



Kinetic studies of the heterogeneous reactions of NaCl particles using a novel experimental approach.

Y. Liu (1), J. P. Cain (2), M. J. Ezell (3), H. Wang (2), B. J. Finlayson-Pitts (3) and A. Laskin (1)

(1) William R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P. O. Box 999, MSIN K8-88, Richland, WA 99352, (2) Department of Aerospace and Mechanical Engineering, University of Southern California, Los Angeles, CA 90089-1453, (3) Department of Chemistry, University of California, Irvine, California 92697-2025 (Alexander.Laskin@pnl.gov / Fax: +1 509 376 6066 / Phone: +1 509 376 8741)

The kinetics of heterogeneous reaction of deliquesced sodium chloride particles (NaCl_{aq}) with gas phase reactants, HNO_3 and $\text{OH}\cdot$, and their uptake on NaCl_{aq} were measured using a novel experimental approach. The technique utilizes the exposure of substrate deposited aerosol particles to reactive gases followed by chemical analysis of the particles using computer controlled scanning electron microscopy with energy dispersive analysis of X-ray (CCSEM/EDX) capability. Experimental conditions were carefully selected based on fluid dynamics calculation results to ensure that effects of fluid mechanics have minimal effect on the accuracy of kinetic measurements. As we discuss in this presentation, fundamental reaction kinetics data may be obtained from these experiments after a theoretical kinetic-diffusion analysis of effects of gaseous reactant transport from the bulk gas to the substrate surface. Such effects arise from the close proximity of the reacting particles mounted on the substrate, which may result in kinetic rates being diffusion controlled. We show that these effects may be quantified and kinetic rates can be obtained where the transport limitations associated with the substrate experiments are decoupled from the reaction kinetics. The apparent, pseudo-first-order and intrinsic, second-order rate constants were obtained based on the changes in the chloride concentration of individual particles upon reaction with HNO_3 or $\text{OH}\cdot$. The lower limits for uptake coefficients of HNO_3 and $\text{OH}\cdot$ on $\sim 1.8 \mu\text{m}$ NaCl_{aq} particles at $\text{RH}=80\%$ have been measured as $\gamma = 0.06$ ($\times/\div 2$) and $\gamma = 0.11$ ($\times/\div 2$) respectively, both in excellent agreement with experimental data and theoretical predictions reported in the literature. The dependences of HNO_3 uptake

coefficients on relative humidity were also probed for NaCl, a mixture of NaCl and MgCl₂, and sea salt particles.