Supplement of Atmos. Chem. Phys., 18, 1895–1907, 2018
https://doi.org/10.5194/acp-18-1895-2018-supplement

Supplement of

Nanoparticle growth by particle-phase chemistry

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Figure S1

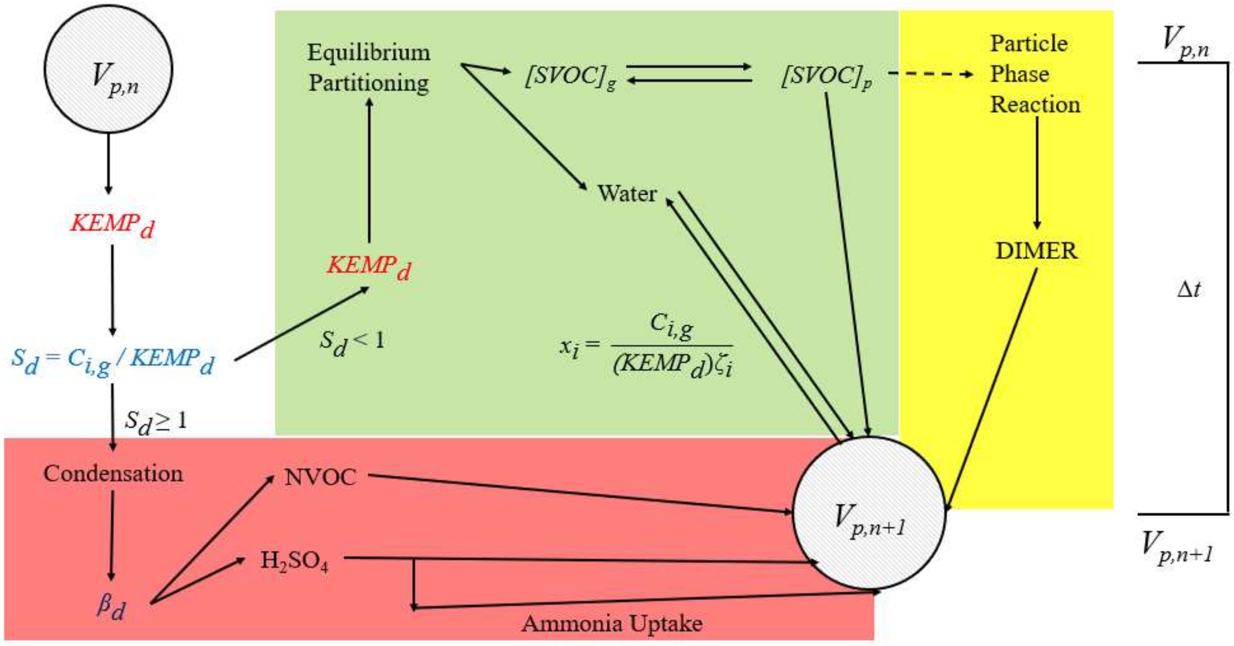


Figure S1 shows a schematic of the iterative calculations, starting with volume $V_{p,n}$, the total volume of the particle at the start of time period *n*. Color shaded regions delineate particle growth by condensation (red), partitioning (green), and particle phase chemistry (yellow). Calculations begin with the Kelvin effect modified vapor pressure ($KEMP_d$):

(S1) $KEMP_d = P_0 \mathrm{e}^{\left[(2\sigma V_{M,p}) / \left(\frac{d}{2} RT\right)\right]}$

where P_0 is the saturation vapor pressure over a flat surface, σ is the surface tension, $V_{M,p}$ is the average molar volume of the particle, *d* is the particle diameter, *R* is the universal gas constant, and *T* is the temperature. The subscript *d*, shown here with $KEMP_d$, and for other variables hereafter, represents the particle diameter and denotes that the variable is particle size dependent. The saturation ratio (S_d) is given by:

(S2) $S_d = C_{I,g}/KEMP_d$

For compounds having $S_d < 1$, uptake occurs at a slower rate than the condensation rate, while for compounds having $S_d >> 1$, uptake occurs at the condensation rate.

For the molecular species considered in this study, those growing the particle at the condensation rate (red shaded region of Figure S1) are sulfuric acid and non-volatile organic compound (NVOC). Equation 1 in the main text gives the uptake rate, which assumes that every collision results in uptake. The Loyalka mass transfer correction factor β_d is given by:

(S3) $\beta_d = \frac{\sqrt{\pi}\, Kn\, (1+1.333)}{1 + Kn\left(1.333 + 1.333\sqrt{\pi}\, Kn + \delta\right)}$

where α is the mass accommodation coefficient (assumed to be 1), δ is the mass transfer jump coefficient equal to 1.0161, and Kn is the Knudsen number:

$$\text{(S4)}\quad Kn = \frac{2\lambda}{d_p + d_i},$$

where λ is the mean free path and d is diameter. Subscripts p and i indicate particle and gas molecule respectively. The mean free path is defined as:

$$\text{(S5)}\quad \lambda = \frac{4\left(D_p + D_i\right)}{\sqrt{\pi}\left(c_p^2 + c_i^2\right)^{1/2}}$$

where D is the gas phase diffusion coefficient and c is the mean thermal speed. The gas phase diffusion coefficient of a particle is defined as

$$\text{(S6)}\quad D_p = \frac{k_B\, T\, C_c}{3\,\pi\,\mu_{air} d_p}$$

where Cc is the Cunningham slip correction factor and μ_{air} is the dynamic viscosity of air ($\mu_{air} = 1.76\times10^{-5}$ kg m^{-1} s^{-1} at 282 K). The gas phase diffusion coefficient of a vapor molecule is estimated from:

$$\text{(S7)}\quad D_i = \frac{0.001\, T^{1.75}}{P\left(\Sigma_{air}^{1/3} + \Sigma_i^{1/3}\right)^2}\sqrt{\frac{1}{MW_{air}} + \frac{1}{MW_i}}$$

where P is atmospheric pressure, Σ is the atomic diffusion volume, and MW is the molecular weight. Eq. S7 is to calculate the gas phase diffusion coefficients for sulfuric acid and ammonia. For Σ_{air} and MW_{air}, the values 19.7 and 28.97 g mol^{-1} are used respectively. A list of atomic diffusion volumes can be found in Poling et al 2001. The diffusion coefficients for SVOC and NVOC vapor molecules were assumed to be 0.05 cm^2 s^{-1}. This value is consistent with Eq. S7 for typical molecular structures of monomer products of monoterpene ozonolysis.

Semi-volatile organic compounds (SVOC) cause particle growth at a rate that is slower than the condensation rate (yellow shaded region in Figure S1). Based on the gas phase mixing ratio and particle properties, a corresponding equilibrium particle phase concentration is calculated (Eq. 2 of the main text). The mass of such species added to the particle is based on $V_{p,n}$, so by $V_{p,n+1}$, the species is no longer in equilibrium and must be re-calculated. Partitioning of water is dependent on the mixing ratio and the $KEMP_d$ to determine the equilibrium mole fraction x_i. For simplicity, the activity coefficient (ζ) is assumed to be 1.

Particle phase chemistry occurs by an accretion reaction (yellow shaded region of Figure S1). Reactions are modeled by the second order decay of SVOC (or in the case of Figures S2 and S3, NVOC) to produce DIMER products. Depletion of SVOC is dependent on the concentration of SVOC existing in the particle at $V_{p,n}$. When equilibrium is re-calculated for SVOC at $V_{p,n+1}$, the mass added to the particle must account for both depletion by reaction and dilution due to particle growth. When the volume changes for all individual species have been calculated, they are summed to give the new particle volume, $V_{p,n+1}$. After volume $V_{p,n+1}$ is achieved, calculations are iteratively repeated.

Figure S2

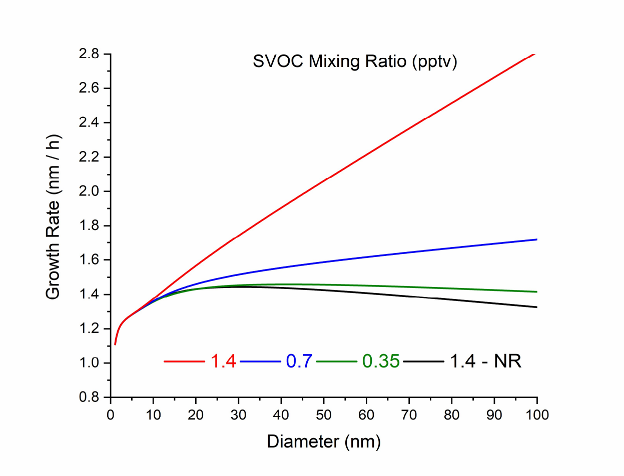
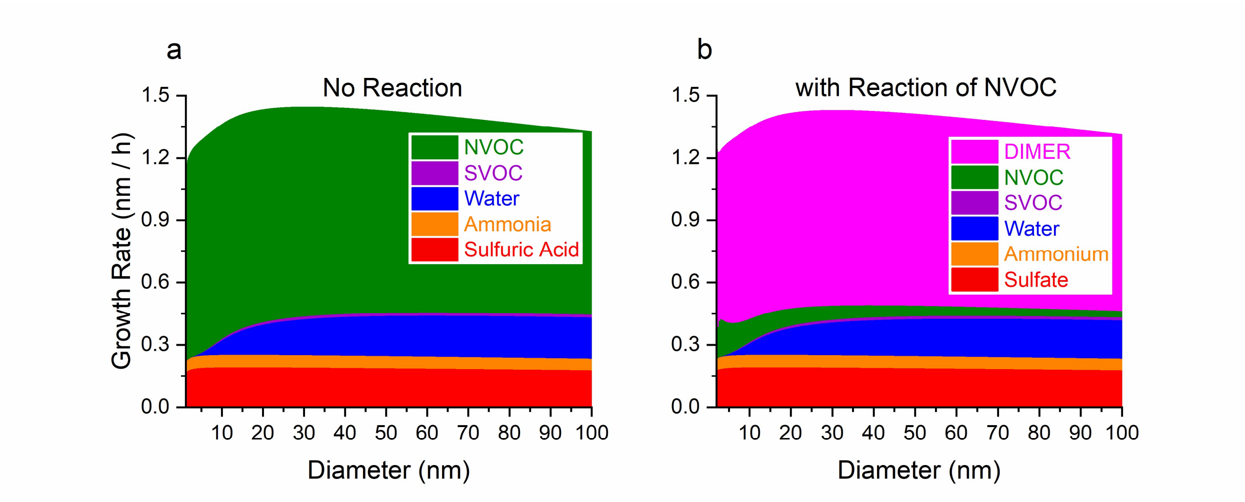


Figure S2 shows growth rate vs particle diameter for the comparison of the growth rate due to particle phase reaction at different gas phase mixing ratios of SVOC. “1.4 - NR” indicates no particle phase reaction occurs and growth is only due to condensation and partitioning.

Figure S3



Figures S3a and b show the size dependent evolution of particle growth rate by a) partitioning alone and b) with dimer formation from NVOC ($k_{II} = 10^{-3}$ M^{-1}s^{-1}). Dimer formation from NVOC does not enhance the growth rate (growth still proceeds at the NVOC collision rate), but it does change the composition.

Figure S4

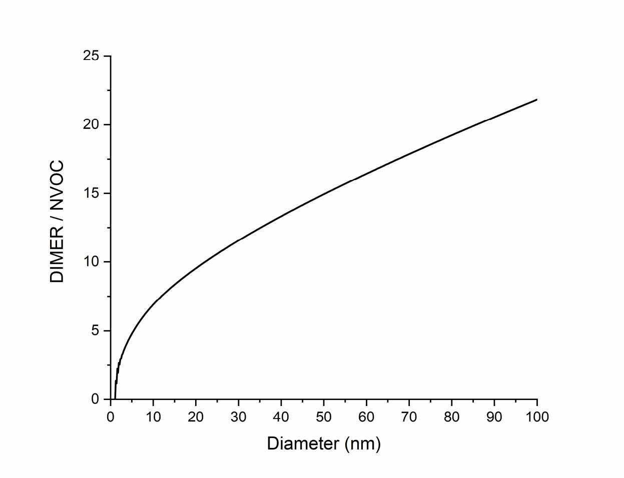


Figure S4 shows the mass fraction ratio of DIMER to NVOC, which monotonically increases with increasing particle diameter.