



Kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB): the influence of interfacial transport and bulk diffusion on the oxidation of oleic acid by ozone

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Aerosols are ubiquitous in the atmosphere and have strong effects on climate and public health. Gas-particle interactions can significantly change the physical and chemical properties of aerosols such as toxicity, reactivity, hygroscopicity and radiative properties. Chemical reactions and mass transport lead to continuous transformation and changes in the composition of atmospheric aerosols (“chemical aging”). Resistor model formulations are widely used to describe and investigate heterogeneous reactions and multiphase processes in laboratory, field and model studies of atmospheric chemistry. The traditional resistor models, however, are usually based on simplifying assumptions such as steady state conditions, homogeneous mixing, and limited numbers of non-interacting species and processes.

In order to overcome these limitations, Pöschl, Rudich and Ammann have developed a kinetic model framework (PRA framework) with a double-layer surface concept and universally applicable rate equations and parameters for mass transport and chemical reactions at the gas-particle interface of aerosols and clouds [1]. Based on the PRA framework, we present a novel kinetic multi-layer model that explicitly resolves mass transport and chemical reaction at the surface and in the bulk of aerosol particles (KM-SUB) [2]. The model includes reversible adsorption, surface reactions and surface-bulk exchange as well as bulk diffusion and reaction. Unlike earlier models, KM-SUB does not require simplifying assumptions about steady-state conditions and radial mixing. The temporal evolution and concentration profiles of volatile and non-volatile species at the gas-particle interface and in the particle bulk can be modeled along with surface concentrations and gas uptake coefficients.

In this study we explore and exemplify the effects of bulk diffusion on the rate of reactive gas uptake for a simple reference system, the ozonolysis of oleic acid particles, in comparison to experimental data and earlier model studies. We demonstrate how KM-SUB can be used to interpret and analyze experimental data from laboratory studies, and how the results can be extrapolated to atmospheric conditions. In particular, we show how interfacial transport and bulk transport, i.e., surface accommodation, bulk accommodation and bulk diffusion, influence the kinetics of the chemical reaction. Sensitivity studies suggest that in fine air particulate matter oleic acid and compounds with similar reactivity against ozone (C=C double bonds) can reach chemical life-times of multiple hours only if they are embedded in a (semi-)solid matrix with very low diffusion coefficients ($\sim 10^{-10}$ cm² s⁻¹).

Depending on the complexity of the investigated system, unlimited numbers of volatile and non-volatile species and chemical reactions can be flexibly added and treated with KM-SUB. We propose and intend to pursue the application of KM-SUB as a basis for the development of a detailed master mechanism of aerosol chemistry as well as for the derivation of simplified but realistic parameterizations for large-scale atmospheric and climate models.

References

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- [2] Shiraiwa et al., *Atmos. Chem. Phys. Discuss.*, 10, 281-326 (2010).