Supplement of

Nocturnal Atmospheric Synergistic Oxidation Reduces the Formation of Low-volatility Organic Compounds from Biogenic Emissions

Han Zang[1], Zekun Luo[1], Chenxi Li[1], Ziyue Li[1], Dandan Huang[2,*], Yue Zhao[1,*]

[1]School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China

[2]Shanghai Academy of Environmental Sciences, Shanghai, 200233, China

[*]Correspondence: Yue Zhao (yuezhao20@sjtu.edu.cn); Dandan Huang (huangdd@saes.sh.cn);

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Table S1. Summary of experimental conditions.

Exp #	α-pinene Conc	O_3 Conc	NO_3 Conc (simulated)	N_2O_5 Conc (simulated)	Reacted α-pinene
1	100	394	-	-	4.20
2	200	394	-	-	8.37
3	300	394	-	-	12.51
4	400	394	-	-	16.63
5	500	394	-	-	20.72
6	100	394	2.74	11.51	14.11
7	200	394	2.74	11.51	18.41
8	300	394	2.74	11.51	22.59
9	400	394	2.74	11.51	26.73
10	500	394	2.74	11.51	30.84
11*	100	397	-	-	2.26
12*	100	397	2.74	11.51	12.39
13[#]	300	270	-	-	54.22
14[#]	300	270	2.00	12.00	65.88

Note: All species concentrations are in ppb.

*100 ppm cyclohexane was added as an OH scavenger in these experiments.

[#]SOA formation experiments. The total air flow in the reactor was 5 L min^{-1} and the residence time was 180 seconds.

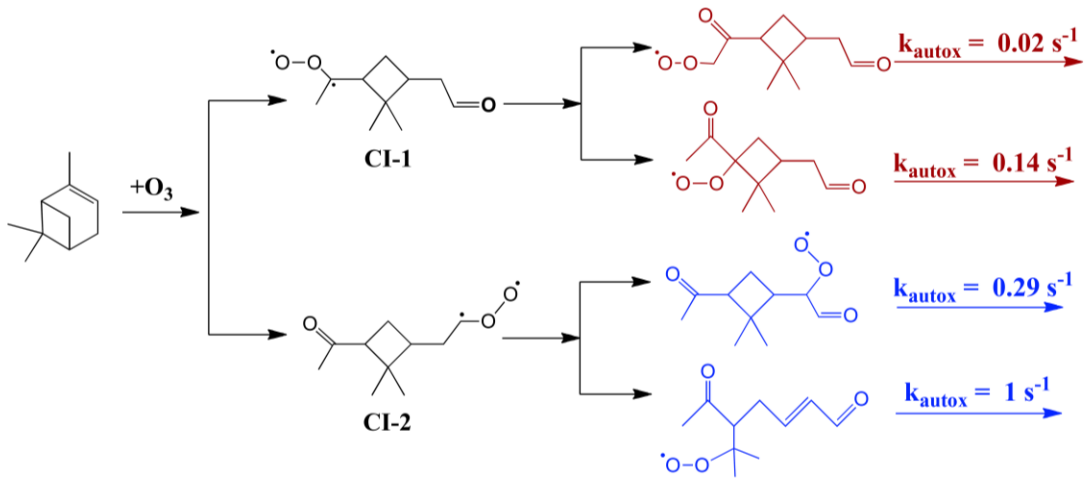
Table S2. Observed molecular formula, molar mass, and saturation vapor concentration of HOM-ONs in the O_3 + NO_3 regime.

Molecular formula	Molar mass (g mol^{-1})	Saturation vapor conc., C^* (μg m^{-3})	Molecular formula	Molar mass (g mol^{-1})	Saturation vapor conc., C^* (μg m^{-3})
C7H9NO8	235.0328	2.114784	C18H21NO6	347.1368	0.563055
C7H13NO11	287.0488	-1.75213	C18H23NO6	349.1525	0.563055
C8H11NO5	201.0637	5.000419	C18H21NO7	363.1318	-0.09533
C8H15NO10	285.0696	-0.44685	C18H23NO7	365.1474	-0.09533
C8H13NO11	299.0488	-1.73627	C18H27NO7	369.1787	-0.09533
C8H13NO12	315.0437	-3.06641	C18H33NO8	391.2206	-0.83685
C8H15NO12	317.0594	-3.06641	C18H35NO8	393.2362	-0.83685
C9H11NO8	261.0484	1.793846	C18H21NO9	395.1216	-1.65153
C9H11NO9	277.0433	0.663671	C18H29NO9	403.1842	-1.65153
C9H17NO9	283.0903	0.663671	C18H21NO10	411.1165	-2.53093
C9H17NO11	315.0801	-1.77195	C18H23NO10	413.1322	-2.53093
C9H15NO13	345.0543	-4.38285	C18H31NO10	421.1948	-2.53093
C10H15NO5	229.095	4.300331	C18H23NO11	429.1271	-3.46785
C10H15NO6	245.0899	3.500375	C18H29NO11	435.174	-3.46785
C10H15NO7	261.0848	2.586279	C18H21NO12	443.1063	-4.45614
C10H13NO8	275.0641	1.579446	C18H23NO12	445.122	-4.45614
C10H15NO8	277.0798	1.579446	C18H29NO12	451.169	-4.45614
C10H17NO8	279.0954	1.579446	C18H21NO13	459.1013	-5.49047
C10H13NO9	291.059	0.49624	C18H29NO13	467.1639	-5.49047
C10H15NO9	293.0747	0.49624	C18H21NO14	475.0962	-6.56625
C10H19NO9	297.106	0.49624	C19H31NO5	353.2202	0.708682
C10H13NO10	307.0539	-0.65061	C19H23NO7	377.1474	-0.47287
C10H15NO10	309.0696	-0.65061	C19H23NO9	409.1372	-1.98218
C10H17NO10	311.0852	-0.65061	C19H29NO9	415.1842	-1.98218
C10H19NO10	313.1009	-0.65061	C19H31NO10	433.1948	-2.83699
C10H13NO11	323.0488	-1.85105	C19H25NO11	443.1427	-3.74903
C10H15NO11	325.0645	-1.85105	C19H33NO11	451.2053	-3.74903
C10H17NO11	327.0801	-1.85105	C19H23NO12	457.122	-4.71237
C10H15NO12	341.0594	-3.09705	C19H31NO12	465.1846	-4.71237
C10H19NO12	345.0907	-3.09705	C19H33NO12	467.2003	-4.71237
C10H15NO13	357.0543	-4.3821	C19H31NO13	481.1795	-5.72189
C14H21NO8	331.1267	0.488146	C19H35NO13	485.2108	-5.72189
C14H19NO9	345.106	-0.44079	C19H37NO13	487.2264	-5.72189
C14H19NO10	361.1009	-1.43582	C19H33NO14	499.1901	-6.77312
C14H19NO11	377.0958	-2.48832	C19H33NO15	515.185	-7.86214
C14H23NO12	397.122	-3.59112	C20H25NO6	375.1682	-0.23872
C14H19NO13	409.0856	-4.73817	C20H23NO7	389.1474	-0.85605
C14H19NO14	425.0805	-5.92438	C20H25NO7	391.1631	-0.85605
C14H21NO14	427.0962	-5.92438	C20H25NO8	407.158	-1.55328

C15H17NO7	323.1005	0.994946	C20H27NO8	409.1737	-1.55328
C15H23NO11	393.1271	-2.7078	C20H31NO8	413.2049	-1.55328
C15H25NO13	427.1325	-4.89625	C20H33NO8	415.2206	-1.55328
C15H23NO14	441.1118	-6.05289	C20H27NO9	425.1686	-2.32154
C15H23NO16	473.1016	-8.46949	C20H29NO9	427.1842	-2.32154
C16H19NO7	337.1161	0.639584	C20H31NO9	429.1999	-2.32154
C16H21NO7	339.1318	0.639584	C20H27NO10	441.1635	-3.1532
C16H19NO8	353.111	-0.15311	C20H29NO10	443.1791	-3.1532
C16H27NO8	361.1737	-0.15311	C20H31NO10	445.1948	-3.1532
C16H19NO9	369.106	-1.02087	C20H33NO10	447.2104	-3.1532
C16H23NO9	373.1372	-1.02087	C20H31NO11	461.1897	-4.04171
C16H27NO10	393.1635	-1.95432	C20H33NO11	463.2053	-4.04171
C16H27NO15	473.1381	-7.36903	C20H35NO11	465.221	-4.04171
C17H21NO6	335.1368	0.957198	C20H29NO12	475.169	-4.98139
C17H21NO7	351.1318	0.275791	C20H31NO12	477.1846	-4.98139
C17H21NO8	367.1267	-0.49036	C20H33NO12	479.2003	-4.98139
C17H27NO8	373.1737	-0.49036	C20H31NO13	493.1795	-5.96728
C17H21NO9	383.1216	-1.33067	C20H33NO13	495.1951	-5.96728
C17H21NO10	399.1165	-2.23623	C20H31NO14	509.1744	-6.99505
C17H25NO10	403.1478	-2.23623	C20H33NO14	511.1901	-6.99505
C17H27NO11	421.1584	-3.19952	C20H39NO14	517.237	-6.99505
C17H31NO14	473.1744	-6.37603	C20H31NO15	525.1693	-8.0609

Table S3. Molecular formula and molar mass of highly oxygenated $^{NO3}RO_2$ and $C_xH_yO_z$-HOM monomers which have very close molar masses.

$^{NO3}RO_2$	molar mass (g mol^{-1})	CHO-HOM	molar mass (g mol^{-1})
C10H16NO6	246.10	C10H14O7	246.07
C10H16NO7	262.09	C10H14O8	262.07
C10H16NO8	278.09	C10H14O9	278.06
C10H16NO9	294.08	C10H14O10	294.06
C10H16NO10	310.08	C10H14O11	310.05



Scheme S1. Simplified pathways leading to the formation of four different primary ${}^{CI}RO_2$ radicals.

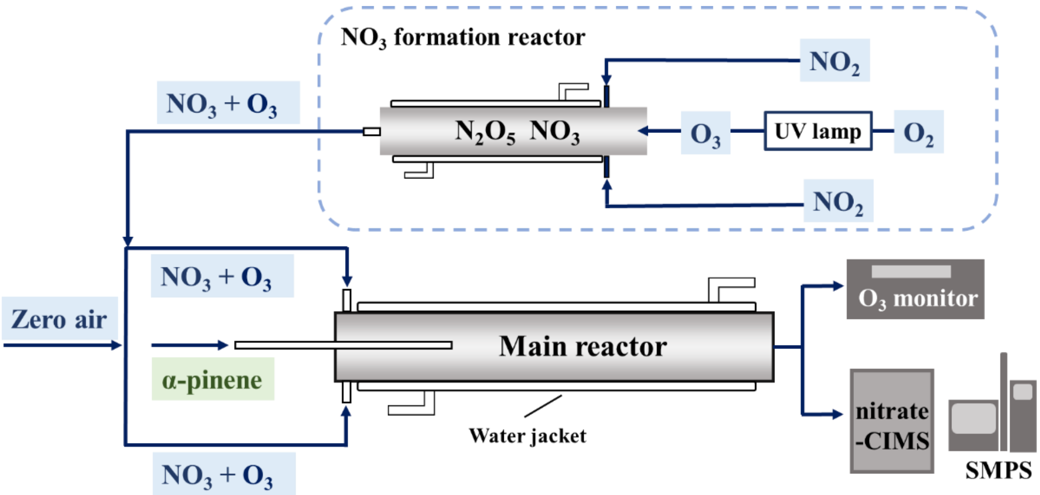


Figure S1. Schematic diagram of the flow tube system used for synergistic oxidation experiments.

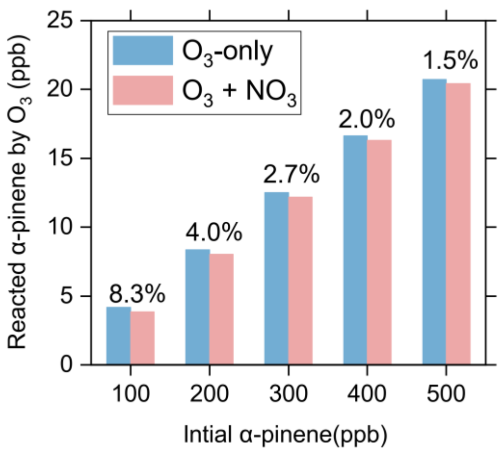


Figure S2. Simulated reacted α-pinene by O_3 as a function of initial α-pinene concentrations in O_3-only and O_3 + NO_3 regimes (Exps 1-10).

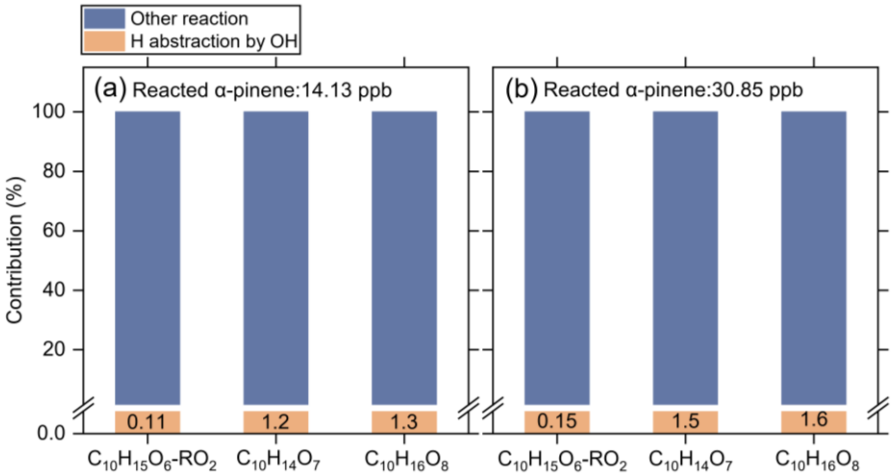


Figure S3. Simulated contributions of the H-abstraction pathways by OH radicals (yellow) and OH-addition and ozonolysis pathways (blue) to the formation of typical HOMs under different reacted α-pinene conditions. The cross-reaction rate constant was set to 1×10^{-13} cm^3 $molecule^{-1}$ s^{-1} for the primary $C_{10}H_{15}O_2$-RO_2 and 1×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for the more oxygenated RO_2. The reaction rate of RO_2 + NO_3 is the same as default value in MCM v3.3.1.

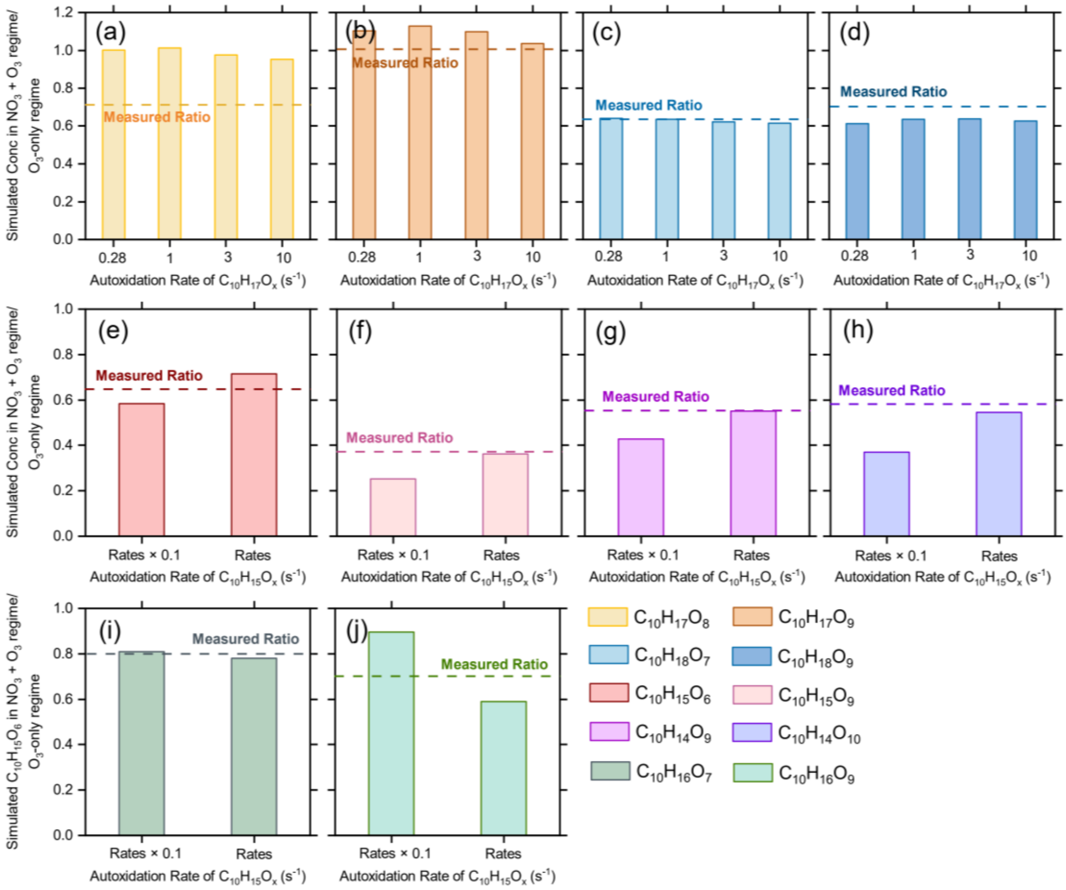


Figure S4 Sensitivity analysis of the autoxidation rate of $^{OH}RO_2$ and $^{CI}RO_2$. The cross-reaction rates of $^{NO3}RO_2$ + $^{CI}RO_2$ and $^{NO3}RO_2$ + $^{OH}RO_2$ were set to 1×10^{-12} cm^3 $molecule^{-1}$ s^{-1} and 1×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, respectively. The autoxidation rate of $^{OH}RO_2$ varies from 0.28 – 10 s^{-1}, and the autoxidation rates of the four different $^{CI}RO_2$ are lowered by a factor of 10.

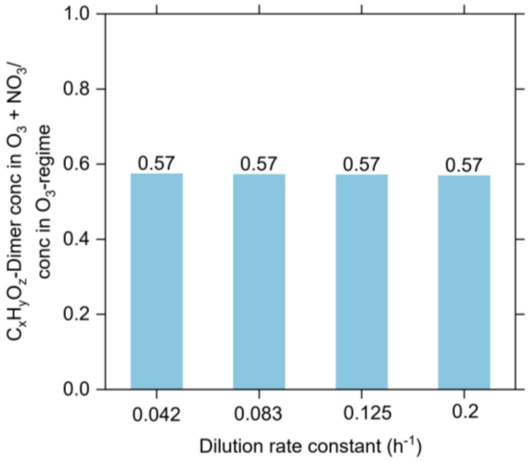


Figure S5 Influence of the dilution rate constant on the reduction of $C_xH_yO_z$-HOM dimers in the O_3 + NO_3 synergistic regime.

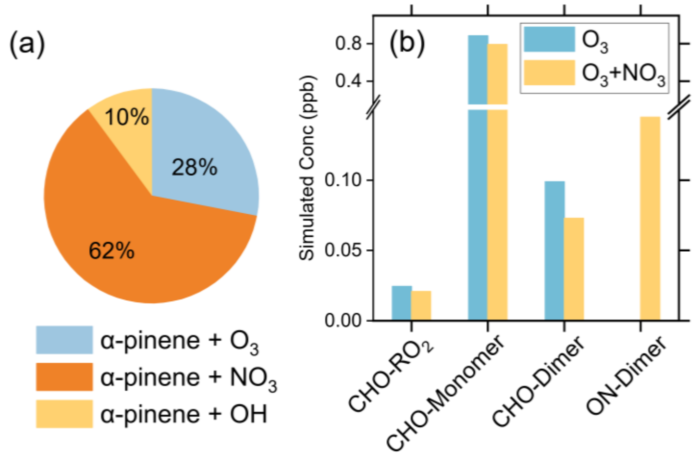


Figure S6 Simulated (a) contributions of different loss pathways of α-pinene by different oxidants and (b) concentration of $C_xH_yO_z$-HOMs and ONs in the absence and presence of NO_3 radicals under typical nighttime ambient conditions with an OH concentration of 5 × 10^5 molecules cm^{-3} (Stone et al., 2012;Geyer et al., 2003).

References:

Geyer, A., Bächmann, K., Hofzumahaus, A., Holland, F., Konrad, S., Klüpfel, T., Pätz, H. W., Perner, D., Mihelcic, D., Schäfer, H. J., Volz-Thomas, A., and Platt, U.: Nighttime formation of peroxy and hydroxyl radicals during the BERLIOZ campaign: Observations and modeling studies, J. Geophys. Res.-Atmos., 108, 10.1029/2001jd000656, 2003.

Stone, D., Whalley, L. K., and Heard, D. E.: Tropospheric OH and HO_2 radicals: field measurements and model comparisons, Chem. Soc. Rev., 41, 10.1039/c2cs35140d, 2012.