Characterization of nighttime formation of particulate organic nitrates based on high-resolution aerosol mass spectrometry in an urban atmosphere in China

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Figure S1. Mass spectra of the OA factors resolved from the PMF analysis on high-resolution merged organic and nitrate mass spectra (i.e., PMF_{org+NO3} analysis) for (a) spring, (b) summer and (c) autumn.

Table S1. Average concentration, reaction branching and SOA production of α -pinene and limonene with respect to different oxidants at night.

Text S1: Estimation of SOAs from VOC+NO₃ at nighttime

In this section, we focus on SOA formation from the NO₃ oxidation of limonene and α -pinene, which accounts for a total of approximately 90% of NO₃ lost with respect to the reaction with VOCs. And the analysis approach follows to Xu et al. (2015). However, at night (excluding NO₃), ozone is another main oxidant for SOA formation via VOCs. Based on the mass concentrations of oxidants and the reaction rate constants for limonene and α -pinene with NO₃ and ozone, the branching ratio of each BVOC that reacts with NO₃ can be estimated. In addition, by combining the estimated branching ratios and SOA yields from the chamber studies (Table S1), SOAs from these two dominant VOCs can be calculated (Xu et al., 2015):

$$branching\ ratio_{species\ i+NO_3} = \frac{k_{[species\ i+NO_3]} \times [NO_3]}{k_{[species\ i+NO_3]} \times [NO_3] + k_{[species\ i+O_3]} \times [O_3]} \quad (1)$$

$$[SOA]_{species, oxidant} = [species] \cdot branching\ ratio_{species, oxidant} \cdot yield_{species, oxidant} \quad (2)$$

Table S3 lists the average estimated reaction branchings and SOA productions of limonene and α -pinene with different oxidants. The results show that 96.2% and 95.7% of α -pinene and limonene, respectively, react with NO₃, and the SOA yield from this pathway is 0.015 $\mu\text{g m}^{-3}$ for α -pinene and 0.14-1.28 $\mu\text{g m}^{-3}$ for limonene. To summarize, the estimated mass concentration range for total SOA from the NO₃ chemistry is approximately 0.16 to 1.29 $\mu\text{g m}^{-3}$ at night, which is comparable

to the range of estimated nighttime organic nitrate concentrations (0.38-0.87 $\mu\text{g m}^{-3}$) based on the HR-AMS observation data; this suggests that limonene and α -pinene are two key VOC precursors for organic nitrate and SOA formations at night in South China.

Figure S1. Mass spectra of OA factors resolved from the PMF analysis on high-resolution merged organic and nitrate mass spectra (i.e., PMF_{org+NO₃} analysis) for (a) spring, (b) summer and (c) autumn.

Table S1 Average concentration, reaction branching and SOA production of α -pinene and limonene with respect to different oxidants at night.

Species	Concentration (ppbv)	Rate coefficient ^a		Branching ratio		SOAs yielded from the literature (NO ₃)	SOA from BVOC + NO ₃ ($\mu\text{g m}^{-3}$)
		NO ₃	O ₃	NO ₃	O ₃		
α-pinene	0.39	6.64*10 ⁻¹²	7.2*10 ⁻¹⁷	0.962	0.038	0.007 ^b	0.015
Limonene	0.14	1.22*10 ⁻¹¹	1.54*10 ⁻¹⁶	0.957	0.043	0.2-1.74 ^c	0.14-1.28

^a Rate constants are from the Master Chemical Mechanism model (<http://mcm.leeds.ac.uk/MCM/>; under 25 °C)

^b Hallquist et al., 1999

^c Fry et al., 2011, 2014; Spittler et al., 2006; Boyd et al., 2017

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