OXIDATION OF NaBr AEROSOL BY OZONE: IMPORTANCE OF A SURFACE REACTION

MARTINA ROESELOVÁ, SHERRI W. HUNT, WEIHONG WANG, LISA M. WINGEN, *School of Physical Sciences, Department of Chemistry, University of California, Irvine, CA 92697*; ELADIO M. KNIPPING, *EPRI, Palo Alto, CA 94304*; DONALD DABDUB, *The Henry Samueli School of Engineering, Department of Mechanical and Aerospace Engineering, University of California, Irvine, CA 92697*; DOUGLAS J. TOBIAS and BARBARA J. FINLAYSON-PITTS[a], *School of Physical Sciences, Department of Chemistry, University of California, Irvine, CA 92697*.

The release of Br atoms from photolyzable bromine species, such as Br_2, is responsible for the almost complete destruction of ground-level ozone observed in the Arctic after polar sunrise, and is likely to play a role in the partial destruction of ozone observed in the marine boundary layer at mid-latitudes.

To investigate the mechanism of the reactions of O_3 with NaBr aerosol, experiments were carried out at room temperature and atmospheric pressure in a 561 L aerosol chamber above the deliquescence point of NaBr aerosol. Fourier transform infrared spectroscopy was used to measure the concentrations of O_3 and molecular bromine concentrations were monitored using atmospheric pressure chemical ionization mass spectrometry.

A computer kinetics model, including gas and aqueous phase chemical reactions, gas and aqueous phase diffusion, and mass transfer between the liquid aerosol droplets and the gas phase, was used to evaluate the mechanism for bromine production. Experimental results are not reproduced well by known gas phase and aqueous phase bromine chemistry alone, and thus, a reaction occurring at the air-water interface between gaseous ozone and aqueous bromide ion to produce Br_2 via an $O_3 \ldots Br^-$ surface complex is proposed. With the inclusion of this interface reaction, the model satisfactorily reproduces experimental results.

While there is no direct spectroscopic evidence of the surface complex, molecular dynamics simulations provide further support for the proposed heterogeneous reaction mechanism. They show that O_3 strongly prefers to reside at the interface rather than in the bulk solution, and that it makes frequent and long enough contacts with bromide ion for the surface reaction to be feasible. The atmospheric implications will be discussed.

[a]Support by NSF Collaborative Research in Chemistry grant is gratefully acknowledged.