Supporting Information

A. Derivation of γ from N_2O_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, number of molecules per second) is proportional to the gradient of reactive

$$F_d = \big(\rho(\infty) - \rho(r^*)\big) r^* 4\pi D_{N2O5} \qquad \text{(A1)}$$

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_{N2O5} the diffusion constant. Within the boundary, typically within one mean free path above the particle surface, simple molecular collision is assumed for

$$F_c = \rho(r^*) f \gamma A \frac{\langle v \rangle}{4} \qquad \text{(A2)}$$

surface-bound transport, represented as a function of $\rho(r^*)$ in equation A2 where *f* denotes the equilibrium ratio of $[NO_3]/[N_2O_5]$, A the surface area of the particle under consideration and $<v>$ the average molecular speed of 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 N_2O_5 loss rate through NO_3 uptake is shown in equation A3 in which n_p denotes the particle number concentration.

$$-\frac{d[N_2O_5]}{dt} = n_p \frac{[N_2O_5]}{\frac{1}{r^* 4\pi D_{N2O5}} + \frac{4}{f\gamma A\langle v \rangle}} \qquad \text{(A3)}$$

Derivation of equation A3 assumes diffusional transport of reactive nitrogen as N_2O_5, based on the fact that N_2O_5 has a much longer lifetime than NO_3. Also there is minimal NO_2 concentration enhancement near the particle surface from loss of NO_3 by N_2O_5 decomposition and *f* is calculated from directly measured 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).

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 cm^2/cm^3. C_NO_3 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, NO_2 concentration and N_2O_5 concentrations are used as starting parameters for each simulation run for various aerosol loading conditions.

#	Rate Expression	Rate Constant 293K	Ref.
1	$NO_2+NO_3 \rightarrow N_2O_5$	1.25×10^{-12}	ATK
2	$N_2O_5 \rightarrow NO_2+NO_3$	2.39×10^{-2}	ATK
3	$NO_3+NO_3 \rightarrow NO_2+NO_2+O_2$	1.99×10^{-16}	DEM
4	$NO_3 \rightarrow$ wall loss	0.41	This study
5	$NO_3 \rightarrow NO_2$ (wall conversion)	1.3	This study
6	NO_3+Surface → C_NO_3	13	This study
7	NO_3+Surface → NO_2	24	This study
8	N_2O_5+Surface → C_NO_3+NO_2	0.13	This study
9	N_2O_5+Surface → NO_2+NO_2	0.22	This study

References: ATK = Atkinson et al., 2004.[1]; DEM = DeMore et al., 1997.[2]

C. Calculation of oxidation ratio as a function of time

Consider a particle of certain diameter, the inbound flux of NO_3 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 NO_3 flux yields the total number of NO_3 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.

$$N_{NO_3} = \int_0^T Z_{NO_3} \cdot A \cdot \gamma(x)\, dt \quad ; x = \frac{N_{NO_3}}{N} \tag{A4}$$

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.

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

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 τ. 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_2O_5, the N_2O_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

1. R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi and J. Troe, *Atmospheric Chemistry and Physics*, 2004, **4**, 1461-1738.
2. S. P. S. W.B. DeMore, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.E. Kolb, M.J. Molina, *JPL Publication 97-4*, 1997, 1-266.