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Iodine activation photosensitized by imidazole carboxaldehyde

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Ocean surface water and sea spray aerosol deriving from the latter contain chromophoric dissolved organic matter (CDOM). CDOM species (especially carbonyls, dicarbonyls or aromatic carbonyls such as imidazole-2-carboxaldehyde (IC)), referred to as photosensitizers, form triplet excited states upon UV-VIS light absorption. These triplet-excited states may react with halides generating halogen radicals and additionally molecular halogen compounds, which can be released into the gas phase and may thus contribute to halogen activation. In this work we study the influence of bromide and iodide on condensed phase radical cycling by irradiated coated wall flow tube (CWFT) experiments in mixtures of halides with citric acid (CA) as matrix and IC as photosensitizer. Iodine release was measured by post-oxidation of iodine compounds and detected as ultrafine I_2O_5 particles. We use a kinetic model to interpret our results and to assess radical production and iodine release in sea-spray particles. As indicated by the experimental results and confirmed by the model, significant recycling of halogen species occurs via scavenging reactions with HO₂, to prevent the full and immediate release of the molecular halogen (bromine and iodine) produced, while partially shutting down the HO_x chemistry. The recycling efficiency is higher under the effect of diffusion limitations at high viscosity prevailing at lower relative humidity or temperature. Photosensitized iodine activitation becomes competitive with oxidation by ozone under those conditions.