

Tuesday Afternoon, November 5, 2002

Surface Science

Room: C-110 - Session SS2-TuA

Atmospheric Surface Chemistry

Moderator: C.H.F. Peden, Pacific Northwest National Laboratory

2:00pm **SS2-TuA1 Surface Chemistry of Size-Selected Soot Nano-Aerosol Particles.** *J.T. Roberts, K.K. Higgins, A. Wensmann, M.R. Zachariah*, University of Minnesota

A method has been developed to conduct surface chemistry and extract surface kinetic rates from size-selected aerosol nanoparticles. The measurements encompass broad ranges of particle size, phase, and composition. Results will be presented on the growth and oxidation of soot nanoparticles (particle radius between 10 and 40 nm). The particles are investigated for changes in surface area using on-line nanoparticle characterization instrumentation. Experiments emphasize two classes of reactive conditions: high temperature oxidation by O_2 and NO_x , and room temperature addition of hydrocarbons. We believe these to be the first measurements of soot oxidation and condensation kinetics that have been conducted on size-selected particles. The results are important because soot emission from combustion sources is dictated by the competing surface processes of growth and oxidation. More generally, the results represent one of the first kinetic and mechanistic studies of gas-phase nanoparticle reactivity.

2:20pm **SS2-TuA2 Uptake and Reaction of Ozone on NaCl and Bromide-doped NaCl.** *J.N. Newberg, J.C. Hemminger*, University of California, Irvine

Sea-salt significantly affects the chemistry and composition of the marine boundary layer. For example, gas-phase bromine compounds resulting from sea-salt aerosol particles and sea ice have been implicated in tropospheric ozone depletion events in the arctic spring time, as well as in the deposition of mercury from the atmosphere in the marine troposphere. While there have been significant advances in our knowledge of gas-phase and bulk aqueous-phase reactions of sea-salt, little is known about the fundamental surface interactions of sea-salt with important gas-phase constituents (e.g., O_3 and OH) at the air-particle interface. This is due in part to the paucity of conventional atmospheric chemistry methods with the ability to monitor surface reactions on a fundamental molecular-level. Using X-ray photoelectron spectroscopy (XPS), we monitored the surface chemistry of solid sea-salt substrates upon exposure to ozone. Past studies under steady-state conditions indicate that O_3 is essentially unreactive towards dry and aqueous NaCl in the dark. Our results show unequivocally that under UHV conditions and continuous exposure to O_3 , oxygen uptake occurs on NaCl. For NaCl doped with bromide, an increase in oxygen uptake was observed. Moreover, as the amount of doped bromide increased, the total uptake of oxygen increased. Based on our experimental results and ab initio calculations, it is suggested that the products of the surface reaction of O_3 on dry bromide-doped NaCl yield ClO^- and BrO^- . Neither of these species has been reported in the XPS literature. Exposing the bromide-doped NaCl samples to water vapor leads to the segregation of Br^- to the salt surface. Exposure of this surface enriched Br^- to ozone leads to enhanced uptake of oxygen, likely in the form of BrO^- .

2:40pm **SS2-TuA3 XPS Study on Surface Segregation of Bromide in Bromide-doped NaCl Crystals by Water Vapor Exposure.** *K. Inazu, J.T. Newberg, J.C. Hemminger*, University of California, Irvine

Drastic decrease of tropospheric ozone in the Arctic at polar spring has been observed accompanying an increase of particulate bromide.¹ The chain reactions involving sea salt bromide were proposed to be responsible for the ozone depletion.² While current model calculations for the tropospheric ozone depletion have applied the available abundance of bromide for the atmospheric reactions estimated from the bromide concentration in bulk sea water, the availability of bromide in sea salt particles must be reevaluated if the selective surface enrichment of bromide takes place on sea salt particles. In order to verify the feasibility of the surface bromide enrichment in sea salt particles, water-vapor exposure experiments were conducted for bromide-doped NaCl (100) single crystals with different bromide concentration using X-ray photoelectron spectroscopy and scanning electron microscopy. Segregation of bromide to the surface of the NaCl crystals uniformly doped with bromide at Br/Cl ratio below the level in sea water was observed even when the crystals were exposed to water vapor at lower pressure than the deliquescence points of NaCl and NaBr. The initial

segregation rate of bromide was dependent on water vapor pressure and steeply increased when the employed water vapor pressure approached the deliquescence point of NaBr. At the initial stage of the segregation, segregated NaBr crystallites were highly dispersed on the crystal with ca. 0.2 μm on a side. As segregation proceeded by further water vapor exposure, the NaBr crystallites fused each other to achieve three-dimensional growth similarly to the case of water-induced reorganization of the ultra thin nitrate film formed by the reaction of NaCl single crystal with nitric acid.³

¹L. A. Barrie et al., Nature, 334, 138(1988).

²K. W. Oum et al., Geophys. Res. Lett., 25, 3923-3926(1998).

³J. C. Hemminger, Int. Rev. Phys. Chem., 18, 387(1999).

3:00pm **SS2-TuA4 Chemical Reactions Induced by Ionizing and Electron-beam Irradiation in Organohalide/Water (Ice) Films.** *C.C. Perry*, Johns Hopkins University, *N.S. Faradzhev*, Rutgers, The State University of New Jersey, *A.J. Wagner*, *C. Vecitis*, *G. Wolfe*, *D.H. Fairbrother*, Johns Hopkins University, *T.E. Madey*, Rutgers, The State University of New Jersey

We report on the reactions of organohalides (CCl_4 , $CHCl_3$, CH_2Cl_2 , $PhCl$, CF_2Cl_2) in water (ice) films (~50 nm) at ~100K under the influence of ionizing and electron beam irradiation using reflection-absorption infrared spectroscopy, X-ray photoelectron spectroscopy and mass spectrometry. The final neutral gas phase products of electron-stimulated degradation of chlorocarbons CCl_4 , $CHCl_3$, CH_2Cl_2 , and $PhCl$, were identified as CO_2 , CO , and HCl . Product species identified in the film include a thermally stable partially chlorinated (C_xCl_y) overlayer, CO_2 , H_3O^+ and Cl^- . Phosgene ($COCl_2$) was also observed except in the case of $PhCl$. For CCl_4/H_2O mixtures, the product branching distributions are sensitive to the films initial H_2O/CCl_4 composition. In CCl_4 rich films, the dominant reaction products in the film were C_2Cl_4 and the C_xCl_y overlayer; CO was the dominant gas phase species. In H_2O rich films, CO_2 becomes dominant at the expense of C_2Cl_4 and C_xCl_y species. For films concentrated with CCl_4 chlorine is lost principally into the gas phase while in water rich films chlorine is partitioned principally as HCl , producing HO^+ and Cl^- . In contrast, Freon-12 (CF_2Cl_2) / water mixtures subject to ebeam or X-ray irradiation produced carbonyl fluoride (COF_2), a major source of fluorine in the stratosphere. H_3O^+ and CO_2 were also detected as stable reaction products as well as Cl^- and F^- , consistent with a recent study of negative ion yields in ESD from CF_2Cl_2 /water films. The decomposition rate of different organohalides in ice film under electron beam irradiation varied dramatically (~100): Freon being much more sensitive to electron exposure than the chlorocarbons.

3:20pm **SS2-TuA5 Heterogeneous Uptake of HNO_3 in the Troposphere: From Sand to Cirrus.** *M.A. Tolbert*, University of Colorado, Boulder **INVITED**

One longstanding issue in tropospheric chemistry is the observation that the ratio of HNO_3/NO_x often shows atmospheric values two to ten times lower than those modeled. This implies either a missing sink of HNO_3 , a missing source of NO_x species, or a missing conversion from HNO_3 to NO_x in the models. There are several dominant particle types in the free troposphere that may provide surfaces for loss of HNO_3 . In this paper, we present laboratory studies of HNO_3 uptake on two systems modeling global tropospheric particulate: ice surfaces representative of cirrus clouds and mineral particles representative of atmospheric dust. The results from current laboratory experiments will be discussed and, where possible, comparisons with recent atmospheric data will be presented.

4:00pm **SS2-TuA7 Surface Chemistry of Oxide and Carbonate Particles in the Atmosphere.** *V.H. Grassian, B.J. Krueger, S. Carlos-Cuellar*, University of Iowa

While there is a growing body of evidence which suggests that reactions on mineral aerosol may play an important role in the troposphere, there is very little understanding of what chemistry occurs on the surface of these particles. The focus of this talk is on recent laboratory studies of surface reactions of inorganic and organic acids found in the atmosphere on oxide and carbonate particles. These particles are used as laboratory surrogates for mineral aerosol. Kinetic measurements are made of these potentially important atmospheric reactions so as to quantify the rates of these reactions. Spectroscopic measurements along with atomic force and scanning electron microscopy provide additional information about surface reaction mechanisms. The laboratory data are then used as input into atmospheric chemistry models in order to assess the importance of these surface reactions in the troposphere.

4:20pm **SS2-TuA8 Variable-Temperature Studies of Sulfur Dioxide Reactions with Carbon Clusters**, *W.T. Wallace*, Georgia Institute of Technology, *A.J. Leavitt*, State University of West Georgia, *M.G. Arredondo*, Georgia Institute of Technology, *D. Doby*, State University of West Georgia, *R.L. Whetten*, Georgia Institute of Technology

The variable-temperature reactions of SO_2 with thermalized carbon cluster anions, C_N^- , are reported. Carbon clusters were produced via laser vaporization of a graphite rod and exposed to a dilute SO_2 :He mixture in a pulsed variable-temperature flow tube reactor (FTR). The products of these reactions were detected using time-of-flight mass spectrometry. A series of reactions were monitored at FTR temperatures of 96 °C, 73 °C, 55 °C, 47 °C, 38 °C, and 24 °C. At all temperatures, the products C_NO^- and C_NO_2^- were detected corresponding to the depletion of the parent C_N^- concentration in the mass balance for selected values of $N = 8$ to 40. At each increasing temperature, the reaction was driven closer to completion when compared to $\text{C}_N^-:\text{SO}_2$ reactivity at room temperature. These studies probe the reactive nature of atmospheric soot with SO_x that are linked to respiratory problems.

4:40pm **SS2-TuA9 Heterogeneous Reactivity of Ozone on Mineral Oxides**, *A.E. Michel*, *C.R. Usher*, *V.H. Grassian*, University of Iowa

Mineral aerosols, or wind-blown soil particles, are emitted into the atmosphere where they can provide numerous sites for the heterogeneous reaction, physisorption and chemisorption of tropospheric gases. Understanding the role of mineral aerosol in the troposphere is important for its potential impact on chemical processes in the atmosphere. Laboratory measurements of the various processes are desired for the development of accurate atmospheric computer models. The uptake of ozone on various mineral oxide particles was observed using a Knudsen cell apparatus equipped with a quadrupole mass spectrometer. Mineral oxide samples included both commercially available powders ($\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$ and SiO_2) and authentic dusts (Saharan sand and China loess). Initial reactive uptake coefficients, γ_{BET} , were measured for the various particles and ranged from 10^{-5} to 10^{-4} . In this investigation, it was observed that both the mineral oxide powders and authentic dusts exhibited catalytic behavior towards the destruction of ozone. Additionally, variations in the reactivity of the authentic dusts were observed as a function of sample treatment.

5:00pm **SS2-TuA10 Alkali Halide Nanocrystal Growth and Etching Studied by AFM and Modeled MD Simulation**, *S. Garcia-Manyes*, *A. Verdaguier*, University of Barcelona, Spain, *P. Gorostiza*, University of California at Berkeley, *F. Sanz*, University of Barcelona, Spain

Adsorption of water on alkali halides single crystals plays a key role in many fields ranging from interstellar dust grains, biochemistry, industrial applications and environmental processes, such as nucleation of clouds or sea salt spray. To understand the atomistic details of the wetting and dissolution processes that take place in, we combined Atomic Force Microscopy and Molecular Dynamics to study the adsorption of water vapor on a stepped (100)-oriented crystals surface prepared by cleavage. The AFM microscope, placed in a humidity-controlled chamber is used to induce local step nanostructures forming hillocks. A few seconds of contact between the cantilever tip and the crystal surface are enough to create a hillock of a few monatomic steps due to the water neck formed on account of capillary forces. The shape and distribution of the monatomic steps in the formed hillock follows the minimization of the interface free energy established between the aqueous ionic solution and the air phase in order to reduce surface tension. After hillock creation the AFM tip is retracted and the hillock starts to dissolve and ions migrates until the hillock disappears. Terraces in the hillock disappear one by one, from the upper one to the lowest in order to minimize again the free energy of the whole system. We have studied creation and free evolution of hillocks for alkali halides single crystals by AFM under chosen humidity conditions. Imaging during experiments is performed in tapping mode so as to reduce the surface perturbation. We performed molecular dynamics simulations of the interface between the single crystal and water using a hillock-like surface model and results are compared with experimental data in order to understand the dynamics of the system. Ionic migration, steps mobility and dissolution directly calculated by the simulations have been used to modeling the hillock evolution according to experimental data.

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