Multiphase chemical kinetics of OH radical uptake by semisolid organic aerosol particles

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Multiphase reactions of OH radicals are among the most important pathways of chemical aging of organic aerosols in the atmosphere. Reactive uptake of OH by organic compounds has been observed in a number of studies, but the kinetics of mass transport and chemical reaction are still not fully understood. Here we apply the kinetic multilayer model of gas– particle interactions (KM-GAP) to experimental data from OH exposure studies of levoglucosan and abietic acid, which serve as surrogates and molecular markers of biomass burning aerosol (BBA). The model accounts for gas-phase diffusion within a cylindrical coated wall flow tube, reversible adsorption of OH, surface-bulk exchange, bulk diffusion, and chemical reactions at the surface and in the bulk of the condensed phase. The nonlinear dependence of OH uptake coefficients on reactant concentrations and time can be reproduced by KM-GAP. We find that the bulk diffusion coefficient of the organic molecules is approximately 10^{-16} cm^2 s^{-1}, reflecting an amorphous semisolid state of the organic substrates. The OH uptake is governed by reaction at or near the surface and can be kinetically limited by surface-bulk exchange or bulk diffusion of the organic reactants. Estimates of the chemical half-life of levoglucosan in 200 nm particles in a biomass burning plume increase from 1 day at high relative humidity to 1 week under dry conditions. In BBA particles transported to the free troposphere, the chemical half-life of levoglucosan can exceed 1 month due to slow bulk diffusion in a glassy matrix at low temperature. The fi ndings demonstrate that multiphase chemical aging of condensed-phase organic material by OH depends strongly on environmental conditions such as RH and temperature. This has important implications for source apportionment studies but also for the evolution of organic aerosol in the atmosphere in general, and as such for aerosol radiative properties and aerosol cloud formation potential.