Modeling aerosol surface chemistry and gas-particle interaction kinetics with K2-SURF: PAH oxidation

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Atmospheric aerosols are ubiquitous in the atmosphere. They have the ability to impact cloud properties, radiative balance and provide surfaces for heterogeneous reactions. The uptake of gaseous species on aerosol surfaces impacts both the aerosol particles and the atmospheric budget of trace gases. These subsequent changes to the aerosol can in turn impact the aerosol chemical and physical properties. However, this uptake, as well as the impact on the aerosol, is not fully understood. This uncertainty is due not only to limited measurement data, but also a dearth of comprehensive and applicable modeling formalizations used for the analysis, interpretation and description of these heterogeneous processes. Without a common model framework, comparing and extrapolating experimental data is difficult. In this study, a novel kinetic surface model (K2-SURF) [Ammann & Pöschl, 2007; Pöschl et al., 2007] was used to describe the oxidation of a variety of polycyclic aromatic hydrocarbons (PAHs).

Integrated into this consistent and universally applicable kinetic and thermodynamic process model are the concepts, terminologies and mathematical formalizations essential to the description of atmospherically relevant physicochemical processes involving organic and mixed organic-inorganic aerosols. Within this process model framework, a detailed master mechanism, simplified mechanism and parameterizations of atmospheric aerosol chemistry are being developed and integrated in analogy to existing mechanisms and parameterizations of atmospheric gas-phase chemistry. One of the key aspects to this model is the defining of a clear distinction between various layers of the particle and surrounding gas phase. The processes occurring at each layer can be fully described using known fluxes and kinetic parameters. Using this system there is a clear separation of gas phase, gas-surface and surface bulk transport and reactions. The partitioning of compounds can be calculated using the flux values between the layers. By describing these layers unambiguously, the interactions of all species in the system can be appropriately modeled.

In describing the oxidation of PAHs, the focus was on the interactions between the sorption layer and quasi-static surface layer. The results from a variety of published experimental studies [Pöschl et al., 2001; Kahan et al., 2006; Kwamena et al., 2004, 2006, 2007; Mmereki and Donaldson, 2003; Mmereki et al., 2004; Dubowski et al., 2004; Donaldson et al., 2005; Segal-Rosenheimer and Dubowski, 2007] were analyzed and compared utilizing K2-SURF. The heterogeneous reaction of PAH and O3 are found to follow a Langmuir-Hinshelwood mechanism, in which ozone first absorbs to the surface and then reacts with PAH. The Langmuir equilibrium constants and second-order-rate coefficients of surface reaction were estimated. In PAH/O3/solid substrate system, they showed similar reaction rate ($\times 10$), but large difference ($\times 1000$) in adsorption. The mean residence time and adsorption enthalpy were estimated for O3 at the surface of substrates, suggesting the chemisorption of O3 molecules or O atoms, respectively. Initial uptake coefficients of O3 under different conditions were also investigated. The observed dependence on gas-phase O3 concentration was well explained with K2-SURF model in five-order range. In addition, competitive adsorption of other gas phase species (NO2, H2O) was well described by the model. Possible mechanism of PAH degradation system and atmospheric implications are discussed.