Modeling SOA formation of α- and β- pinene in smog chambers

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Organic aerosol consists of primary and secondary organic aerosol, whereby secondary organic aerosol (SOA) serves the major burden of the atmospheric organic particulate matter with 140 – 910 TgC/yr (Hallquist *et al.*, 2009). SOA particles are formed via the oxidation of organic precursors, where the volatility of the VOCs is lowered due to the increasement of their functionalization as well as their binding ability. Therefore, gaseous compounds can either nucleate to form new particles or condense on existing particles, which may dominate particle mass. The framework of SOA formation is under natural conditions very complex, because there are a multitude of gas-phase precursors, atmospheric degradation processes and products after oxidation. Thus, a lacking understanding of chemical and physical processes associated with SOA formation complicates modeling of SOA processes, which usually causes underestimation of measured SOA values.

The present study utilizes SPACCIM (SPectral Aerosol Cloud Chemistry Interaction Model, Wolke *et al.*, 2005), which is a parcel model that couples a multiphase chemical model with a microphysical model. For SOA modeling a further development of SPACCIM was necessary. Therefore, two components are needed (i) a gas-phase chemistry mechanism for the VOC oxidation and (ii) a partitioning approach for the gas-to-particle phase transfer. An aggregated gas-phase chemistry mechanism for α- and β-pinene was adapted from Chen and Griffin (2005). For the phase transfer an absorptive partitioning approach (Pankow, 1994) was implemented as a first try. The measurements of the institute's own chemistry department in the smog chamber LEAK are a perfect base for model evaluation and process analysis. Comparisons of simulation results with measurements of LEAK and additional literature data show no coherent agreement. Thus, implementation of a kinetic approach (Zaveri *et al.*, 2014) serves a more detailed representation of the gas-to-particle conversion. Thereby, taking into account diffusion and chemical reaction within the particle.

Utilizing the absorptive approach for partitioning of the organic species yields no consistent results for the two precursors α- and β-pinene. Whereby for α-pinene only a slight overestimation of the total SOA mass occur (Fig. 1), the measured SOA mass for β-pinene cannot be reached by the model (here not shown). Different monoterpenes do not exhibit the same behaviour because of their different chemical structures (Hallquist et al, 1999). More precisely, β-pinene has an exocyclic double bond and α-pinene contains an endocyclic double bond.

Thus, this leads to different yields of the oxidation products due to various oxidation pathways. The subsequent gas-to-particle transfer is approached with absorptive partitioning (Pankow, 1994), which implies that the equilibrium between the gas and the particle phase is reached fast enough.

With the implementation of the kinetic approach the organic aerosol can be resolved in different size sections, whereby the particle radius is a parameter included in the partitioning equations. The phase state of the organic material as well as their further reactions in the particle-phase will influence the modeled SOA yields. The aim is to compare the results of the absorptive and the kinetic approach in the way of reached SOA yields by using the same gas phase chemistry mechanisms.
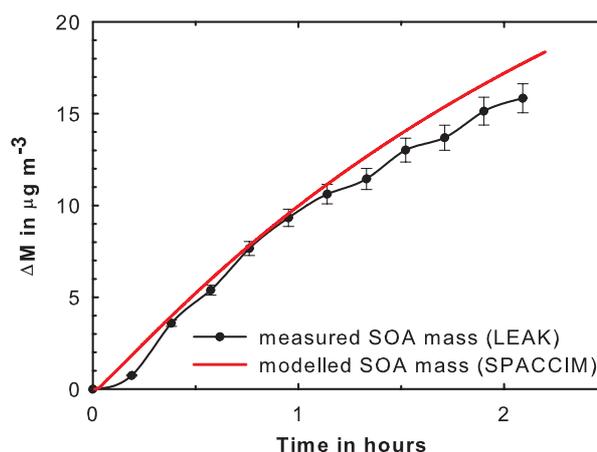

Figure 1. Comparison between measured total SOA mass in LEAK and simulated SOA mass with SPACCIM for the ozonolysis of α-pinene. Error bars denote the measurement uncertainty in the order of 5%.

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