Supplement of

Acylperoxy radicals during ozonolysis of α-pinene: composition, formation mechanism, and contribution to the production of highly oxygenated organic molecules

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S1 Changes in measured RO_2 and closed-shell products as a function of the reacted α-pinene.

The changes of selected RO_2 and the corresponding closed-shell monomers and dimers as a function of the reacted α-pinene are consistent with previous studies (Figure S7) (Zhao et al., 2018). The RO_2 concentration increases rapidly when the reacted α-pinene is relatively low, and the increasing rate slows down due to the elevated removal rate of RO_2 via cross-reactions at higher reacted α-pinene (> 20 ppb). The dimers exhibit opposite trends with RO_2. As the reacted α-pinene increases, the increasing rates of the dimers become slightly higher due to the promoted RO_2 cross-reactions. As for the HOM monomers, their concentrations basically show linear correlations with increasing reacted α-pinene.

Table S1 Summary of experimental conditions of α-pinene ozonolysis with the addition of NO_2.

Exp #	α-pinene conc	O_3 conc	NO_2 conc	Reacted α-pinene
1	500	45	0	2.4
2	500	45	3	2.4
3	500	45	7	2.4
4	500	45	10	2.4
5	500	45	15	2.4
6	500	45	20	2.4
7	500	45	30	2.4
8	1000	45	0	4.8
9	1000	45	3	4.8
10	1000	45	7	4.8
11	1000	45	10	4.8
12	1000	45	15	4.8
13	1000	45	20	4.8
14	1000	45	30	4.8
15	2000	45	0	9.3
16	2000	45	3	9.3
17	2000	45	7	9.3
18	2000	45	10	9.3
19	2000	45	15	9.3
20	2000	45	20	9.3
21	2000	45	30	9.3
22	500	180	0	9.6
23	500	180	3	9.6
24	500	180	7	9.6
25	500	180	10	9.6
26	500	180	15	9.6
27	500	180	20	9.6
28	500	180	30	9.6
29	3000	45	0	13.5
30	1000	180	0	18.9
31	2000	180	0	36.8
32*	2000	45	0	5.0

* 500 ppm cyclohexane was added as an OH scavenger in this experiment.

Table S2 Summary of experimental conditions of α-pinene ozonolysis with the addition of NO.

Exp #	α-pinene conc	O_3 conc	NO conc	Reacted α-pinene
33	500	45	3	2.8
34	500	45	7	3.6
35	500	45	10	4.2
36	500	45	15	4.8
37	500	45	20	5.1
38	500	45	30	5.3
39	1000	45	3	5.2
40	1000	45	7	6.0
41	1000	45	10	6.7
42	1000	45	15	7.8
43	1000	45	20	8.6
44	1000	45	30	9.6
45	2000	45	3	9.6
46	2000	45	7	10.4
47	2000	45	10	11.1
48	2000	45	15	12.3
49	2000	45	20	13.4
50	2000	45	30	15.5
51	500	180	3	9.8
52	500	180	7	10.4
53	500	180	10	10.8
54	500	180	15	11.5
55	500	180	20	12.2
56	500	180	30	13.3

Table S3 Major modifications in MCM mechanisms.

#	Reactions	k (s^{-1} or cm^3 $molecule^{-1}$ s^{-1})
1	APINENE + O3 = 0.5 × APINOOA + 0.5 × APINOOB	8.05E-16.*exp(-640./T)
2	APINOOA = Z-APINAOO	KDEC*0.09
3	APINOOA = E-APINAOO	KDEC*0.09
4	APINOOA = C107O2 + OH	KDEC*0.45
5	APINOOA = C109O2 + OH	KDEC*0.37
6	APINOOB = Z-APINBOO	KDEC*0.10
7	APINOOB = E-APINBOO	KDEC*0.10
8	APINOOB = PINONIC	KDEC*0.16
9	APINOOB = C10H15O4KBRO2 + OH	KDEC*0.49
10	APINOOB = C10H15O4RBRO2 + OH	KDEC*0.5*0.3
11	C107O2 = C10H15O6R1RO2	0.14
12	C109O2 = C10H15O6R1RO2	0.02
13	C10H15O4KBRO2 = C10H15O6KBRO2	0.29
14	C10H15O4RBRO2 = C10H15O6RBRO2	1
15	RO2 + NO2 = ROONO2	7.5E-12
16	ROONO2 = RO2 + NO2	5

Table S4 Wall loss fractions of OH, HO_2, and RO_2 radicals, as well as HOM monomers and dimers under different reaction conditions

Species	D_{gas} (cm^2 s^{-1})	k_{wall} (s^{-1})	Wall loss fractions (%)			
			500 ppb αp +45 ppb O_3	1ppm αp+45 ppb O_3	2ppm αp+45 ppb O_3	500 ppb αp+45 ppb O_3
OH	0.23	0.0537	0.14	0.11	0.08	0.08
HO_2	0.15	0.0354	9.08	6.71	4.89	4.74
C_7-RO_2	0.07	0.0171	13.9	11.9	9.8	9.6
C_8-RO_2	0.07	0.0171	25.5	21.5	18.0	17.7
C_9-RO_2	0.07	0.0171	16.4	16.2	14.5	14.3
C_{10}-RO_2	0.05	0.0125	11.5	9.3	7.4	7.3
C_7-HOM	0.07	0.0171	24.3	23.3	22.5	22.3
C_8-HOM	0.07	0.0171	34.7	31.0	28.1	27.8
C_9-HOM	0.07	0.0171	29.0	27.5	26.1	25.9
C_{10}-HOM	0.05	0.0125	22.3	20.3	18.6	18.4
$C_{14\text{-}15}$-dimers	0.05	0.0125	33.1	30.5	27.8	27.6
$C_{16\text{-}19}$-dimers	0.03	0.0079	25.4	22.6	20.0	19.7
C_{20}-dimers	0.03	0.0079	17.5	15.8	14.4	14.2

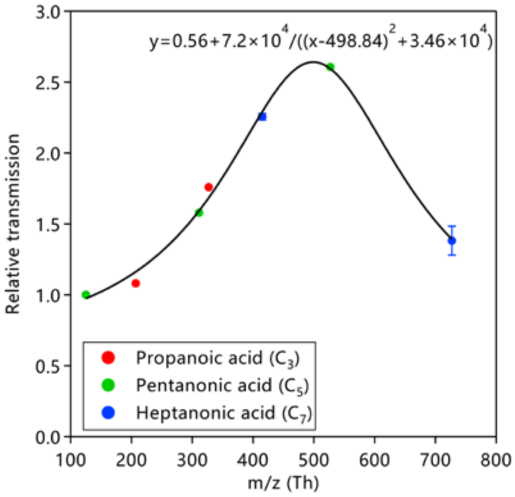

Figure S1 Mass-dependent transmission efficiency of nitrate-CIMS.

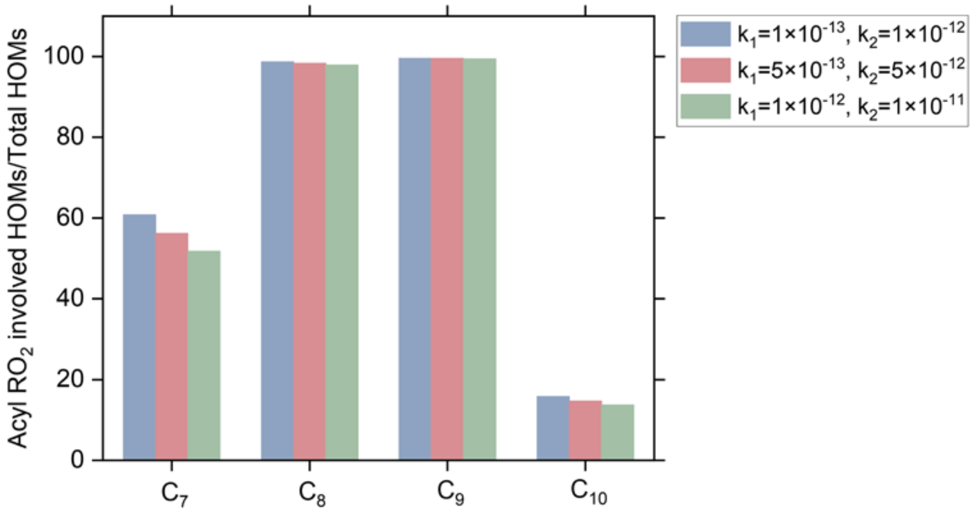

Figure S2 Sensitive analysis of the dimer formation rate to acyl RO_2-involved HOM formation, k_1 and k_2 are the dimer formation rates for alkyl and acyl RO_2, respectively, the unit is cm^3 molecule^{-1} s^{-1}.

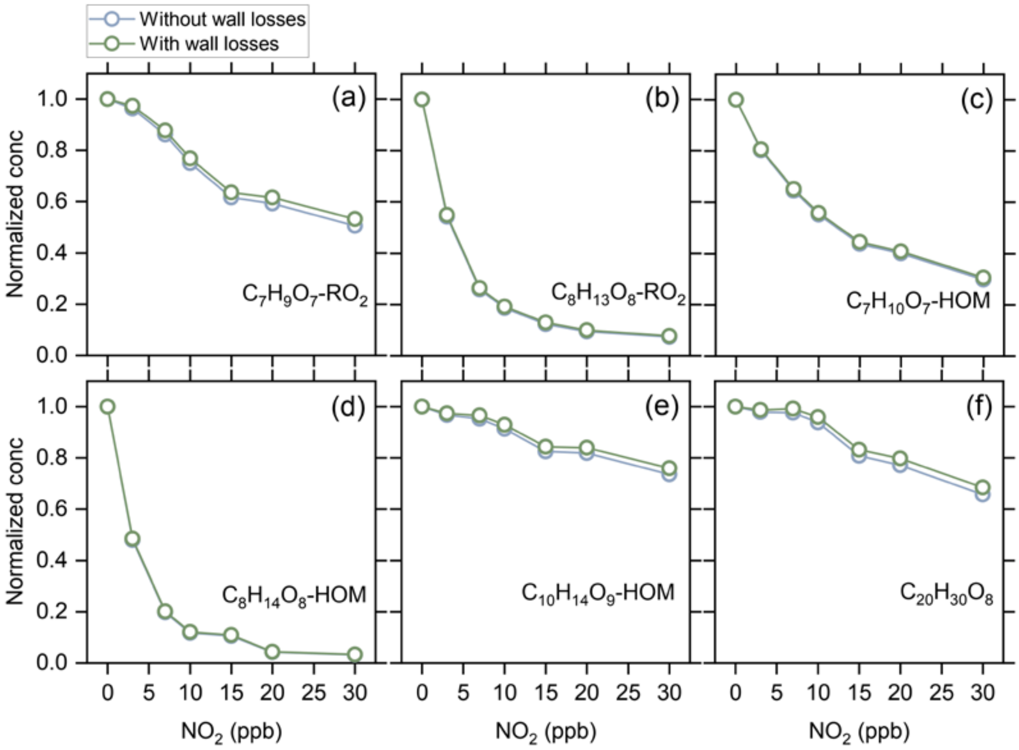

Figure S3 Normalized concentration of typical RO_2, HOM monomers and dimers as a function of the added NO_2 concentration with/without considering wall losses (Taking Exps 8-14 as an example).

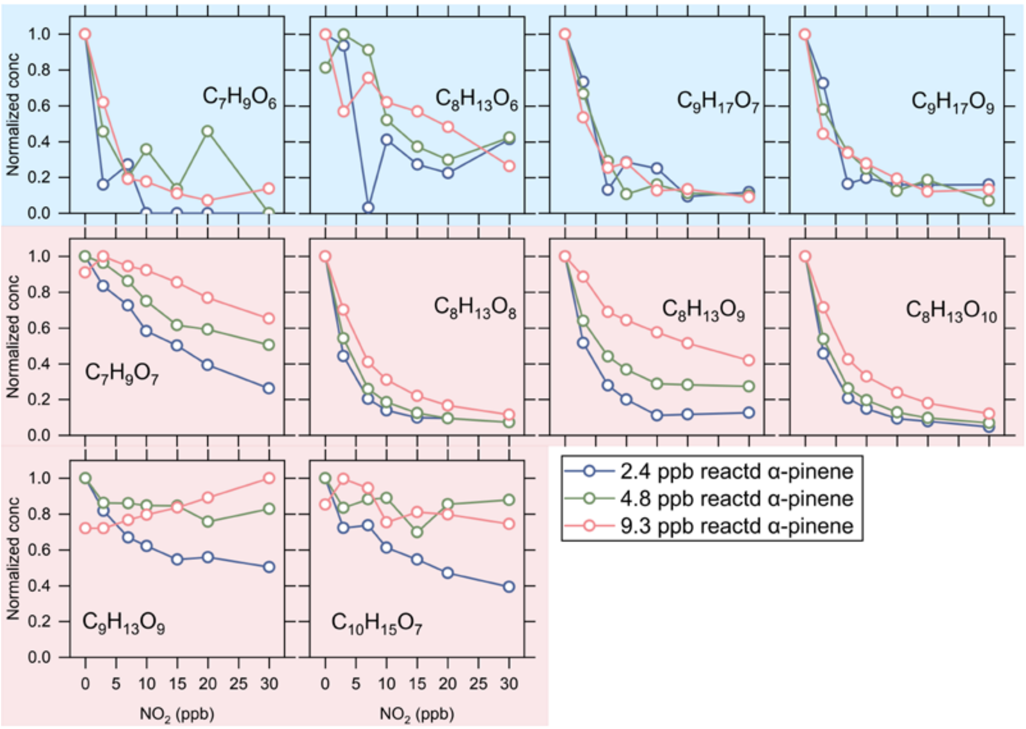

Figure S4 Normalized concentration of the measured acyl RO_2 as a function of the added NO_2 concentration (Exps 1-21). The data are categorized according to the effects of reacted α-pinene on the decreasing extents of acyl RO_2 concentration, which are indicated by different background colors (blue: no obvious effects, pink: the decreasing extent becomes lower when reacted α-pinene increases).

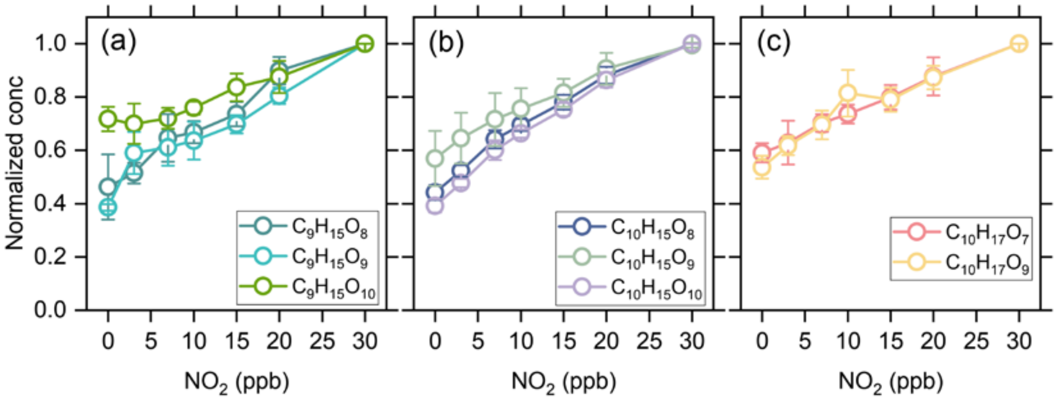

Figure S5 Averaged normalized concentration of the measured alkyl RO_2 as a function of the added NO_2 concentration (Exps 1-28).

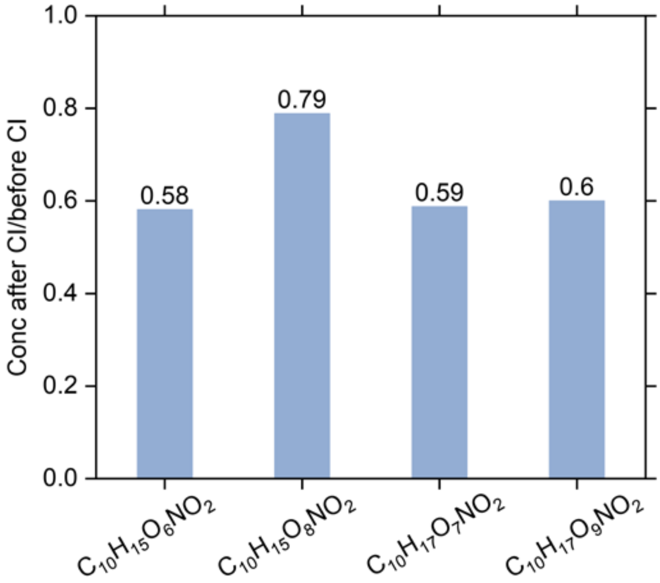

Figure S6 Ratio of simulated concentration of $ROONO_2$ after leaving the CI inlet to the concentration before into the CI inlet (the experimental conditions are same as Exp 14), the acyl RO_2 $C_{10}H_{15}O_8$ reported by Iyer et al. (2021) is included in the model, therefore the decomposition of the whole $ROONO_2$ is relatively lower.

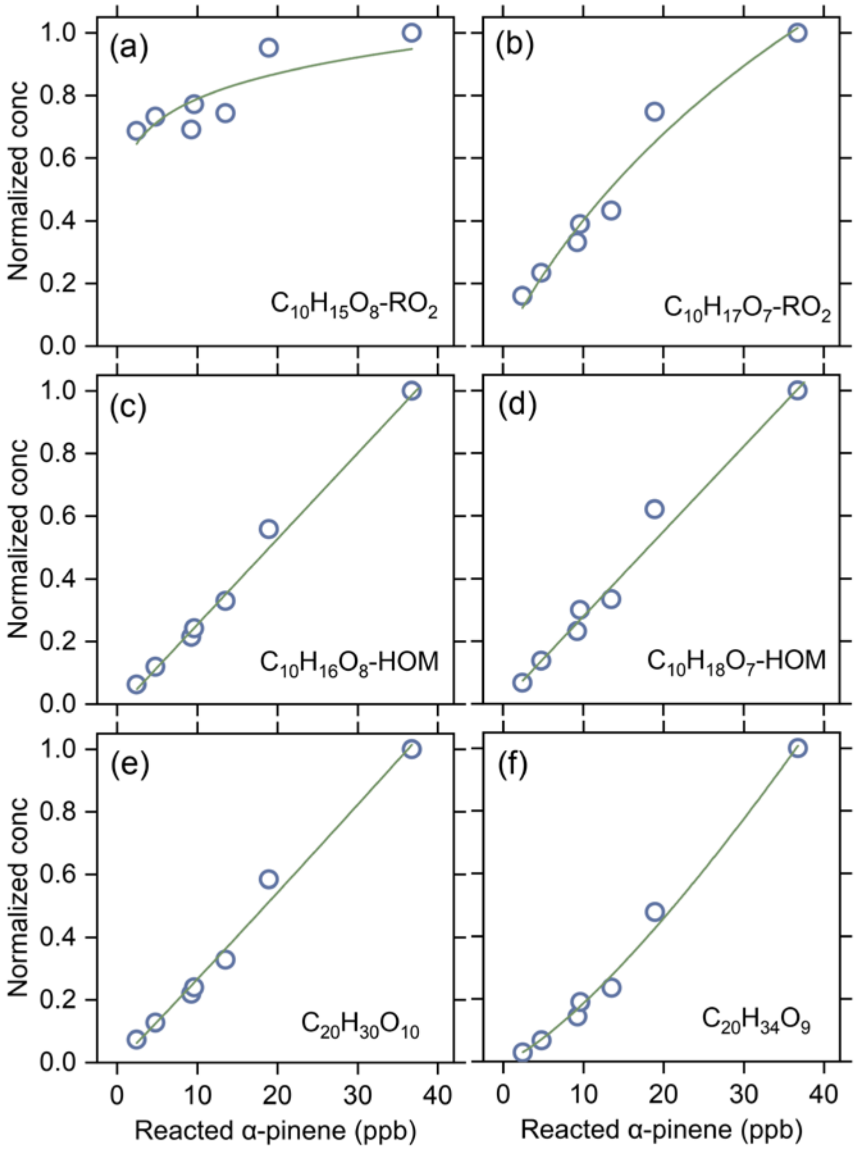

Figure S7 Normalized concentration of selected RO_2 as well as closed-shell monomers and dimers as a function of the reacted α-pinene (Exps 1, 8, 15, 22, and 29-31).

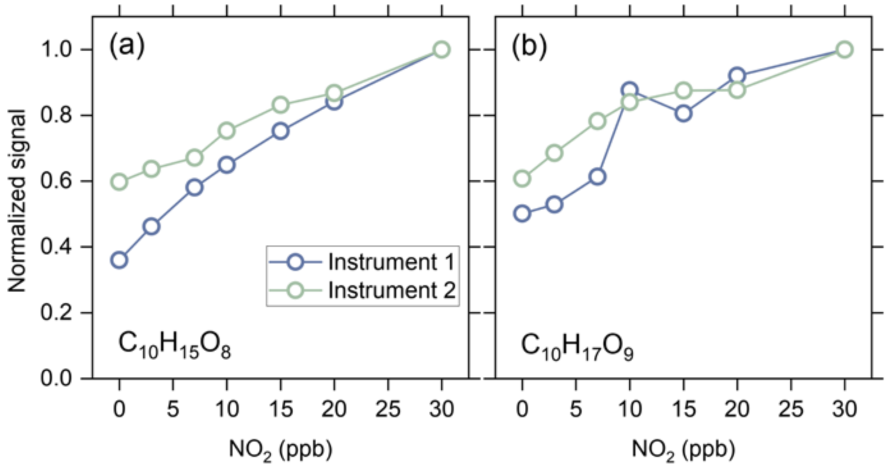

Figure S8 Changes of typical alkyl RO_2 concentration with different NO_2 concentration measured by two nitrate-CIMS under the same experimental conditions (Exps15-21). Instrument 1 is the nitrate-CIMS we used in this study.

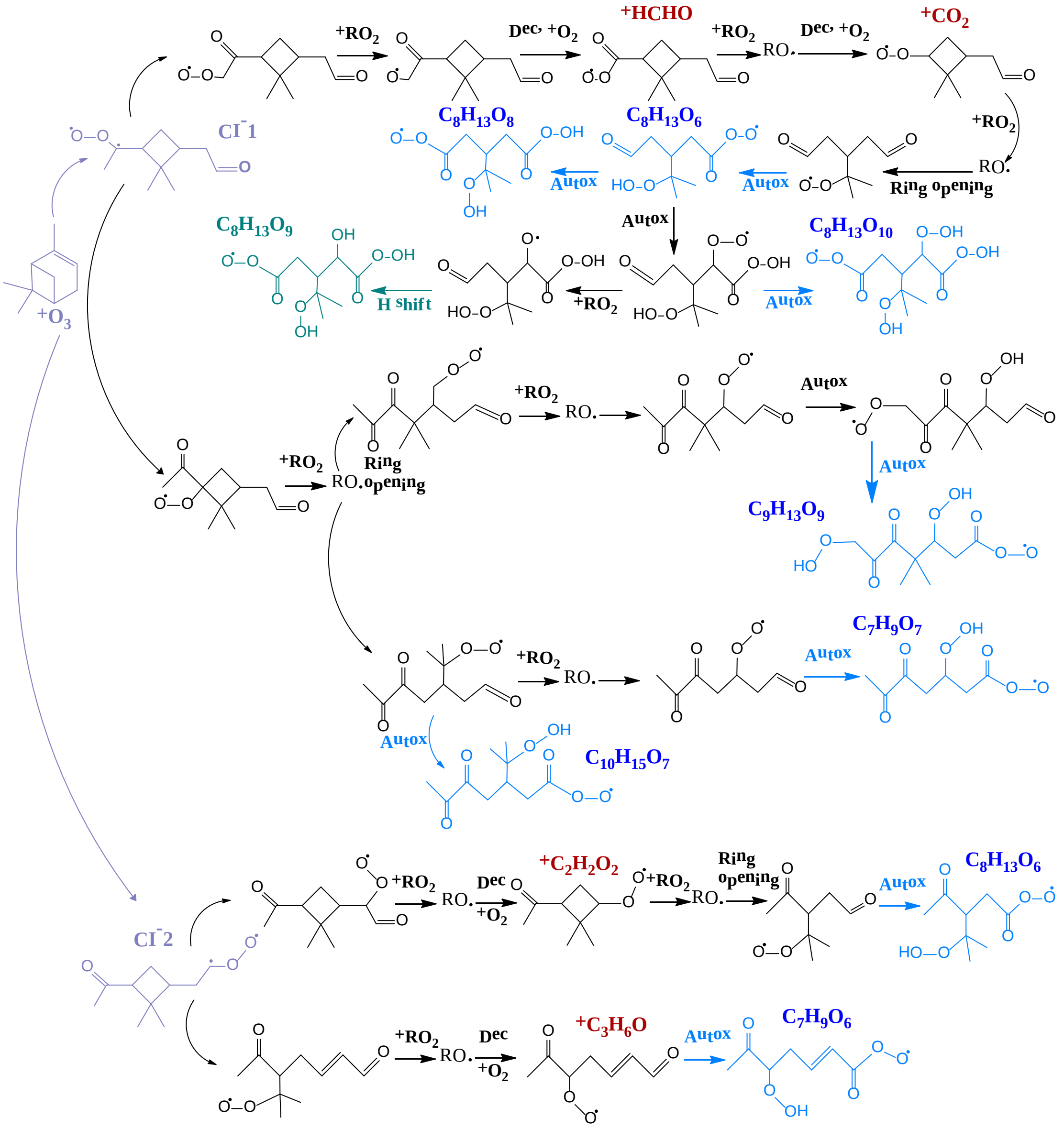

Figure S9 Formation mechanisms of the acyl RO_2 measured in this study.

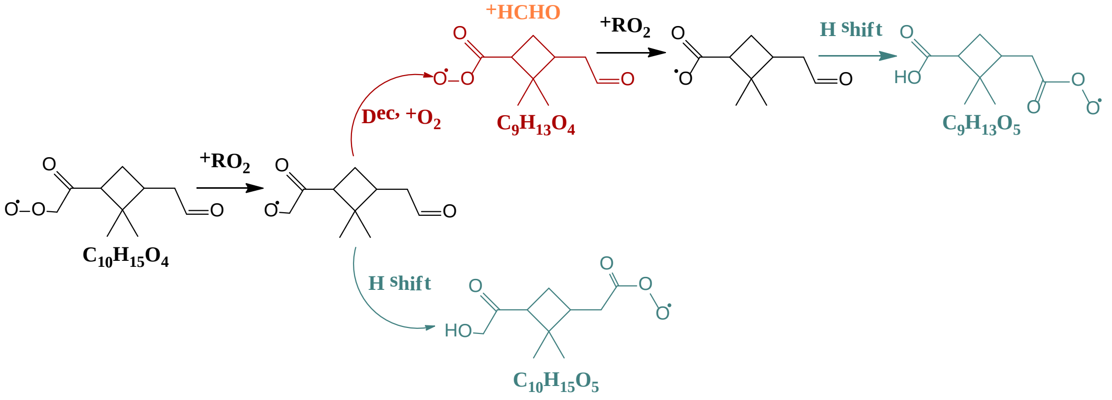

Figure S10 Formation pathways of the acyl RO_2 with oxygen atoms less than 6 in default MCM v3.3.1.

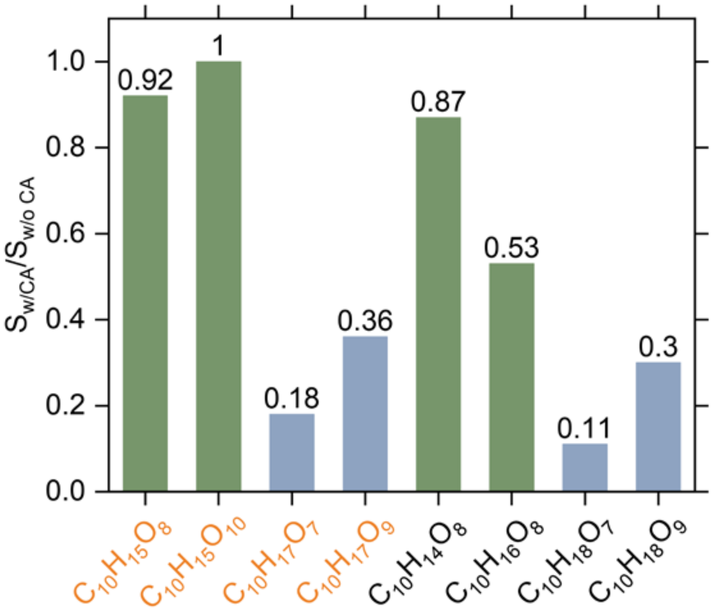

Figure S11 Relative changes in concentration of typical C_{10} RO_2 and HOM monomers due to the addition of 500 ppm cyclohexane (Exp 32), the yellow species are RO_2 radicals.

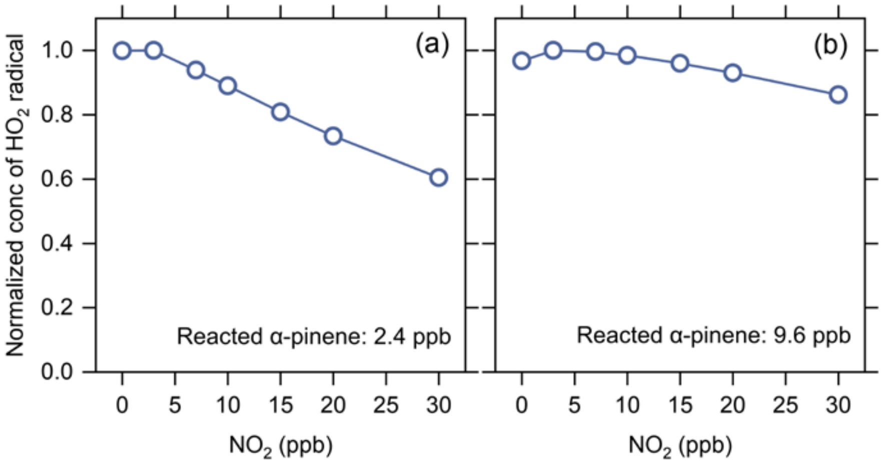

Figure S12 Normalized concentration of the HO_2 radicals as a function of NO_2 concentration under low (2.4 ppb, a) and high (9.6 ppb, b) reacted α-pinene conditions.

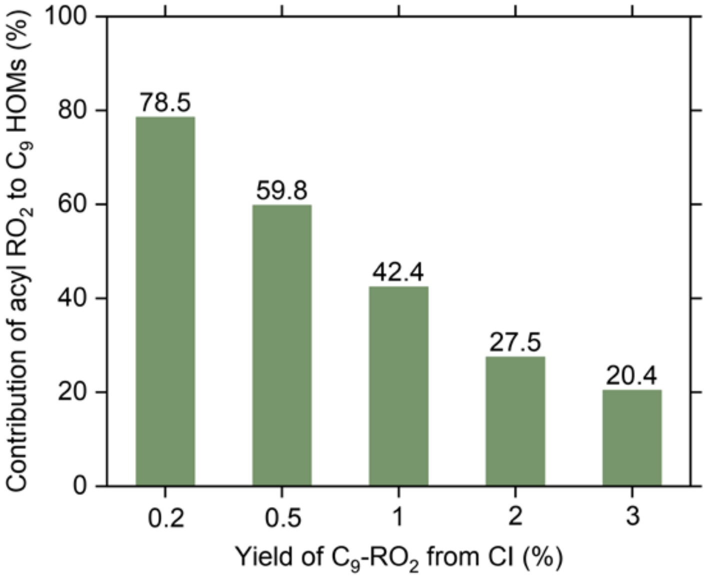

Figure S13 Sensitive analysis of C_9 RO_2 yield from one of the CI to the contribution of C_9 acyl RO_2 related HOMs.

References

Iyer, S., Rissanen, M. P., Valiev, R., Barua, S., Krechmer, J. E., Thornton, J., Ehn, M., and Kurten, T.: Molecular mechanism for rapid autoxidation in alpha-pinene ozonolysis, *Nat. Commun.*, 12, 878, https://doi.org/10.1038/s41467-021-21172-w, 2021.

Zhao, Y., Thornton, J. A., and Pye, H. O. T.: Quantitative constraints on autoxidation and dimer formation from direct probing of monoterpene-derived peroxy radical chemistry, *Proc. Natl. Acad. Sci. U. S. A.* , 115, 12142-12147, https://doi.org/10.1073/pnas.1812147115, 2018.