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Non-conventional halide oxidation pathways : oxidation by imidazole triplet and surface specific oxidation by ozone

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Oxidation of halide ions (chloride, bromide, iodide) are the starting point of halogen release mechanisms out of sea water, marine aerosol or other halide containing continental aerosols. Slow oxidation of chloride and bromide by ozone in the bulk aqueous phase is of limited relevance. Faster surface specific oxidation has been suggested based on heterogeneous kinetics experiments. We provide first insight into very efficient bromide oxidation by ozone at the aqueous solution – air interface by surface sensitive X-ray photoelectron spectroscopy indicating significant build-up of an oxidized intermediate at the surface within millisecond time scales.
The second source of oxidants in the condensed we have considered is the absorption of light by triplet forming photosensitizers at wavelengths longer than needed for direct photolysis and radical formation. We have performed coated wall flow tube experiments with mixtures of citric acid (CA) and imidazole-2-carboxaldehyde (IC) to represent secondary organic material rich marine aerosol. The halide ions bromide and iodide have been observed to act as efficient electron donors leading to their oxidation, HO_2 formation and finally release of molecular halogen compounds. The photosensitization of imidazole-2-carboxaldehyde (IC) involves a well-known mechanism where the triplet excited state of IC is reduced by citric acid to a reduced ketyl radical that reacts with halide ions. A competition kinetics approach has been used to evaluate the rate limiting steps and to assess the significance of this source of halogens to the gas phase.