



Iron-Catalyzed Activation of Chloride from Saline Media

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Iron (Fe) occurs in highly saline media (e.g. sea salt aerosol, salt brines etc.). High salinity, low pH, and organic constituents promote the dissolution of iron, forming photosensitive complexes that are responsible for a gaseous Cl production when irradiated by sunlight [1].

We studied the production of atomic Cl, Br and OH radicals from modeled salt pans [2] and artificial sea-salt aerosols containing Fe(III) ions or pyrogenic Fe₂O₃ particles (Sicotrans Orange, BASF) at various compositions in a Teflon smog-chamber. The samples were either spread on a Teflon sheet or they were nebulized from dilute brines (most abundant particle diameter: ~0.4 μm, initial surface area: up to 3·10⁻² cm²cm⁻³) and exposed to simulated sunlight at 60-90% relative humidity. The photochemical formation of Cl, OH and Br (if possible) in the gas phase was quantified by the radical clock method [3] resulting in time profiles of the radical-production rates and total productions.

Simultaneous monitoring of the aerosol surface area enabled us to determine the initial Cl production rate per cm² aerosol surface. Whereas no significant Cl production was detected employing a molar Cl⁻/Fe(III) ratio of 13, it increased to ~2.8·10¹⁷ atoms cm⁻²s⁻¹ (at a ratio of 101), ~4.1·10¹⁷ atoms cm⁻²s⁻¹ (at a ratio of 53) and ~1.9·10¹⁸ atoms cm⁻²s⁻¹ (at a ratio of 13). The presence of NO₂ (~20 ppb) or O₃ (630 ppb) in the gas phase additionally increased the Fe(III)-induced chloride activation to ~7·10¹⁸ atoms cm⁻²s⁻¹ and ~9·10¹⁸ atoms cm⁻²s⁻¹ (at a Cl⁻/Fe(III) ratio of 13), respectively. SO₂ slightly restrained the Cl formation. Artificial sea salt aerosols doped with Fe₂O₃ (Cl⁻/Fe_{tot} ~13) did not result in detectable Cl concentrations. However, decreasing the pH below 2 favored the dissolution of Fe and led to Cl production rates comparable to the Fe(III) experiments. These observations are in accord with the speciation of the photolabile, aqueous Fe(III) complexes obtained from an equilibrium model (PHREEQC) and supported by SEM-EDX images (Scanning-Electron Microscope with an Energy-Dispersive X-ray detector).

The aerosol experiments result in much higher effective Cl production rates with ~50% of active Fe(III) in zero air compared to the salt pan experiments with a portion of 0.05-0.07% of active Fe(III), caused by the larger active surface area of the homogeneously distributed aerosols.

[1] Lim et al. (2006) *J. Photoch. Photobio. A: Chemistry*, **183**, 126-132 [2] Wittmer et al. (2014) *J. Phys. Chem. A, Article ASAP* [3] Behnke et al. (1988) *Atmos. Environ.*, **22**, 1113-1120