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

Kuangyou Yu\textsuperscript{1,2,*}, Qiao Zhu\textsuperscript{1,*}, Ke Du\textsuperscript{2}, Xiao-Feng Huang\textsuperscript{1}

\textsuperscript{1}Key Laboratory for Urban Habitat Environmental Science and Technology, School of Environment and Energy, Peking University Shenzhen Graduate School, Shenzhen, 518055, China.

\textsuperscript{2}Department of Mechanical and Manufacturing Engineering, University of Calgary, Calgary, Canada.

* Authors have equal contribution.

List of Supporting information:

Text S1: Estimation of SOAs from BVOC+NO\textsubscript{3} at nighttime

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\textsubscript{org+NO\textsubscript{3}} analysis) for (a) spring, (b) summer and (c) autumn.

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

Text S1: Estimation of SOAs from VOC+NO\textsubscript{3} at nighttime

In this section, we focus on SOA formation from the NO\textsubscript{3} oxidation of limonene and \(\alpha\)-pinene, which accounts for a total of approximately 90\% of NO\textsubscript{3} lost with respect to the reaction with VOCs. And the analysis approach follows to Xu et al. (2015). However, at night (excluding NO\textsubscript{3}), 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 \(\alpha\)-pinene with NO\textsubscript{3} and ozone, the branching ratio of each BVOC that reacts with NO\textsubscript{3} 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):

\[
branching\ ratio_{species\;i+NO3} = \frac{k_{[species\;i+NO3]|x[NO3]-1}}{k_{[species\;i+NO3]|x[NO3]-1} + k_{[species\;i+O3]|x[O3]-1}} \tag{1}
\]

\[
[SOA]_{species,\;oxidant} = [species] \cdot branching\ ratio_{species,\;oxidant} \cdot yield_{species,\;oxidant} \tag{2}
\]

Table S3 lists the average estimated reaction branchings and SOA productions of limonene and \(\alpha\)-pinene with different oxidants. The results show that 96.2\% and 95.7\% of \(\alpha\)-pinene and limonene, respectively, react with NO\textsubscript{3}, and the SOA yield from this pathway is 0.015 \(\mu\)g m\textsuperscript{-3} for \(\alpha\)-pinene and 0.14-1.28 \(\mu\)g m\textsuperscript{-3} for limonene. To summarize, the estimated mass concentration range for total SOA from the NO\textsubscript{3} chemistry is approximately 0.16 to 1.29 \(\mu\)g m\textsuperscript{-3} at night, which is comparable.
to the range of estimated nighttime organic nitrate concentrations (0.38-0.87 \( \mu g \ m^{-3} \)) based on the HR-AMS observation data; this suggests that limonene and \( \alpha \)-pinene are two key VOC precursors for organic nitrate and SOA formation 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 \( \alpha \)-pinene and limonene with respect to different oxidants at night.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (ppbv)</th>
<th>Rate coefficient ( a )</th>
<th>Branching ratio</th>
<th>SOA from literature</th>
<th>SOA from BVOC + NO3 (( \mu g \ m^{-3} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-pinene</td>
<td>0.39</td>
<td>( 6.64 \times 10^{-12} )</td>
<td>( 7.2 \times 10^{-17} )</td>
<td>0.962</td>
<td>0.007(^ b )</td>
</tr>
<tr>
<td>Limonene</td>
<td>0.14</td>
<td>( 1.22 \times 10^{-11} )</td>
<td>( 1.54 \times 10^{-16} )</td>
<td>0.957</td>
<td>0.043(^ c )</td>
</tr>
</tbody>
</table>

\(^ a \) 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
References


