



Kinetic regimes for formation and aging of secondary organic aerosol

Manabu Shiraiwa (1), Thomas Berkemeier (1), Katherine Schilling-Fahnestock (2), John Seinfeld (2), and Ulrich Pöschl (1)

(1) Max Planck Institute for Chemistry, Multiphase Chemistry Department, Mainz, Germany (m.shiraiwa@mpic.de), (2) California Institute of Technology, Pasadena, USA

Here we present a conceptual framework of kinetic regime and limiting cases for formation and aging of secondary organic aerosol (SOA). The limiting step of SOA formation can be identified following the developed classification scheme, which is based on three fundamental properties of oxidation products: the reaction location, the saturation ratio, and the heterogeneity in the gas and particle phases. Using the kinetic multi-layer model of gas-particle interactions (KM-GAP) (Shiraiwa et al., 2012), we have analyzed the experimental data of photooxidation of dodecane and subsequent SOA formation. We have found that the contribution of intermediate gas-phase oxidation products to SOA formation is most likely limited by gas-phase reaction, validating the assumption of instantaneous equilibrium partitioning. For semi-volatile and low volatility gas-phase oxidation products, partitioning into the particle phase can be limited by surface accommodation, and possibly by bulk diffusion when organic aerosols adopt glassy or amorphous solid state. The formation of low volatility particle-phase products, such as oligomers and other high molar mass compounds, may be limited by reaction and diffusion in the particle. The 2D evolution plot of molar mass vs. volatility is useful to overview SOA formation and aging. The average molar mass of the organic compounds can be used as a yardstick to estimate relative contribution of gas- vs. particle-phase chemistry to SOA formation. The relatively high values of measured average molar mass for ambient and laboratory-generated SOA imply the importance of particle-phase chemistry in SOA formation.