Mechanistic Insights into Secondary Organic Aerosol Formation from Particle Growth Characteristics

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1. Background
Several recent studies indicate that secondary organic aerosol (SOA) is a highly viscous liquid/semi-solid, with very low values of diffusivity in the particle phase (on the order 10^{-18} - 10^{-15} cm² s⁻¹), such that it evaporates very slowly (or not at all) upon dilution. However, the mechanism of SOA formation itself remains poorly understood and inadequately represented in models.

In general, SOA can form via two possible mechanisms:

1) **Irreversible condensation** of non-volatile organic vapors formed from oxidation in the gas phase.

2) **Reversible absorption** of semi-volatile and volatile organic vapors according to Raoult’s law, with or without chemical reaction in the particle phase.

The former is gas-phase diffusion limited and the growth will be steady-state term unsteady-state term

xₐᵢ = 3 \left( \frac{\coth \left( \frac{q_i}{q_0} \right) - 1}{q_0^2} \right) \frac{6 \pi}{\pi^2} \sum_{n=1}^{\infty} \exp \left[ -n^2 \pi^2 D_{p,i} / R_{p,i} \right] \left( q_i / q_0^2 + n^2 \right)

= particle-phase reactive diffusion term

steady-state term        unsteady-state term

where

\[ k_m = \frac{4 \pi R^2 N_a \left( \frac{R_{p,m}}{D_{p,i}} + \frac{4}{\alpha_i \pi^2} \right)^{-3}} \]

gas-side mass transfer rate constant

\[ q_i = \sqrt{R_{p,m} / D_{p,i}} \]

diffuso-reactive parameter

\[ \bar{C}_{i,m} \]

average particle-phase concentration of species \( i \) in size bin \( m \)

\[ C_i \]

average gas-phase concentration of species \( i \)

\[ \alpha_i \]

volatility of species \( i \)

2. Schematic Process Representation

3. Model Development

Mass transfer of species \( i \) to spherical particles (size section \( m \)), with unsteady-state diffusion \( (D_b) \) and first-order reaction \( (k_{rxn}) \) inside the particle can be described by the following set of differential equations (based on work of Schwartz and Frieberg, 1981, Atmos. Environ.):

\[ \frac{dC_{i,m}}{dt} = k_{m,i} \left( \bar{C}_{i,m} \frac{C_{i,m}}{X_{i,m}} \right) - k_{n,i} \bar{C}_{i,m} \]

where

\[ k_{m,i} = 4 \pi R^2 N_a \left( \frac{R_{p,m}}{D_{p,i}} + \frac{4}{\alpha_i \pi^2} \right)^{-3} \]

gas-side mass transfer rate constant

\[ X_{i,m} = 3 \left( \frac{\coth \left( \frac{q_i}{q_0} \right) - 1}{q_0^2} \right) \frac{6 \pi}{\pi^2} \sum_{n=1}^{\infty} \exp \left[ -n^2 \pi^2 D_{p,i} / R_{p,i} \right] \left( q_i / q_0^2 + n^2 \right) \]

= particle-phase reactive diffusion term

4. Nonreactive Evaporation

\[ \alpha = 0.1, \ C' = 28.5 \ \mu g \ m^{-3}, \ k_{n,i} = 0 \]

\[ R_{p,m} \]

volume average particle-phase concentration

\[ C_i(t) = \frac{1}{R_p} \int C_i(r,t) \, dr \]

Raoult's law equilibrium at the surface

\[ C_{i,m}(t) = \frac{1}{R_{p,m}} \int C_{i,m}(r,t) \, dr \]

The model is successfully able to reproduce the observed evaporation of pyrene that was initially uniformly mixed in SOA particles of 0.175 μm diameter. Note that evaporation is rather slow, with ~40% remaining after 24 hours. The diffusivity in the bulk particle phase was determined to be 2.5 - 5.0 × 10^{-17} cm² s⁻¹.

5. Nonreactive Uptake

\[ \alpha = 0.1, \ C' = 10 \ \mu g \ m^{-3}, \ k_{n,i} = 0 \]

\[ D_b = 10^{-18} \text{ cm}^2 \text{ s}^{-1} \]

Decay of gas-phase concentration as the rate constant increases from 0 to 0.1 s⁻¹ for two bulk diffusivity values: \( D_b = 10^{-18} \) cm² s⁻¹ (left) and \( D_b = 10^{-12} \) cm² s⁻¹ (right).

6. Reactive Uptake

\[ \alpha = 0.1, \ C' = 10 \ \mu g \ m^{-3} \]

\[ D_b = 10^{-17} \text{ cm}^2 \text{ s}^{-1} \]

Decay of gas-phase concentration due to nonreactive mass transfer to a preexisting SOA (0.2 μm diameter) with different bulk particle-phase diffusivities \( D_b = 10^{-14} \) to \( 10^{-18} \) cm² s⁻¹. The equilibration time scale (\( \tau \)) ranges from ~2 min at \( D_b = 10^{-14} \) to 6 days at \( D_b = 10^{-18} \). These results are generally consistent with Shiraiwa and Seinfeld, 2012, GRL.

7. Ongoing and Future Work

- Analyze the behavior of reactive uptake for polydisperse aerosols
- Apply the model to interpret laboratory and field observations of aerosol growth and evaporation.
- Implement actual particle-phase reactions that produce oligomers, organosulfates, etc.

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