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IO radical yield from iodide oxidation by ozone on aqueous aerosol proxy surfaces

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Recently, Koenig et al. [1] measured both gas phase iodine species and particulate iodine (iodate and iodide) in the lower stratosphere indicating that tropospheric multiphase redox reactions prevent poorly soluble gaseous iodine species from removal by wet deposition leading to injections of inorganic iodine into the lower stratosphere. This may influence stratospheric ozone depletion both indirectly through activation of iodide (I^-) to molecular halogens and directly through the aqueous phase reaction of ozone (O_3) with iodide. Also in the troposphere, measurements indicate higher than expected iodide to iodate ratios in the aerosol phase [2], suggesting the reaction of O_3 with I^- to be part of iodine cycling throughout the troposphere. The reaction of O_3 with I^- in the aqueous phase, leading to IO^- and to I_2 through the secondary reaction of IO^- with I^-, is rather well established and one of the main iodine source from oceans [3]. However, for the reaction in the aerosol phase, uncertainties exist with respect to the temperature dependence, effects of pH and ionic strength, and also the extent of a surface reaction pathway [4,5]. In addition, Sakamoto et al. [4] have suggested that from this reaction IO(g) may be released. The objectives of this work has been to determine the temperature dependence of the oxidation of I^- by O_3 as well as to have a better understanding of the parameters that lead to IO radical and I_2 formation. We used a trough reactor [5] coupled to Cavity Enhanced – Differential Optical Absorption Spectroscopy (CE-DOAS) [6] to study the reactivity in dilute aqueous solution (273 – 291 K) and in concentrated ammonium sulfate solutions (255 – 291 K). Measurements at varying O_3 mixing ratios indicate a substantial surface reaction component, especially at lower temperature. The IO/I_2 ratio is in the range of 10^{-3} – 10^{-2}. IO formation seems to result predominantly from a surface process. The experiments are also compared with results from theory.

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