



## Freezing halide ion solutions and the release of interhalogens to the atmosphere

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Tropospheric ozone depletion events observed during polar spring in the Northern Hemisphere have been ascribed to the release of active bromine following reaction between HOBr and bromide ions in acidic solutions. The challenging issue with regard to the operation of this mechanism throughout the Arctic region is the necessity for acid involvement in waters that are effectively buffered to about pH 8. Here we report a novel mechanism for the release of bromine and chlorine interhalogens, which is promoted by the freezing of known sea salt components in the presence of nitrite ions. This discovery was made as a result of our initial work on the low-temperature chemistry associated with nitrite ions and iodide ions. In room temperature solution, reaction between  $\text{NO}_2^-$  and  $\text{I}^-$  proceeds to form iodine and nitric oxide only at  $\text{pH} < 5$ . In contrast we have shown that if such solutions at  $\text{pH} > 5$  are frozen to  $-30^\circ\text{C}$ , the reaction also occurs and the same products are formed.

Initially, the effect of freezing solutions of pre-acidified 0.5 mM nitrite ions at pH 1.5 to 3 was studied. A peak at  $\lambda_{max}$  300nm, characteristic of the nitrate ion was readily observed as previously reported. Similarly the freezing of acidified 0.5mM iodide ion solutions between pH 1.5 and 3 was shown to yield the  $\text{I}_3^-$  ion as expected. The reaction between the two components was then studied at pH values between 1.5 and 3.0 where hydrochloric acid (HCl) was used to acidify the system. In addition to iodine formation, a new band appeared in the UV/Vis spectrum at 248nm, which, from the literature, can readily be assigned to the polyhalide ionic species,  $\text{I}_2\text{Cl}^-$  ( $[\text{I-I-Cl}]^-$ ). However upon freezing this solution to a solid, under both oxygenated and deoxygenated conditions, two unexpected features were observed in the UV/Vis spectra upon thawing – bands at 224 and 342nm. Again from earlier publication, the peaks can be assigned to the dichloroiodate ion,  $\text{ICl}_2^-$  ( $[\text{Cl-I-Cl}]^-$ ).

Possible analogous chemistry for bromide-driven processing was also investigated. Hence sodium bromide was added to nitrite/iodide solutions acidified by sulfuric acid. Before freezing, a peak due to  $I_2Br^-$  at 267nm was observed in the UV/Vis spectrum, while after freezing, a new band was observed at 254nm, which is assigned, from a previous study, to  $IBr_2^-$ .

The transformation of sea salt components to  $I_2Cl^-$ ,  $ICl_2^-$ ,  $I_2Br^-$  and  $IBr_2^-$  ions by freezing represents a potentially important process in a polar atmospheric context. This is because the dichloro- and dibromo-trihalide ions can release chlorine- and bromine-containing gases, which are key intermediates in ozone destruction. Furthermore all these tri-halide ions contain iodine atoms, which can be transformed to IO after reaction with ozone. Finally the observation that the freezing process can lead to acidification in reactant cavities may also help explain the mechanism by which HOBr and  $Br^-$  ions react in polar regions.