Supporting Information

A. Derivation of \( \gamma \) from \( \text{N}_2\text{O}_5 \) loss

Consider an aerosol particle suspended in air with radial transport of reactive nitrogen onto the particle surface. In the far field where transport is governed by Fick’s diffusion, the total radial molecular flux \( (F, \text{number of molecules per second}) \) is proportional to the gradient of reactive nitrate concentration, as shown in equation A1 where \( r^* \) represents the radius of inner boundary beyond which diffusion transport is assumed, \( \rho(\infty) \) and \( \rho(r^*) \) the concentration at infinity and at the boundary, respectively and \( D_{\text{N}_2\text{O}_5} \) the diffusion constant. Within the boundary, typically within one mean free path above the particle surface, simple molecular collision is assumed for surface-bound transport, represented as a function of \( \rho(r^*) \) in equation A2 where \( f \) denotes the equilibrium ratio of \([\text{NO}_3]/[\text{N}_2\text{O}_5]\), \( A \) the surface area of the particle under consideration and \( \langle v \rangle \) the average molecular speed of \( \text{NO}_3 \). It is noted here that the factor \((1/4)\) comes from accounting for half of molecules having velocity component going toward the particle surface and steric angle considerations. By requiring \( F_d = F_c \) under steady state condition, \( \rho(r^*) \) may be solved and the flux presented as a function of \( \rho(\infty) \). Assuming the concentration depletion region from each particle does not overlap, the \( \text{N}_2\text{O}_5 \) loss rate through \( \text{NO}_3 \) uptake is shown in equation A3 in which \( n_p \) denotes the particle number concentration.

\[
F_d = (\rho(\infty) - \rho(r^*))r^*4\pi D_{\text{N}_2\text{O}_5} \quad (A1)
\]

\[
F_c = \rho(r^*)f\gamma A \frac{\langle v \rangle}{4} \quad (A2)
\]

Derivation of equation A3 assumes diffusional transport of reactive nitrogen as \( \text{N}_2\text{O}_5 \), based on the fact that \( \text{N}_2\text{O}_5 \) has a much longer lifetime than \( \text{NO}_3 \). Also there is minimal \( \text{NO}_2 \) concentration enhancement near the particle surface from loss of \( \text{NO}_3 \) by \( \text{N}_2\text{O}_5 \) decomposition and \( f \) is calculated from directly measured \( \text{NO}_2 \) concentration. Noting that diffusion resistance is only around \( 10^{-5} \) of the collisional resistance for the particle size range we used, dropping it in equation A3 gives the corresponding simplified formulation for second order \( k \) (per area density per second) measurable in this experiment (equation 2).

\[
- \frac{d[N_2O_5]}{dt} = n_p \frac{[N_2O_5]}{r^*4\pi D_{\text{N}_2\text{O}_5} + f\gamma A \langle v \rangle} \quad (A3)
\]

B. Brief description of box model

A box model with simplified aerosol evolution module has been developed to simulate surface uptake behavior of squalane. Gas phase and condensed phase components are represented in the same manner, while aerosol surface concentrations are allowed to evolve due to coagulation and wall loss. Condensed phase components are assumed to be homogeneous and not size dependent. For the aerosol module, measured particle distributions were re-binned with uniform bin width \((\log(2)/3)\) under log scale so that coagulation of 2 particles of the same size will fall to the next
size bin. Only brownian and 2-body coagulations were accounted within each time step assuming unity coagulation efficiency for liquid particles.

Reactions incorporated in squalane simulations are listed below. All rate constants are calculated at 293 K and 1 atm. “Surface” denotes surface concentration from aerosol in unit of cm²/cm³. C_NO₃ represents the collective species from all chain-termination products in equation 3 in the aerosol phase. It is noted that the wall loss reactions (4 and 5) are set using blank runs with no particle added to the flow tube and are flow tube dependent. Measured particle size distributions, NO₂ concentration and N₂O₅ concentrations are used as starting parameters for each simulation run for various aerosol loading conditions.

<table>
<thead>
<tr>
<th>#</th>
<th>Rate Expression</th>
<th>Rate Constant 293K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NO₂+NO₃ → N₂O₅</td>
<td>1.25×10⁻¹²</td>
<td>ATK</td>
</tr>
<tr>
<td>2</td>
<td>N₂O₅ → NO₂+NO₃</td>
<td>2.39×10⁻²</td>
<td>ATK</td>
</tr>
<tr>
<td>3</td>
<td>NO₃+NO₃ → NO₂+NO₂+O₂</td>
<td>1.99×10⁻¹⁶</td>
<td>DEM</td>
</tr>
<tr>
<td>4</td>
<td>NO₃ → wall loss</td>
<td>0.41</td>
<td>This study</td>
</tr>
<tr>
<td>5</td>
<td>NO₃ → NO₂ (wall conversion)</td>
<td>1.3</td>
<td>This study</td>
</tr>
<tr>
<td>6</td>
<td>NO₃+Surface → C_NO₃</td>
<td>13</td>
<td>This study</td>
</tr>
<tr>
<td>7</td>
<td>NO₃+Surface → NO₂</td>
<td>24</td>
<td>This study</td>
</tr>
<tr>
<td>8</td>
<td>N₂O₅+Surface → C_NO₃+NO₂</td>
<td>0.13</td>
<td>This study</td>
</tr>
<tr>
<td>9</td>
<td>N₂O₅+Surface → NO₂+NO₂</td>
<td>0.22</td>
<td>This study</td>
</tr>
</tbody>
</table>

References: ATK = Atkinson et al., 2004.; DEM = DeMore et al., 1997.

C. Calculation of oxidation ratio as a function of time

Consider a particle of certain diameter, the inbound flux of NO₃ molecule can be calculated using known value of the particle surface area (A), molecular collision rate (Z_NO₃) and reactive uptake coefficient (γ) for any given instant. The time integration of the NO₃ flux yields the total number of NO₃ molecules (N_NO₃) reacted in the condensed phase. Dividing N_NO₃ by the number of squalene molecules in the particle gives us the oxidation ratio (x), as shown in equation A4.

\[ N_{NO₃} = \int_0^\tau Z_{NO₃} \cdot A \cdot \gamma(x) \, dt \; ; \; x = \frac{N_{NO₃}}{N} \quad (A4) \]
Since reactive uptake coefficient is a function of oxidant ratio $x$ as shown in our experiment, we may rearrange and collect terms in equation A4. Integrating on both sides gives us equation A5.

$$\int_0^{x_\tau} \frac{1}{\gamma(x)} \, dx = \int_0^{\tau} \frac{Z_{NO_3} \cdot A}{N} \, dt \quad (A5)$$

Equation A5 relates oxidation ratio to the reaction time in an atmosphere specified by the NO$_3$ collision rate and aerosol surface area and may be integrated numerically to give $x$ at time $\tau$. It is implied that diffusion in the gas phase does not become limiting in supporting the inbound NO$_3$ flux, which is true in our experimental condition. For a typical nighttime condition of 5 ppb NO$_2$ and the NO$_3$ uptake coefficient of 1 with established equilibrium between NO$_3$ and N$_2$O$_5$, the N$_2$O$_5$ concentration near the surface of a 126 nm diameter particle is only attenuated by 5% comparing with concentration at theoretical infinite separation from particle hence we may ignore diffusion transport in this case.

**References**
