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Chlorine Activation in Coastal and Remote Marine Boundary Layer

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There is evidence of high chlorine concentrations in the polluted coastal troposphere. In [1] we suggested a double phase autocatalytic process that could be responsible for chlorine formation in NO_x-enriched coastal air. A "chlorine explosion" may take place in a chain branched process

Cl_2 (hν) => 2Cl (+$2O_3$) => 2ClO (+$2NO_2$) => 2$ClONO_2$ (+NaCl) => 2Cl_2

in which the $ClONO_2$ + NaCl reaction plays a key role.

Using a coated-insert flow tube reactor combined with a quadruple mass spectrometer we have studied the heterogeneous $ClONO_2$ + NaCl reaction under dry and wet conditions. The uptake coefficient was found to be time dependent and decrease from initial high to steady-state values. Two channels of the heterogeneous reaction were found to be formation of Cl_2 and HOCl. The former increases chlorine abundance while the latter diminishes effect of chlorine activation. A kinetic model describing the uptake mechanism and effect of humidity was proposed and its elementary parameters were determined. The model allows to parameterize the experimental data and to extrapolate them to real conditions of the troposphere. Under wet conditions the uptake coefficient depends on $ClONO_2$ concentration. At high $ClONO_2$ (up to 250 ppt in the troposphere), an uptake has to be considered as steady-state, with the total probability, $\gamma \cong 0.023$, and branching ratio of the product yield [Cl_2]/[HOCl]=0.8$\pm$0.3. At low $ClONO_2$ of $\sim$5 ppt, a time-dependent component of the uptake probability becomes significant with the uptake probability of 0.077 and the product ratio of [Cl_2]/[HOCl]=1.1.

We also explored the possibility of Cl release in the gas phase from a NaCl surface under exposure to OH of (1-2)10^{12} molecule cm^{-3} at 100 Torr and room temperature. The possible gas-phase products were initially collected using a liquid nitrogen trap during 1.5 hours and then detected with a chemical ionization mass spectrometer using SF_6^- as a parent ion. Except of HCl in a trace amount, no any other Cl-containing species were observed at noticable concentrations.

Our preliminary experimental results suggest that the heterogeneous OH + NaCl reaction is likely inefficent in formation of photoactive Cl-containing products.

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Reference

1. M.Yu. Gershenzon, V.M. Grigorieva, V.V. Zelenov, Yu.M. Gershenzon, R. Zellner, and B.J. Finlayson-Pitts; "Mechanism of "chlorine explosion" in the NO_x-enriched coastal troposphere"; 1^{st} General Assembly of European Geosciences Union, Nice, France, 25-30 April 2004; published in Geophys. Res. Abstracts, 2004, V. 6, abstract 05542.