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pH-Dependent production of molecular chlorine, bromine, and iodine from frozen saline surfaces

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The mechanisms of molecular halogen production from frozen saline surfaces remain incompletely understood, limiting our ability to predict atmospheric oxidation and composition in the polar regions. Here we describe results from a laboratory study of mechanisms and environmental controls on halide oxidation to produce molecular halogens, i.e. Cl2, Br2, and I2. We used a temperature-controlled ice-coated flowtube, connected to a chemical ionization mass spectrometer (CIMS) to examine rates of molecular halogen production. The pH of the thin ice coating was controlled with buffers. Condensed-phase hydroxyl radicals (OH) were photochemically generated in the frozen saltwater solutions using H_2O_2 or NO_2- and sunlamps. We found that Cl2, Br2 and I2 were produced via OH-radical oxidation of Cl-, Br-, and I-, via highly pH-dependent processes, with much greater production as pH was lowered to <2. This finding is consistent with mechanisms proposed from recent Arctic field studies for observed snowpack molecular halogen production. Production of Br2 and I2 was enhanced from gas-ice interactions in the presence of added O_3. Our results suggest the relative halogen production rates are dependent on the relative concentrations of halides at the ice surface. Here we discuss the implications of this study in the context of field observations of these three molecular halogens, and future Arctic change.