Geophysical Research Abstracts,
Vol. 11, EGU2009-13762, 2009
EGU General Assembly 2009
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Heterogeneous Processes of ClO Radicals on the Sea Salts Surface

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The compositions of atmospheric aerosols vary widely. Interaction of atmospheric gases with aerosols alters the gas phase composition as well as the aerosols surface characteristics. Sea salt aerosols represent an unlimited halogen reservoir. Together with salt deposited on shelf ice they are considered the most likely source of reactive halogens in the Arctic. Heterogeneous reactions on sea salt aerosols or deposits are therefore suspected to be a potential source of gas phase halogen compounds. The heterogeneous reactivity of HOCl on solid KBr at ambient temperature reveal the formation of Br- and Cl- containing reaction products such as BrCl and Cl2. Photolysis of these reaction products with subsequent reaction with ozone lead to the chlorine oxide formation. The issue of ozone depletion within the Arctic boundary layer in springtime represents a relatively new area of uncertainty in atmospheric chemistry. However catalytic destruction, especially through reactions involving active bromine on the surface of aerosol particles, does appear to be involved. There is considerable uncertainty as to the processes by which active halogen is liberated from the organic (e.g. CH3X) and inorganic forms (e.g. sea salt) of the halogen source. This is unsurprising because a quantitative description of stratospheric heterogeneous chemistry is much less developed than the gas-phase chemistry.

The reaction between chlorine atoms and ozone generates up to (2-4) 1012 ClO radicals/cm3 in the flow reactor:

Cl + O3 → ClO + O2

ClO → Sea Salt (determined)

Study of the heterogeneous processes of the halogen containing radical was carried out in the temperature range 240 – 370 K and at a total pressure ca. 1-10 mbar using the discharge-flow technique. He was used as the carrier gas. The reactants were detected by two different molecular beam mass spectrometers with electron impact detectors. Uptake coefficient measurements were obtained using an MS 7303 quadrupole mass spectrometer.

A major problem in the identification of free radicals using the mass spectrometric technique is linked to the presence of mass peaks of the same mass, but originating from dissociative ionization of other components in the mixture. Mass spectrometric identification of the paramagnetic component of a molecular beam was used for the identification of radicals. Method a non-uniform magnetic field created by a focusing six-pole magnetic lens was used to deviate paramagnetic particles. The action of such a lens on a beam of neutral paramagnetic particles is similar to that of an optical lens with large chromatic aberrations. The molecular beam was modulated by chopper and the alternating component of the ion current was measured. The uptake coefficients radicals ClO on the surface of NaCl, KBr, NaBr were determined (3.7 ± 1.5)•10-4, (12.3 ± 3.6)•10-4, (9.6 ± 5.7)•10-4, respectively.

Acknowledgment. The work was supported by RFBR; NATO CLG - ESP.EAP.CLG 983035; Department of Chemistry and Material Sciences RAS.