/T\right)$
58	$\mathrm{HO_2 + apOx_1RO_2 \longrightarrow apOx_1ROOH}$	10^{-11}
59	$\mathrm{apOx_1RO_2 + apOx_0RO_2 \longrightarrow \gamma apOx_1Ox_0ROOR + \alpha(apOx_0RO + apOx_1RO)}$	$2\sqrt{\mathrm{k_{apOx_1RO_2}\,k_{apOx_0RO_2}}}$
60	$\mathrm{2\,apOx_1RO_2 \longrightarrow \gamma apOx_1Ox_1ROOR + 2\,\alpha apOx_1RO}$	$\mathrm{k_{apOx_2RO_2}}$
61	$\mathrm{apOx_1RO_2 \longrightarrow apOx_1RO}$	6×10^{-8}
62	$\mathrm{apOx_2RO_2 \longrightarrow apOx_3RO_2}$	$A_{\mathrm{ap_3}} \exp\left(-\mathrm{E}_a/T\right)$
63	$\mathrm{HO_2 + apOx_2RO_2 \longrightarrow apOx_2ROOH}$	10^{-11}
64	$\mathrm{apOx_2RO_2 + apOx_0RO_2 \longrightarrow \gamma apOx_2Ox_0ROOR + \alpha(apOx_0RO + apOx_2RO)}$	$2\sqrt{\mathrm{k_{apOx_2RO_2}\,k_{apOx_0RO_2}}}$
65	$\mathrm{apOx_1RO_2 + apOx_2RO_2 \longrightarrow \gamma apOx_2Ox_1ROOR + \alpha(apOx_2RO + apOx_1RO)}$	$2\sqrt{\mathrm{k_{apOx_1RO_2}\,k_{apOx_2RO_2}}}$
66	$\mathrm{2\,apOx_2RO_2 \longrightarrow \gamma apOx_2Ox_2ROOR + 2\,\alpha apOx_2RO}$	$\mathrm{k_{apOx_2RO_2}}$
67	$\mathrm{apOx_2RO_2 \longrightarrow apOx_2RO}$	6×10^{-8}
68	$\mathrm{HO_2 + apOx_3RO_2 \longrightarrow apOx_3ROOH}$	10^{-11}
69	$\mathrm{apOx_3RO_2 + apOx_0RO_2 \longrightarrow \gamma apOx_3Ox_0ROOR + \alpha(apOx_0RO + apOx_3RO)}$	$2\sqrt{\mathrm{k_{apOx_3RO_2}\,k_{apOx_0RO_2}}}$
70	$\mathrm{apOx_1RO_2 + apOx_3RO_2 \longrightarrow \gamma apOx_3Ox_1ROOR + \alpha(apOx_3RO + apOx_1RO)}$	$2\sqrt{\mathrm{k_{apOx_1RO_2}\,k_{apOx_3RO_2}}}$
71	$\mathrm{apOx_2RO_2 + apOx_3RO_2 \longrightarrow \gamma apOx_3Ox_2ROOR + \alpha(apOx_3RO + apOx_2RO)}$	$2\sqrt{\mathrm{k_{apOx_2RO_2}\,k_{apOx_3RO_2}}}$
72	$\mathrm{2\,apOx_3RO_2 \longrightarrow \gamma apOx_3Ox_3ROOR + 2\,\alpha apOx_3RO}$	$\mathrm{k_{apOx_3RO_2}}$
73	$\mathrm{apOx_3RO_2 \longrightarrow apOx_3RO}$	6×10^{-8}

* First-order coefficients have units $\mathrm{s^{-1}}$; second-order coefficients have units $\mathrm{cm^3\ s^{-1}}$.
γ and α represent the branching between dimer formation and alkoxy radical formation, respectively, as discussed in section 2.1.

Reactions specified with k_0 and k_∞ are pressure-dependent with the rate coefficient at a specific pressure given by

$$k = \left(\frac{k_0\, c_{\mathrm{M}}}{1 + \frac{k_0\, c_{\mathrm{M}}}{k_\infty}} \right) 0.6^{\left(1 + \left(\log\left(\frac{k_0\, c_{\mathrm{M}}}{k_\infty}\right)\right)^2\right)^{-1}} \quad (1)$$

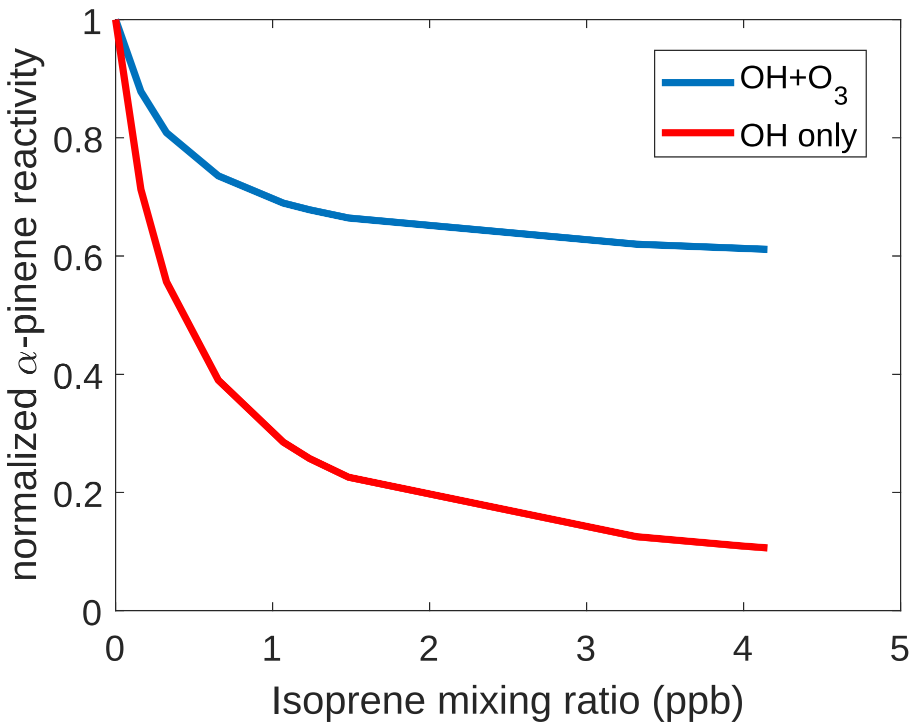

Figure S1: The α-pinene reactivity normalized to the α-pinene reactivity with no isoprene present. Shown is the case simulated in this work where α-pinene mainly reacts with ozone (blue) and a case where no ozone is present, and α-pinene only reacts with OH (red).