

The enhanced iodide oxidation in frozen environment and the following release of gaseous iodine molecules (I₂) to the atmosphere

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Active halogens play a significant role in Earth's environmental systems. Especially, iodine species are known to be related to perturbation of HO_x/NO_x cycles, ozone depletion event, formation of CCN (cloud condensation nuclei), controlling the atmospheric oxidizing capacity. However, the mechanism for abiotic generation of iodine compounds is still not clear. Although the reaction processes taking place in ice matrix are greatly different from those in aqueous solution, chemical reactions of halogens in frozen condition have rarely been investigated compared to those in water. In this work, we investigated the formation of tri-iodide (I₃⁻) through iodide oxidation in ice phase under UV irradiation ($\lambda > 300$ nm) and dark condition. The oxidative formation of I₃⁻ through iodide oxidation, which is very slow in aqueous solution, was significantly accelerated in polycrystalline ice even in the absence of UV irradiation. The following release of gaseous iodine molecule (I₂) to the atmosphere was also monitored by CRDS (cavity ring-down spectroscopy). We suspect that the highly enhanced oxidation of iodide in ice is owing to the freeze concentration of iodides, protons, and dissolved oxygen in the ice crystal grain boundaries. The outdoor experiments carried out under ambient solar radiation of the Antarctic region (King George Island, 62°13'S 58°47'W, sea level) also confirmed that the generation of I₃⁻ via photooxidative process is enhanced when iodide is trapped in ice. The observed authentic redox transformation of iodide in ice phase suggests a previously unknown generation pathway for the considerable release of reactive halogen compounds to the atmosphere consequently influencing O₃ and Hg depletion event, perturbation of OH_x/NO_x cycles, and DMS oxidation to form CCN.