



Smog Chamber Investigation on the Iron-Catalyzed Activation of Chloride from Modeled Saltpans

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Halogen activation on sea spray aerosols and other halide surfaces and thus the formation of reactive halogen species (RHS), influencing trace and greenhouse gases, has become an important topic of research in recent years. In this context the chloride and bromide activation, in particular the formation of RHS by photochemically induced halogen release from (sea) salt surface and reactions with ozone (O_3) and nitrogen oxides (NO_x), came into focus [1,2].

Our studies concentrate on the quantification of atomic chlorine (Cl), bromine (Br) and hydroxyl (OH) radicals in the gas phase above lab-models of salt pans, enriched in iron(III) chloride ($FeCl_3$), that are exposed to simulated sunlight in a smog chamber. The applied radical clock method [3] results in time profiles and source strengths for Cl, Br and OH, which are combined with the various compositions of humidified salts. In particular, the influence of bromine, sulfate, oxalate, and catechol on the $FeCl_3$ enriched salt is investigated. Comparable investigations only exist for the aqueous phase chemistry of $FeCl_3$ (e.g. [4]).

Driven by the photolytic reduction from Fe(III) to Fe(II), an enormous amount of chlorine atoms ($>10^7 \text{ cm}^{-3}$) could be detected for sodium chloride (NaCl) salt pans with low addition of $FeCl_3$ (0.5 - 2 wt%), even in an O_3 and NO_x free environment. The Cl_2 source strength reaches a maximum of $8 \times 10^{11} \text{ Cl}_2 \text{ molecules per cm}^3$ within the first hour of the experiment, corresponding to a Cl_2 mixing ratio of 30 ppbv at standard pressure. These concentrations exceeded the release above pure NaCl samples by a factor of 1000. A crucial factor for the Cl_2 release is the pH and thus the formation of iron(III) complexes on the salt crystals that differ in their sensitivity for photolysis. Whereas the presence of sodium bromide normally strengthens the chlorine release, a suppression accompanied by strong bromine activation ($>10^{10} \text{ cm}^{-3}$) could be observed for iron enriched samples. Furthermore, the addition of sodium sulfate, sodium oxalate and catechol to NaCl/ $FeCl_3$ samples restrains the activation of chloride. The observations are in accord with a simple equilibrium model that shows the pH-dependence of the formed species in the quasi-liquid layer on the salt.

[1] Vogt et al. (1996) *Nature*, **383**, 327-330 [2] Buxmann et al. (2012) *Int. J. Chem. Kinetics*, **44**, 312-326 [3] Behnke et al. (1988) *Atmos. Environ.*, **22**, 1113-1120 [4] Lim et al. (2006) *Journal of Photochemistry and Photobiology A: Chemistry*, **183**, 126-132