Supplement to

Impact of the chemical regimes on highly oxygenated molecule and secondary organic aerosol formation: Effects of varying the importance of NO, $HO_2\cdot$, $RO_2\cdot$ reactions on α-pinene photooxidation products

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S1 Scheme of internal $RO_2\cdot$ termination pathway

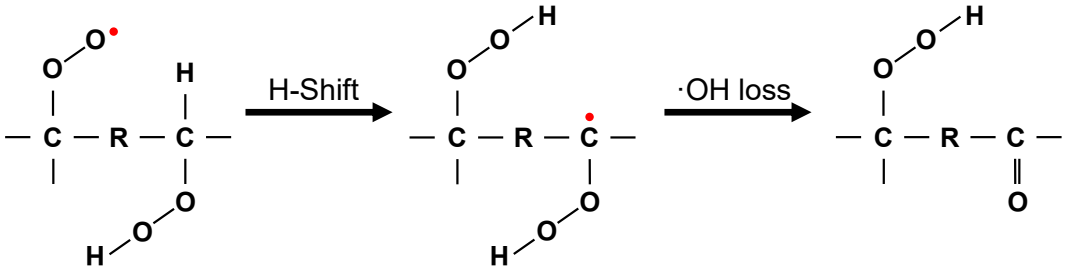

Figure S1 Internal $RO_2\cdot$ termination scheme with carbonyl formation and ·OH loss from a hydroperoxide group.

S2 Correction of drift in NO_x monitor signal

In two experiments with NO (experiment number 3 and 4, for explanation of the experiment numbers see **Tab. S4**) the NO_x monitor (NCLD899, Eco Physics GmbH with a home-built photolytic converter) measurement in the NO inflow was off compared to the expectation. Measurement of the NO inflow in exactly the same set-up (same gas bottle, flow controllers and flow settings) yielded the expected measured concentration in other experiments. Therefore, we decided to correct the NO_x measurement data for these two experiments by multiplication with a correction factor. The correction factor was determined individually for each steady state from the expected NO concentration in the inflow divided by the NO concentration measured in the inflow.

S3 Identified compounds in NO_3-CIMS

Table S1 Peaklist NO_3-MION-CIMS for base and high HO_2· cases. All compounds were detected as clusters with $(NO_3)^-$. The table is sorted into fragments, monomers, and accretion products. Some compounds were just assignable in certain experiments, this is indicated by the superscript, no superscript indicated that the compound was assigned in all experiments. For experiment numbers see Tab. S4.

Fragments		Monomers	Accretion products			
$C_5H_6O_4$[1]	$C_8H_{10}O_6$	$C_{10}H_{14}O_5$	$C_{14}H_{20}O_9$	$C_{17}H_{24}O_7$	$C_{19}H_{26}O_8$[1,2,5]	$C_{20}H_{28}O_9$
$C_5H_6O_5$	$C_8H_{10}O_7$	$C_{10}H_{14}O_6$	$C_{14}H_{22}O_{10}$	$C_{17}H_{24}O_9$	$C_{19}H_{28}O_7$	$C_{20}H_{28}O_{11}$
$C_5H_6O_6$	$C_8H_{10}O_{10}$[1]	$C_{10}H_{14}O_7$	$C_{14}H_{22}O_{11}$[1,2,5]	$C_{17}H_{24}O_{10}$[1,2,5]	$C_{19}H_{28}O_8$	$C_{20}H_{30}O_6$
$C_5H_6O_7$	$C_8H_{12}O_5$[1,2,4]	$C_{10}H_{14}O_8$	$C_{14}H_{26}O_{11}$	$C_{17}H_{24}O_{11}$	$C_{19}H_{28}O_9$	$C_{20}H_{30}O_7$
$C_5H_6O_8$[2,5]	$C_8H_{12}O_6$	$C_{10}H_{14}O_9$		$C_{17}H_{24}O_{13}$[1,2,5]	$C_{19}H_{28}O_{10}$	$C_{20}H_{30}O_8$
$C_5H_7O_8$	$C_8H_{12}O_7$	$C_{10}H_{14}O_{10}$	$C_{15}H_{20}O_{14}$[1]	$C_{17}H_{26}O_8$	$C_{19}H_{28}O_{11}$	$C_{20}H_{30}O_9$
$C_5H_8O_7$	$C_8H_{12}O_8$	$C_{10}H_{14}O_{11}$	$C_{15}H_{22}O_9$	$C_{17}H_{26}O_9$	$C_{19}H_{28}O_{12}$[1,2]	$C_{20}H_{30}O_{10}$
	$C_8H_{12}O_9$		$C_{15}H_{22}O_{10}$	$C_{17}H_{26}O_{10}$	$C_{19}H_{28}O_{13}$[1,2,4]	$C_{20}H_{30}O_{11}$
$C_6H_6O_4$[1,4,5]	$C_8H_{13}O_8$	$C_{10}H_{15}O_5$	$C_{15}H_{22}O_{11}$	$C_{17}H_{26}O_{11}$	$C_{19}H_{28}O_{14}$[1,2]	$C_{20}H_{30}O_{12}$
$C_6H_{10}O_5$	$C_8H_{13}O_9$	$C_{10}H_{15}O_6$	$C_{15}H_{22}O_{12}$[1,2,5]	$C_{17}H_{26}O_{12}$	$C_{19}H_{28}O_{15}$[1]	$C_{20}H_{30}O_{13}$
$C_6H_{10}O_6$	$C_8H_{14}O_5$	$C_{10}H_{15}O_7$	$C_{15}H_{22}O_{13}$[1]	$C_{17}H_{26}O_{13}$[1,2]	$C_{19}H_{28}O_{16}$[1,2]	$C_{20}H_{30}O_{14}$
$C_6H_{10}O_7$	$C_8H_{14}O_6$	$C_{10}H_{15}O_8$	$C_{15}H_{22}O_{14}$[1]	$C_{17}H_{26}O_{14}$[1,2,5]	$C_{19}H_{30}O_6$	$C_{20}H_{30}O_{15}$
$C_6H_{12}O_6$[5]	$C_8H_{14}O_7$	$C_{10}H_{15}O_9$	$C_{15}H_{24}O_{13}$[1,2,5]	$C_{17}H_{28}O_8$	$C_{19}H_{30}O_7$	$C_{20}H_{30}O_{16}$
	$C_8H_{14}O_8$	$C_{10}H_{15}O_{10}$	$C_{15}H_{26}O_{10}$[1,2,5]	$C_{17}H_{28}O_9$	$C_{19}H_{30}O_8$	$C_{20}H_{30}O_{17}$[5]
$C_7H_8O_5$[4,5]	$C_8H_{14}O_9$	$C_{10}H_{15}O_{11}$		$C_{17}H_{28}O_{10}$	$C_{19}H_{30}O_9$	$C_{20}H_{30}O_{18}$
$C_7H_8O_6$[4]		$C_{10}H_{15}O_{12}$	$C_{16}H_{22}O_9$[1,2,5]	$C_{17}H_{28}O_{11}$	$C_{19}H_{30}O_{10}$	$C_{20}H_{32}O_6$
$C_7H_8O_7$	$C_9H_{12}O_4$[5]		$C_{16}H_{24}O_9$	$C_{17}H_{28}O_{12}$	$C_{19}H_{30}O_{11}$	$C_{20}H_{32}O_7$
$C_7H_8O_8$	$C_9H_{12}O_5$	$C_{10}H_{16}O_3$[5]	$C_{16}H_{24}O_{10}$		$C_{19}H_{30}O_{12}$	$C_{20}H_{32}O_8$
$C_7H_{10}O_5$[1,4,5]	$C_9H_{12}O_6$	$C_{10}H_{16}O_4$	$C_{16}H_{24}O_{11}$	$C_{18}H_{26}O_9$	$C_{19}H_{30}O_{13}$	$C_{20}H_{32}O_9$
$C_7H_{10}O_6$	$C_9H_{12}O_7$	$C_{10}H_{16}O_5$	$C_{16}H_{24}O_{12}$[1,2,5]	$C_{18}H_{26}O_{10}$	$C_{19}H_{30}O_{14}$[1,2,5]	$C_{20}H_{32}O_{10}$
$C_7H_{10}O_7$	$C_9H_{12}O_8$	$C_{10}H_{16}O_6$	$C_{16}H_{26}O_8$	$C_{18}H_{26}O_{11}$	$C_{19}H_{30}O_{15}$[1,2]	$C_{20}H_{32}O_{11}$
$C_7H_{10}O_8$	$C_9H_{12}O_9$	$C_{10}H_{16}O_7$	$C_{16}H_{26}O_9$	$C_{18}H_{26}O_{15}$[1]	$C_{19}H_{30}O_{16}$[1,5]	$C_{20}H_{32}O_{12}$
$C_7H_{10}O_9$[1,2,5]	$C_9H_{12}O_{12}$[2]	$C_{10}H_{16}O_8$	$C_{16}H_{26}O_{10}$	$C_{18}H_{28}O_6$	$C_{19}H_{32}O_7$	$C_{20}H_{32}O_{13}$
$C_7H_{10}O_{10}$	$C_9H_{13}O_9$[1,2,4]	$C_{10}H_{16}O_9$	$C_{16}H_{26}O_{11}$	$C_{18}H_{28}O_8$	$C_{19}H_{32}O_8$	$C_{20}H_{32}O_{14}$
$C_7H_{14}O_5$[1,2,5]	$C_9H_{13}O_{10}$	$C_{10}H_{16}O_{10}$	$C_{16}H_{26}O_{12}$	$C_{18}H_{28}O_9$[1,5]	$C_{19}H_{32}O_9$	$C_{20}H_{32}O_{15}$
$C_7H_{14}O_6$	$C_9H_{14}O_4$	$C_{10}H_{16}O_{11}$	$C_{16}H_{26}O_{13}$[2,5]	$C_{18}H_{28}O_{10}$	$C_{19}H_{32}O_{10}$	$C_{20}H_{34}O_6$
	$C_9H_{14}O_5$		$C_{16}H_{28}O_{18}$[1,2,5]	$C_{18}H_{28}O_{11}$	$C_{19}H_{32}O_{11}$	$C_{20}H_{34}O_7$
	$C_9H_{14}O_6$	$C_{10}H_{17}O_6$		$C_{18}H_{28}O_{12}$[1,2,5]	$C_{19}H_{32}O_{12}$	$C_{20}H_{34}O_8$
	$C_9H_{14}O_7$	$C_{10}H_{17}O_7$		$C_{18}H_{28}O_{13}$	$C_{19}H_{32}O_{13}$[1,5]	$C_{20}H_{34}O_9$
	$C_9H_{14}O_8$	$C_{10}H_{17}O_8$		$C_{18}H_{28}O_{14}$[1,4,5]	$C_{19}H_{32}O_{14}$[1,2,5]	$C_{20}H_{34}O_{10}$
	$C_9H_{14}O_9$	$C_{10}H_{17}O_9$		$C_{18}H_{28}O_{15}$[1,5]		$C_{20}H_{34}O_{11}$
	$C_9H_{14}O_{10}$	$C_{10}H_{17}O_{10}$[1,4]		$C_{18}H_{28}O_{16}$[1,4,5]		$C_{20}H_{34}O_{12}$
	$C_9H_{16}O_5$	$C_{10}H_{17}O_{11}$[4]		$C_{18}H_{30}O_7$		$C_{20}H_{34}O_{13}$
	$C_9H_{16}O_6$			$C_{18}H_{30}O_8$		$C_{20}H_{34}O_{14}$[5]
	$C_9H_{16}O_7$	$C_{10}H_{18}O_4$		$C_{18}H_{30}O_9$		$C_{20}H_{34}O_{16}$[5]
	$C_9H_{16}O_8$	$C_{10}H_{18}O_5$		$C_{18}H_{30}O_{10}$		
		$C_{10}H_{18}O_6$		$C_{18}H_{30}O_{11}$		
		$C_{10}H_{18}O_7$		$C_{18}H_{30}O_{12}$		
		$C_{10}H_{18}O_8$		$C_{18}H_{30}O_{13}$		
		$C_{10}H_{18}O_9$		$C_{18}H_{30}O_{14}$[1,5]		

Table S2 Peaklist NO_3-MION-CIMS for cases with NO (Fragments). All compounds were detected as clusters with $(NO_3)^-$. Some compounds were just assignable in certain experiments, this is indicated by the superscript, no superscript indicated that the compound was assigned in all experiments. For experiment numbers see Tab. S4.

Fragments				
$C_5H_5NO_7$	$C_6H_6N_2O_6$[3,4]	C_7H_6O	$C_8H_{10}O_6$	$C_9H_{12}O_4$[5]
$C_5H_5NO_8$[3,4]			$C_8H_{10}O_7$	$C_9H_{12}O_5$
$C_5H_5NO_9$	$C_6H_6O_4$	$C_7H_7NO_4$	$C_8H_{10}O_{10}$	$C_9H_{12}O_6$
	$C_6H_6O_5$	$C_7H_7NO_6$[5]		$C_9H_{12}O_7$
$C_5H_6O_5$		$C_7H_7NO_8$	$C_8H_{11}NO_6$[3]	$C_9H_{12}O_8$
$C_5H_6O_6$[4,5]	$C_6H_7NO_6$	$C_7H_7NO_9$	$C_8H_{11}NO_7$[5]	$C_9H_{12}O_9$
$C_5H_6O_7$	$C_6H_7NO_8$		$C_8H_{11}NO_8$[3,4]	
$C_5H_6O_8$[3,4]		$C_7H_8O_6$	$C_8H_{11}NO_9$	$C_9H_{13}NO_8$
	$C_6H_8O_6$	$C_7H_8O_7$	$C_8H_{11}NO_{11}$	$C_9H_{13}NO_9$
$C_5H_7NO_6$	$C_6H_8O_7$	$C_7H_8O_8$		$C_9H_{13}NO_{10}$
$C_5H_7NO_7$			$C_8H_{12}O_5$[3,4]	$C_9H_{13}NO_{11}$
$C_5H_7NO_8$	$C_6H_9NO_6$	$C_7H_9NO_6$	$C_8H_{12}O_6$	
$C_5H_7NO_9$	$C_6H_9NO_7$	$C_7H_9NO_7$	$C_8H_{12}O_7$	$C_9H_{13}O_{10}$
$C_5H_7NO_{10}$	$C_6H_9NO_8$	$C_7H_9NO_8$	$C_8H_{12}O_8$	
	$C_6H_9NO_9$	$C_7H_9NO_9$	$C_8H_{12}O_9$	$C_9H_{14}O_4$
$C_5H_8O_5$[5]	$C_6H_9NO_{10}$	$C_7H_9NO_{10}$		$C_9H_{14}O_5$[4,5]
$C_5H_8O_7$		$C_7H_9NO_{11}$	$C_8H_{13}NO_6$	$C_9H_{14}O_6$
	$C_6H_{10}O_5$		$C_8H_{13}NO_7$	$C_9H_{14}O_7$
$C_5H_9NO_6$	$C_6H_{10}O_6$	$C_7H_{10}O_5$[5]	$C_8H_{13}NO_8$	$C_9H_{14}O_8$
	$C_6H_{10}O_7$	$C_7H_{10}O_6$	$C_8H_{13}NO_9$	$C_9H_{14}O_9$
		$C_7H_{10}O_7$	$C_8H_{13}NO_{10}$	$C_9H_{14}O_{10}$
	$C_6H_{11}NO_6$[5]	$C_7H_{10}O_8$	$C_8H_{13}NO_{11}$	
	$C_6H_{11}NO_7$[5]	$C_7H_{10}O_9$		$C_9H_{15}NO_6$[3,5]
	$C_6H_{11}NO_8$[5]	$C_7H_{10}O_{10}$	$C_8H_{13}O_8$	$C_9H_{15}NO_7$[3,5]
	$C_6H_{11}NO_9$[5]			$C_9H_{15}NO_8$
		$C_7H_{11}NO_6$	$C_8H_{14}O_5$	$C_9H_{15}NO_9$
		$C_7H_{11}NO_7$[5]	$C_8H_{14}O_6$	$C_9H_{15}NO_{10}$
		$C_7H_{11}NO_9$	$C_8H_{14}O_7$	
			$C_8H_{14}O_8$	$C_9H_{16}O_5$
		$C_7H_{12}O_5$	$C_8H_{14}O_9$	$C_9H_{16}O_6$
		$C_7H_{12}O_5$		$C_9H_{16}O_7$
		$C_7H_{13}NO_7$[5]		$C_9H_{16}O_8$
		$C_7H_{14}O_6$[5]		

Table S3 Peaklist NO_3-MION-CIMS for cases with NO (monomers and accretion products). All compounds were detected as clusters with $(NO_3)^-$. Some compounds were just assignable in certain experiments, this is indicated by the superscript, no superscript indicated that the compound was assigned in all experiments. For experiment numbers see Tab. S4.

Monomers		Accretion products		
$C_{10}H_{13}NO_7$	$C_{10}H_{16}O_4$	$C_{14}H_{22}O_{10}$	$C_{18}H_{26}O_9$[5]	$C_{20}H_{28}O_9$
$C_{10}H_{13}NO_8$	$C_{10}H_{16}O_5$		$C_{18}H_{26}O_{10}$[5]	$C_{20}H_{28}O_{11}$
$C_{10}H_{13}NO_9$	$C_{10}H_{16}O_6$	$C_{15}H_{22}O_9$[5]	$C_{18}H_{26}O_{11}$	
$C_{10}H_{13}NO_{10}$	$C_{10}H_{16}O_7$	$C_{15}H_{22}O_{10}$	$C_{18}H_{26}O_{12}$	$C_{20}H_{30}O_6$[5]
$C_{10}H_{13}NO_{11}$	$C_{10}H_{16}O_8$	$C_{15}H_{22}O_{11}$		$C_{20}H_{30}O_7$
$C_{10}H_{13}NO_{12}$	$C_{10}H_{16}O_9$	$C_{15}H_{22}O_{12}$	$C_{18}H_{28}O_8$[4,5]	$C_{20}H_{30}O_8$
	$C_{10}H_{16}O_{10}$	$C_{15}H_{22}O_{13}$[3,4]	$C_{18}H_{28}O_9$	$C_{20}H_{30}O_9$
$C_{10}H_{14}N_2O_9$	$C_{10}H_{16}O_{11}$		$C_{18}H_{28}O_{10}$	$C_{20}H_{30}O_{10}$
$C_{10}H_{14}N_2O_{10}$		$C_{15}H_{24}O_{13}$[3,4]	$C_{18}H_{28}O_{11}$	$C_{20}H_{30}O_{11}$
$C_{10}H_{14}N_2O_{11}$	$C_{10}H_{17}NO_6$[5]		$C_{18}H_{28}O_{12}$	$C_{20}H_{30}O_{12}$
$C_{10}H_{14}N_2O_{12}$	$C_{10}H_{17}NO_7$	$C_{16}H_{24}O_{11}$[5]	$C_{18}H_{28}O_{13}$	$C_{20}H_{30}O_{13}$
$C_{10}H_{14}N_2O_{13}$	$C_{10}H_{17}NO_8$	$C_{16}H_{24}O_{12}$[5]	$C_{18}H_{28}O_{14}$	$C_{20}H_{30}O_{14}$
	$C_{10}H_{17}NO_9$			$C_{20}H_{30}O_{15}$
$C_{10}H_{14}O_5$	$C_{10}H_{17}NO_{10}$	$C_{16}H_{26}O_8$	$C_{18}H_{30}O_7$[5]	$C_{20}H_{30}O_{16}$
$C_{10}H_{14}O_6$	$C_{10}H_{17}NO_{11}$	$C_{16}H_{26}O_9$	$C_{18}H_{30}O_8$[5]	
$C_{10}H_{14}O_7$		$C_{16}H_{26}O_{10}$	$C_{18}H_{30}O_9$	$C_{20}H_{32}O_6$[5]
$C_{10}H_{14}O_8$	$(C_{10}H_{17}O_5)$	$C_{16}H_{26}O_{11}$	$C_{18}H_{30}O_{10}$	$C_{20}H_{32}O_7$
$C_{10}H_{14}O_9$	$(C_{10}H_{17}O_6)$	$C_{16}H_{26}O_{12}$	$C_{18}H_{30}O_{11}$	$C_{20}H_{32}O_8$
$C_{10}H_{14}O_{10}$	$(C_{10}H_{17}O_7)$	$C_{16}H_{26}O_{13}$[5]	$C_{18}H_{30}O_{12}$	$C_{20}H_{32}O_9$
$C_{10}H_{14}O_{11}$	$(C_{10}H_{17}O_8)$		$C_{18}H_{30}O_{13}$	$C_{20}H_{32}O_{10}$
	$(C_{10}H_{17}O_9)$			$C_{20}H_{32}O_{11}$
$C_{10}H_{15}NO_6$	$(C_{10}H_{17}O_{10})$	$C_{17}H_{24}O_9$	$C_{19}H_{28}O_7$[5]	$C_{20}H_{32}O_{12}$
$C_{10}H_{15}NO_7$	$(C_{10}H_{17}O_{11})$	$C_{17}H_{24}O_{10}$	$C_{19}H_{28}O_8$	$C_{20}H_{32}O_{13}$
$C_{10}H_{15}NO_8$		$C_{17}H_{24}O_{11}$[5]	$C_{19}H_{28}O_9$	$C_{20}H_{32}O_{14}$
$C_{10}H_{15}NO_9$	$C_{10}H_{18}N_2O_8$	$C_{17}H_{24}O_{12}$	$C_{19}H_{28}O_{10}$	$C_{20}H_{32}O_{15}$
$C_{10}H_{15}NO_{10}$	$C_{10}H_{18}N_2O_9$	$C_{17}H_{24}O_{13}$[5]	$C_{19}H_{28}O_{11}$	
$C_{10}H_{15}NO_{11}$	$C_{10}H_{18}N_2O_{10}$			$C_{20}H_{34}O_6$[5]
$C_{10}H_{15}NO_{12}$	$C_{10}H_{18}N_2O_{11}$	$C_{17}H_{26}O_8$[5]	$C_{19}H_{30}O_6$	$C_{20}H_{34}O_7$[5]
$C_{10}H_{15}NO_{13}$		$C_{17}H_{26}O_9$	$C_{19}H_{30}O_7$	$C_{20}H_{34}O_8$
$C_{10}H_{15}NO_{14}$	$C_{10}H_{18}O_4$[4,5]	$C_{17}H_{26}O_{10}$	$C_{19}H_{30}O_8$	$C_{20}H_{34}O_9$
	$C_{10}H_{18}O_5$	$C_{17}H_{26}O_{11}$	$C_{19}H_{30}O_9$	$C_{20}H_{34}O_{10}$
$C_{10}H_{15}O_6$	$C_{10}H_{18}O_6$	$C_{17}H_{26}O_{12}$	$C_{19}H_{30}O_{10}$	$C_{20}H_{34}O_{11}$
$C_{10}H_{15}O_7$	$C_{10}H_{18}O_7$	$C_{17}H_{26}O_{14}$	$C_{19}H_{30}O_{11}$	$C_{20}H_{34}O_{12}$
$C_{10}H_{15}O_8$	$C_{10}H_{18}O_8$		$C_{19}H_{30}O_{12}$	$C_{20}H_{34}O_{13}$[5]
$C_{10}H_{15}O_{10}$	$C_{10}H_{18}O_9$	$C_{17}H_{28}O_9$[5]	$C_{19}H_{30}O_{13}$	
		$C_{17}H_{28}O_{10}$	$C_{19}H_{30}O_{14}$	
$C_{10}H_{16}N_2O_7$		$C_{17}H_{28}O_{11}$	$C_{19}H_{30}O_{15}$[5]	
$C_{10}H_{16}N_2O_8$		$C_{17}H_{28}O_{12}$[5]		
$C_{10}H_{16}N_2O_9$			$C_{19}H_{32}O_7$[5]	
$C_{10}H_{16}N_2O_{10}$			$C_{19}H_{32}O_8$[5]	
$C_{10}H_{16}N_2O_{11}$			$C_{19}H_{32}O_9$	
$C_{10}H_{16}N_2O_{12}$			$C_{19}H_{32}O_{10}$	
$C_{10}H_{16}N_2O_{13}$			$C_{19}H_{32}O_{11}$	
			$C_{19}H_{32}O_{12}$	
			$C_{19}H_{32}O_{13}$[5]	

S4 HOM-RO_2· detection with NO_3-LTOF-CIMS in systems with high RO_2·+NO

At high importance of RO_2·+NO the detection of HOM-RO_2· with the utilized NO_3-LTOF-CIMS had higher uncertainties due to two factors. Firstly, in the mass spectrum the peaks of the HOM-RO_2· compounds can be found at the same nominal m/Q ratios as the peaks of different ON products. Both are found at odd m/Q ratios, which in the base and high HO_2· case had little contribution besides HOM-RO_2· (only ^{13}C-isotope peaks of closed-shell products). The resolution of the mass spectrum was not sufficient to fully separate the ON species and the HOM-RO_2· as shown on the example in **Fig. S2**.

Secondly, the strong reduction in the HOM-RO_2· signal led to low signal levels, in some cases even close or below the detection level. The low signals were an issue especially in the $C_{10}H_{17}O_x$· family, which already had low signals in the base case. The combination of small signals with assignment on the shoulder of an often much larger product peak led to high uncertainties in the determined HOM-RO_2· levels.

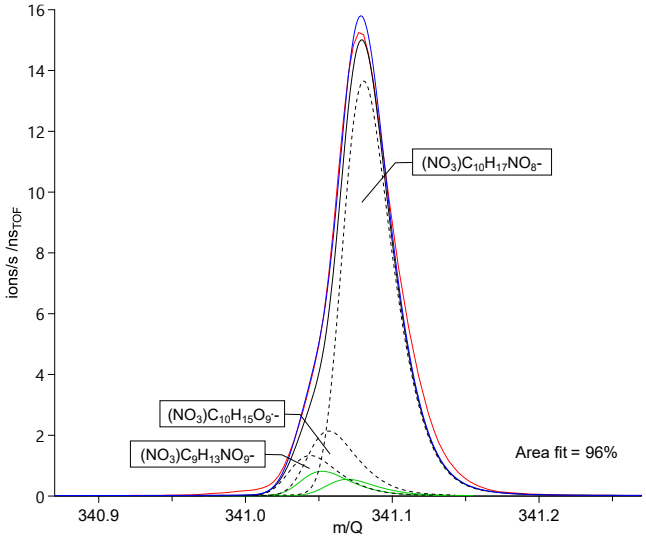

Figure S2 Peak assignment of $C_{10}H_{15}O_9$· between organic nitrate compounds at middle NO level. Red line shows peak shape. Dashed lines show calculated individual compound peaks, black line is fit of assigned compounds. Green lines are ^{13}C-isotope peaks, blue line is the fit of assigned compounds including ^{13}C-isotopes.

S5 Details for box model calculations and modeled HO_2· and RO_2· sum concentrations

Two additional important input parameters for the box model were the ·OH background reactivity (·OH loss in the absence of any VOC) and the wall loss of HO_2· and RO_2·. No product species wall loss was implemented as it is assumed that the product species included in the MCM are too volatile to have significant wall losses. A detailed description of the determination of wall loss and ·OH background reactivity can be found in the Supplement of Baker et al. (2024) in Sec. S3.

Table S4 Overview of modeled HO_2·, RO_2· and NO concentrations in all experiments. Experiments are seperated by number and phase (particle-free or seeded)

Case description	Exp. nr.	Particle-free experiment phase			Seeded experiment phase		
		HO_2· (cm^{-3})	RO_2· (cm^{-3})	NO (cm^{-3})	HO_2· (cm^{-3})	RO_2· (cm^{-3})	NO (cm^{-3})
Base	1	$3.8 \cdot 10^7$	$6.0 \cdot 10^9$	0	-	-	-
	2	$4.7 \cdot 10^7$	$6.9 \cdot 10^9$	0	$4.6 \cdot 10^7$	$6.8 \cdot 10^9$	0
	3	$5.7 \cdot 10^7$	$7.5 \cdot 10^9$	0	-	-	-
	4	-	-	-	$4.4 \cdot 10^7$	$6.3 \cdot 10^9$	0
	5	$3.7 \cdot 10^7$	$5.0 \cdot 10^9$	0	$3.6 \cdot 10^7$	$4.7 \cdot 10^9$	0
High HO_2·	1	$1.2 \cdot 10^9$	$1.9 \cdot 10^9$	0	-	-	-
	2	$1.5 \cdot 10^9$	$1.9 \cdot 10^9$	0	$1.5 \cdot 10^9$	$2.0 \cdot 10^9$	0
	4	-	-	-	$1.7 \cdot 10^9$	$1.7 \cdot 10^9$	0
Low NO	3	$1.7 \cdot 10^8$	$4.6 \cdot 10^9$	$7.6 \cdot 10^8$ (0.03 ppbv)	$1.8 \cdot 10^8$	$4.2 \cdot 10^9$	$8.3 \cdot 10^8$ (0.03 ppbv)
Middle NO	3	$3.7 \cdot 10^8$	$1.8 \cdot 10^9$	$4.3 \cdot 10^9$ (0.17 ppbv)	$3.6 \cdot 10^8$	$1.7 \cdot 10^9$	$4.6 \cdot 10^9$ (0.18 ppbv)
High NO	3	$2.7 \cdot 10^8$	$6.7 \cdot 10^8$	$1.8 \cdot 10^{10}$ (0.71 ppbv)	$2.7 \cdot 10^8$	$6.7 \cdot 10^8$	$1.8 \cdot 10^{10}$ (0.71 ppbv)
Middle NO, high HO_2·	4	$1.9 \cdot 10^9$	$8.9 \cdot 10^8$	$4.8 \cdot 10^9$ (0.19 ppbv)	$1.9 \cdot 10^9$	$1.0 \cdot 10^9$	$4.5 \cdot 10^9$ (0.18 ppbv)
Intermediate-high NO, high HO_2·	4	$1.6 \cdot 10^9$	$6.5 \cdot 10^8$	$1.1 \cdot 10^{10}$ (0.43 ppbv)	$1.6 \cdot 10^9$	$6.9 \cdot 10^8$	$1.1 \cdot 10^{10}$ (0.42 ppbv)
High NO, high HO_2·	4	$1.3 \cdot 10^9$	$5.2 \cdot 10^8$	$1.6 \cdot 10^{10}$ (0.63 ppbv)	$1.3 \cdot 10^9$	$5.6 \cdot 10^8$	$1.6 \cdot 10^{10}$ (0.62 ppbv)
	5	$1.2 \cdot 10^9$	$4.2 \cdot 10^8$	$1.4 \cdot 10^{10}$ (0.57 ppbv)	$1.2 \cdot 10^9$	$4.9 \cdot 10^8$	$1.4 \cdot 10^{10}$ (0.55 ppbv)

S6 Overview of information for classification of the chemical regime

Table S5 Distribution between RO_2· reaction with HO_2·, NO and RO_2· and overall bimolecular reaction rate as averages for all utilized steady states

Case description	NO steady-state concentration	Contribution to bimolecular reactions			(Pseudo) first order bimolecular reaction rate
		HO_2·	NO	RO_2·	
Base	-	3 %	-	97 %	0.04 s^{-1}
High HO_2·	-	80 %	-	20 %	0.05 s^{-1}
Low NO	0.1 ppbv	12 %	21 %	67 %	0.03 s^{-1}
Middle NO	0.2 ppbv	15 %	70 %	15 %	0.06 s^{-1}
High NO	0.5 ppbv	3 %	95 %	2 %	0.17 s^{-1}
Middle NO, high HO_2·	0.2 ppbv	50 %	45 %	5 %	0.09 s^{-1}
Intermediate-high NO, high HO_2·	0.3 ppbv	28 %	70 %	2 %	0.14 s^{-1}
High NO, high HO_2·	0.4 ppbv	18 %	80 %	2 %	0.17 s^{-1}

S7 ON-HOM-Mon containing two nitrogen

In the HOM-Mon class ON containing two nitrogen atoms were observed, i.e. $C_{10}H_{14}N_2O_z$, $C_{10}H_{16}N_2O_z$ and $C_{10}H_{18}N_2O_z$. Such observations could be due to ON-HOM clustering with dimer reagent ions in the CIMS ($NO_3 \cdot HNO_3$, for example $(C_{10}H_{17}NO_{z-3} \cdot HNO_3 \cdot NO_3)^-$ pretending $(C_{10}H_{18}N_2O_z \cdot NO_3)^-$. No such clusters with reagent ion dimers were observed in the NO_x-free system, because only the NO_3^- ions are guided into the ion molecule reaction zone of the inlet, but HNO_3 becomes available in the ion molecule reaction zone in NO_x experiments due to its production in the chamber. To exclude such CIMS measurement effects the timeseries of the ON-HOM with two nitrogen atoms were compared to the respective ON products with one nitrogen (comparison of $C_{10}H_yN_2O_z$ to $C_{10}H_{(y-1)}NO_{(z-3)}$). The 1-N and 2-N compounds showed clearly different temporal behavior during the experiment, leading to the conclusion that the observation of ON-HOM with two nitrogen atoms was not due to clustering of ON-HOM with dimer reagent ions ($NO_3 \cdot HNO_3$).

ON with two nitrogen containing groups contributed maximally 11 % to the overall ON signal, but their presence indicates that in specific cases 1-N ON-HOM can undergo decay or a second ·OH attack and terminate a second time with NO. However, no nitrogen containing HOM-Acc products could be identified, which would be expected if nitrogen containing HOM-RO_2· are formed in significant concentrations. Either specific formation pathways led to the formation of the observed ON with two nitrogen atoms or the concentration of nitrogen containing HOM-Acc was too small to be detected.

S8 Effect of alkoxy-peroxy step on ON product contribution

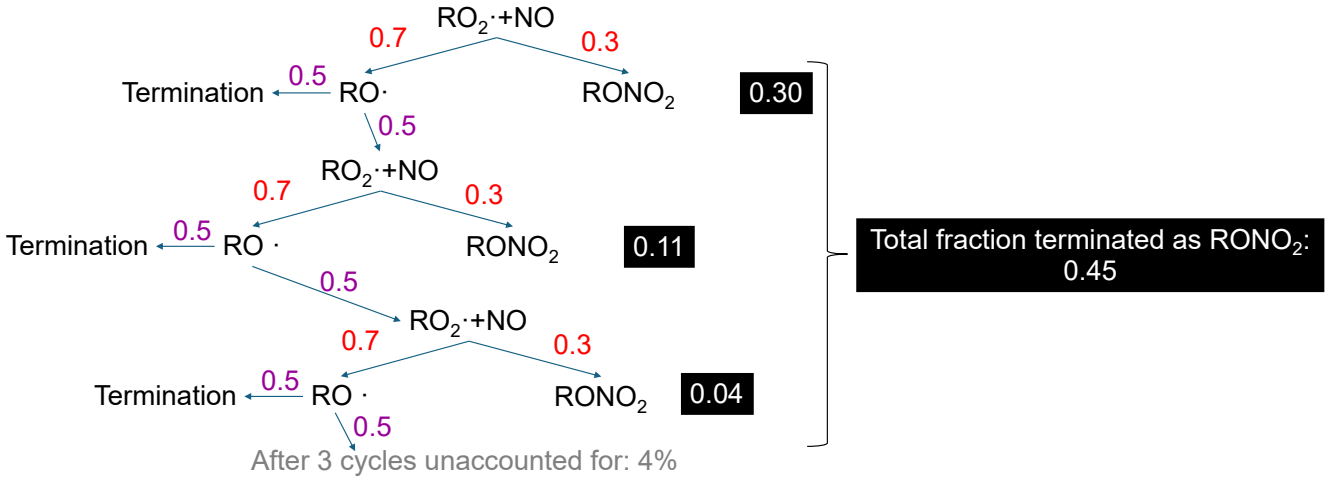

Figure S3 Simple scheme calculating the contribution of $RONO_2$ (shown in black boxes) assuming a 0.3 branching ratio of RO_2·+NO into $RONO_2$ formation and a 0.5 branching ratio of RO· into an alkoxy-peroxy step. Branching ratios based on MCM v3.3.1 (Jenkin et al., 1997; Saunders et al., 2003) and Kang et al. (2025)

S9 Change in HOM-Frag formation as a function of the calculated generic RO_2·+RO_2· and RO_2·+NO reaction rate

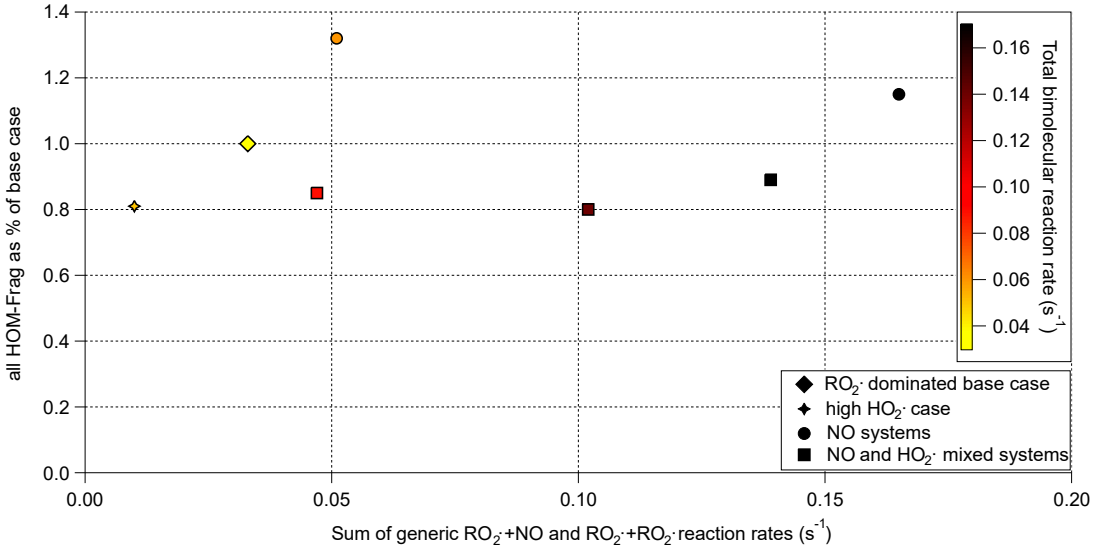

Figure S4 Relative change in the HOM-Frag sum in comparison to the base case as a function of the bimolecular reaction rate for RO· forming pathways (RO_2·+RO_2· and RO_2·+NO). Color scale indicates total bimolecular reaction rate.

S10 Importance of HOM-Frag in the pure NO system

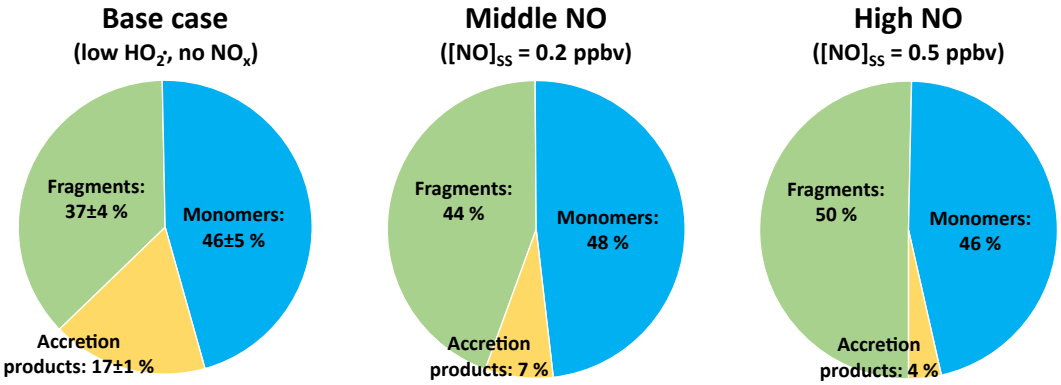

Figure S5 Relative contribution of the different HOM product classes in the pure NO system

Figure S5 and **Fig. S6** show a clear increase in concentration and contribution of HOM-Frag products with increasing NO, which is a clear indication of increased alkoxy radical formation. A more detailed breakdown of the changes in the HOM-Frag grouped by carbon number (non-ON and ON HOM-Frag) can be found in **Fig. S6a)**. The graph shows that fragments with smaller carbon numbers (C_5-C_7) increased in the presence of NO. This fits well to a stepwise fragmentation process as implemented in the MCM chemistry (Jenkin et al., 1997; Saunders et al., 2003) and agrees with the findings of the high HO_2 case (Baker et al 2024).

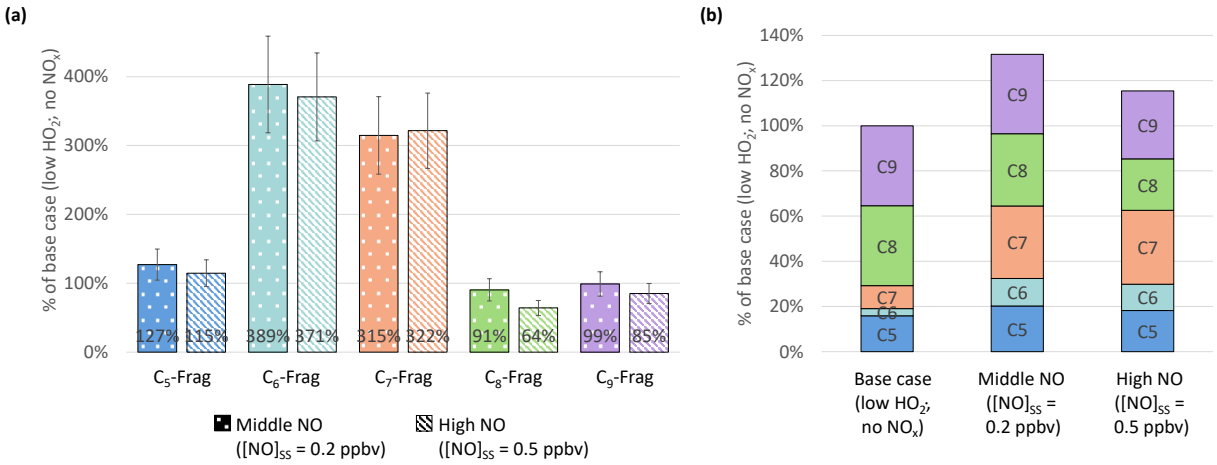

Figure S6 Behavior of HOM-Frag groups in system with NO a) Overview of relative change in HOM-Frag groups detected in NO_3-CIMS at the two NO levels compared to NO_x-free case in unseeded system b) Contribution of each HOM-Frag group in relation to the base case (contribution of each group multiplied with overall relative change compared to base case.) All data normalized to α-pinene ·OH turnover.

The C_8- and C_9-HOM-Frag groups decreased with increasing NO. Besides the C_7-HOM-Frag group, all groups slightly decreased at high NO compared to middle NO. The C_6- and C_7-HOM-Frag groups had the largest increase with NO, though the large relative increase in C_6-HOM-Frag has to be judged in context of the small contribution of C_6-HOM-Frag in general. **Fig. S6b)** visualizes the importance of the different HOM-Frag groups in a stacked bar chart, showing that even though the C_6-HOM-Frag group had the largest relative increase compared to the base case, its importance was still minor.

The contribution of C_6 was only around 3 % in the base case and increased to around 10 % with NO in the system. **Fig. S6b)** also shows that the most significant shift in contribution was the increase in importance of C_7-HOM-Frag.

S11 Ratios of $C_{10}H_{17}O_x\cdot$ and $C_{10}H_{15}O_x\cdot$ products as a function of $RO_2\cdot$+NO importance

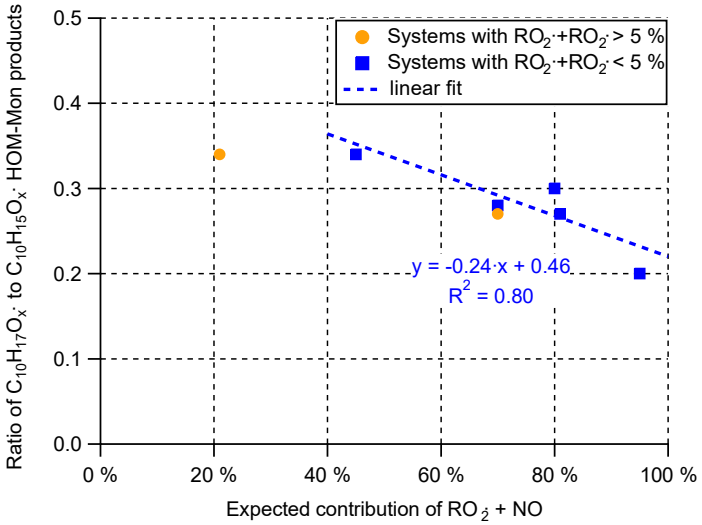

Figure S7 Ratio of $C_{10}H_{17}O_x$ products (sum of $C_{10}H_{18}O_z$ and $C_{10}H_{17}NO_z$) to $C_{10}H_{15}O_x\cdot$ products (sum of $C_{10}H_{14}O_z$, $C_{10}H_{16}O_z$ and $C_{10}H_{15}NO_z$) products as a function of the expected RO_2+NO contribution to the total bimolecular reaction rate. $C_{10}H_{16}O_z$ stemming from internal termination of $C_{10}H_{17}O_x\cdot$ are misassigned. Data set is separated by expected importance of $RO_2\cdot$+$RO_2\cdot$ reactions (threshold 5 %). Linear fit applies to systems with $RO_2\cdot$+$RO_2\cdot$ < 5 %.

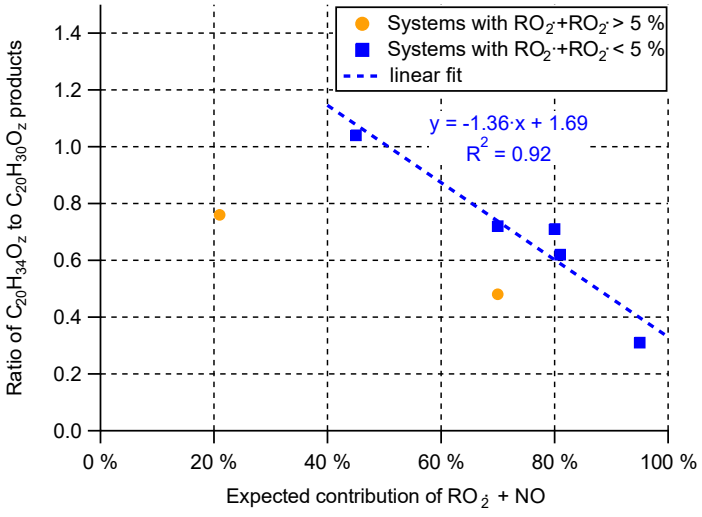

Figure S8 Ratio of the sum of all $C_{20}H_{34}O_z$ products to the sum of all $C_{20}H_{30}O_z$ products as a function of the expected RO_2+NO contribution to the total bimolecular reaction rate. Data set is separated by expected importance of $RO_2\cdot$+$RO_2\cdot$ reactions (threshold 5 %). Linear fit applies to systems with $RO_2\cdot$+$RO_2\cdot$ < 5 %.

S12 Relative changes in HOM-families in the middle and high pure NO system compared to the base case

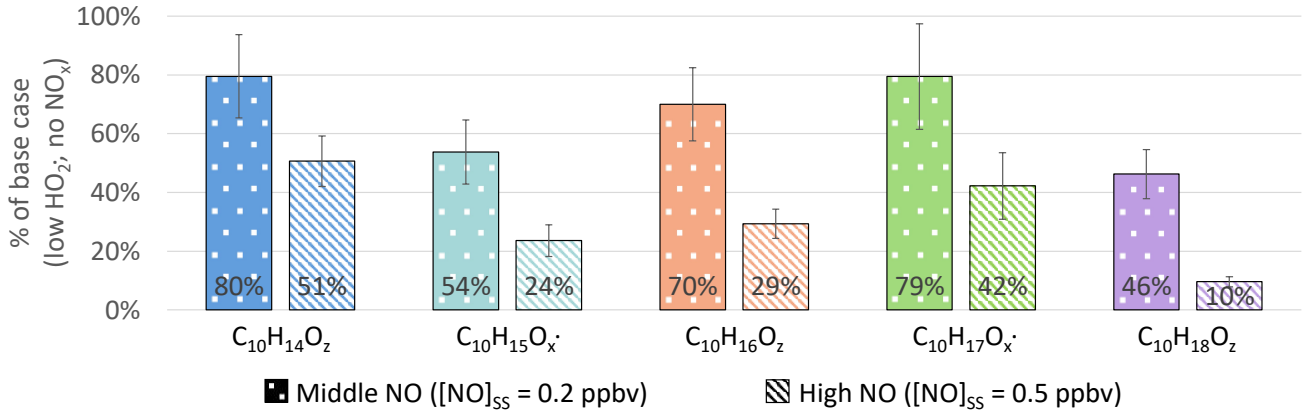

Figure S9 Overview of relative change in monomer families detected in NO_3-CIMS at the two NO levels compared to the base case in unseeded system (All data normalized to α-pinene ·OH turnover. Error bars via error propagation, for more information see Supplement Sec. 14)

S13 Overview of particle-phase data

Table S6 Utilized particle-phase parameters for seeded experiment phases. Total surface area and median particle diameter from SMPS measurements. Organic aerosol and sulfate mass concentrations from AMS measurements. In Experiment Nr. 5 no AMS measurement was available due to instrument issues.

Case description	Exp. nr.	Total surface area ($m^2\ m^{-3}$)	Median particle diameter of surface distribution (nm)	Organic mass ($\mu g\ m^{-3}$)	Sulfate mass ($\mu g\ m^{-3}$)
Base	2	$8.7 \cdot 10^{-4}$	84	3.4	10.2
	4	$6.8 \cdot 10^{-4}$	76	2.7	8.2
	5	$5.9 \cdot 10^{-4}$	79	-	-
High HO_2·	2	$10.1 \cdot 10^{-4}$	89	2.0	13.6
	4	$6.9 \cdot 10^{-4}$	76	1.7	9.6
Low NO	3	$7.8 \cdot 10^{-4}$	80	2.6	9.0
Middle NO	3	$7.4 \cdot 10^{-4}$	81	2.5	8.0
High NO	3	$7.0 \cdot 10^{-4}$	80	1.9	7.1
Middle NO, high HO_2·	4	$7.3 \cdot 10^{-4}$	77	1.9	9.6
Intermediate-high NO, high HO_2·	4	$7.9 \cdot 10^{-4}$	80	1.9	12.6
High NO, high HO_2·	4	$8.6 \cdot 10^{-4}$	83	2.0	13.7
	5	$5.9 \cdot 10^{-4}$	81	-	-

S14 Error propagation

Error propagation was used for the estimation of the error of a derived parameter q. The generic equation to calculate the absolute uncertainty δq can be found in **Eq. *(S1)***. Here, the variables $x,\ldots,z$ are the variables necessary to calculate q and it is the uncertainty of these variables that defines the absolute uncertainty of q. This calculation can only be applied if the uncertainties of the variables $x,\ldots,z$ are independent and random (Taylor, 1997).

$$\delta q = \sqrt{\left(\frac{\partial q}{\partial x}\delta x\right)^2 + \ldots + \left(\frac{\partial q}{\partial z}\delta z\right)^2} \quad \textit{(S1)}$$

S15 Calculation of wall-loss corrected SOA yields

The organic aerosol mass concentration (m_{AMS}) is measured by AMS. For SOA yield calculations this value is then corrected to account for the fraction expected to be lost on the ammonium sulfate seed in comparison to the overall loss on the particle surface and the chamber wall. The equation to calculate the corrected organic mass concentration m_{SOA} is shown in **Eq. *(S2)*** (McFiggans et al., 2019).

$$m_{SOA} = m_{AMS} * \frac{k_{cond} + k_{wall}}{k_{cond}} \quad \textit{(S2)}$$

To estimate the fraction lost to the seed surface we use the condensation rate coefficient k_{cond} calculated for one major HOM-product ($C_{10}H_{16}O_7$) and the average HOM-Mon wall loss rate k_{wall}. For calculation of k_{cond} please refer to Supplement Sec. S8 of Baker et al. (2024)).

Determination of k_{wall} was done experimentally by switching off the UV-C light and observing the decay of HOM-Mon formed by photooxidation in the NO_3-CIMS (for more details see Supplement Sec. S3 of Baker et al. (2024)). The SOA yield is then calculated as shown in , where $[\alpha\text{-}pinene]_{in}$ is the α-pinene concentration flowing into the reactor and $[\alpha\text{-}pinene]_{SS}$ is the α-pinene steady-state concentration.

$$SOA\ yield = \frac{m_{SOA}}{[\alpha\text{-}pinene]_{in} - [\alpha\text{-}pinene]_{SS}} \quad \textit{(S3)}$$

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