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Freezing Halide Ion Solutions and the Release of Interhalogens to the Atmosphere

Paul O'Driscoll, Kathrin Lang, Nicholas Minogue, and John Sodeau*

Department of Chemistry, University College Cork, Ireland

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The effect of freezing on a variety of acidified and neutral, nitrite ion and halide-containing mixtures has been investigated using UV/vis spectroscopy. Several trihalide ions were formed and monitored, including I_2Cl^-, I_2Br^-, ICl_2^- and IBr_2^-. A mechanism to explain the observations is given in terms of steps involving INO and the nitroacidium ion, $[H_2ONO]^+$. The transformation of sea salt components to specific trihalide 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.

Tropospheric ozone depletion events[1,2] 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.[3−5] 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 NO_2^- and I^- proceeds to form iodine and nitric oxide, only at $pH < 5$.[6−13] In contrast, previous work in this laboratory has shown that if such solutions at $pH > 5$ are *frozen to −30 °C*, the reaction also occurs and the same products are formed.[14]

A variety of acidified and neutral, halide-containing mixtures were investigated during the course of the current work to help determine the reasons why the freezing process should have such a dramatic effect on the NO_2^-/I^- reaction. For this purpose, a Hewlett-Packard 8453 diode-array UV/vis spectrophotometer was used to analyze the solution-phase products and a Digilab FTS 3000 IR spectrophotometer was used to monitor the gas phase. An ethanol bath at −30 °C, cooled by a Neslab CC-100 Cryocool refrigerator, was employed to freeze the solution. Pasco ScienceWorkshop sensors were utilized to monitor the pH and dissolved oxygen content.

From inspection of the UV/vis spectra obtained after freezing *neutral* 0.5 mM solutions of both NO_2^- and I^- ions, iodine and triiodide ions (I_3^-) were observed to be formed predominantly. The latter species is formed because the primary iodine product is rapidly converted to triiodide by the presence of iodide ions in the sample. This is a well-known equilibrium process, which lies well to the trihalide ion side of the balance with an equilibrium constant of 698 L mol^{-1}.[15] Thus, I_3^-, with its large molar absorption coefficients at λ_{max} wavelengths 288 and 352 nm, represents a good proxy measure for the iodine product.[16]

The autoxidation of species, such as sulfite[17] and sulfide[18] ions to sulfate ions or iodide[19] ions to molecular iodine, accelerated by freezing has been published. So too has the necessity for a frozen acidic environment in the formation of nitrate ions from nitrous acid.[20−22] However, there are no prior reports of chemistry potentially relevant to the atmosphere being promoted by freezing when molecular oxygen is not one of the reactants. Hence, as a starting point to understand the mechanism by which the iodide/nitrite ion reaction occurs, the ion-partitioning concept, first discussed by Workman and Reynolds,[23] was used. In this proposal, it was suggested that when dilute ionic solutions freeze, ion-partitioning differences in the aqueous and ice phases could generate electric potential. The approach was chosen to explain the current findings because Takenaka et al.,[20−22] in their studies of HONO in solution between pH 3 and 6, outlined a theory depending upon the rejection of hydrogen ions from the ice to solution pockets upon freezing and a subsequent concentrating effect on the reactants. In that work, the formation of nitrate ions was detected by ion chromatography at concentrations down to 10^{-6} mol dm^{-3}. Hence, an increase in acidity promoted by freezing might, by such a theory, lead to the products observed in the current study.

To follow this idea further, the effect of freezing solutions of pre-acidified 0.5 mM nitrite ions at pH 1.5−3 was also studied. A peak at λ_{max} 300 nm, characteristic of the nitrate ion, was readily observed as previously reported.[20−22] Similarly, the freezing of acidified 0.5 mM iodide ion solutions between pH 1.5 and 3 was shown to yield the I_3^- ion as expected.[19] 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 248 nm, which, from the literature, can readily be assigned to the polyhalide ionic species, I_2Cl^- ($[I-I-Cl]^-$)[16,24] However, when this solution was frozen 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 342 nm. Again from an earlier publication,[24] the peaks can be assigned to the dichloroiodate ion, ICl_2^- ($[Cl-I-Cl]^-$). The resultant spectra are shown in Figure 1.

It was further observed that its mechanism of formation must involve the I_2Cl^- ion because the concentrations of the two species are linearly dependent. Clearly, the freezing process also

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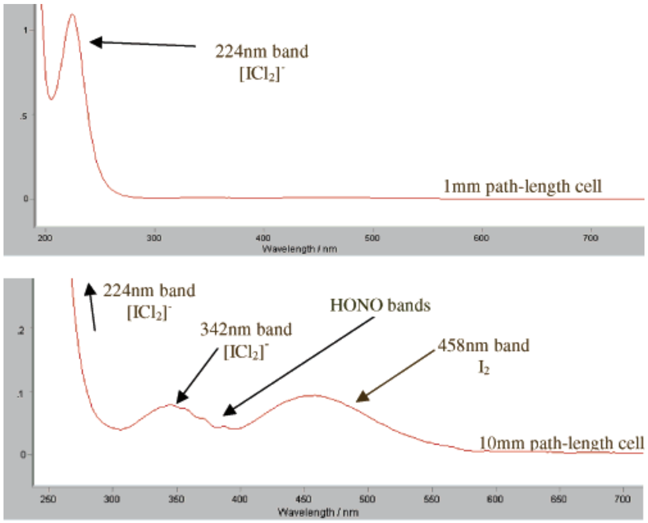

Figure 1. Effect of freezing $I^-/NO_2^-/HCl$ solutions on their UV/vis spectra.

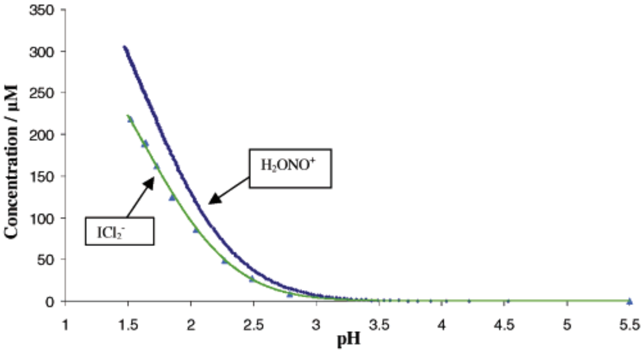

Figure 2. Concentration vs pH plots for $[ICl_2]^-$ and $[H_2ONO]^+$.

plays a key role in the generation of ICl_2^- because it was not observable at room temperature before freezing at these pH values. Indeed, simple cooling of the solution was found not to be effective: frozen solid was a prerequisite. Furthermore, the reaction did not proceed in the presence of chloride ions without acidification. Finally, the formation of the dichloro ion product was not observed when nitrite ions/HONO were absent from the mixture. In other words, it appears that for this freezing reaction, which forms ICl_2^-, to take place, the presence of hydrogen ions and nitrite ions are essential, even though neither species are components of the final product.

Further studies were carried out using a constant chloride ion concentration (56 mM). In these experiments, sodium chloride salt was added to the nitrite/iodide solution and sulfuric acid was used to acidify the system. Again, upon freezing, the ICl_2^- ion was formed. Then, a series of freezing experiments was carried out such that the concentrations of all reactants were kept constant and only the pH was changed. These latter experiments allowed a graph of $[ICl_2^-]$ production vs pH to be plotted. The profile thereby obtained is shown in Figure 2.

The speciation balance associated with the $HONO-NO_2^-$ couple has been the subject of much study over the years due to its importance in tropospheric heterogeneous chemistry. A recent publication[25] shows that a simple one-step equilibrium process is not sufficient to explain the experimental behavior of the system at pH < 3. Therefore, a second step was introduced at these low pH values involving the protonation of HONO to form the nitroacidium ion, $[H_2ONO]^+$. Its computer-modeled concentration vs pH profile is also shown in Figure 2.

It is clear from Figure 2 that the experiments performed in this current freezing study to produce the ICl_2^- ion show a profile similar to that of the model simulation plot for the formation of the nitroacidium ion. As shown, at pH values between 5 and 3, the two graphs track each other exactly with *y*-values close to zero but below pH 3 the concentrations of both species increase with almost the same profile. The two curves can be described very accurately by essentially the same mixed Gaussian/Lorentzian function. This correlation provides strong evidence for suggesting a necessary intermediacy of the nitroacidium ion in the mechanism for production of the dichloroiodate ion, ICl_2^-, from I_2Cl^-. Taken together, the observations lead to the following proposed sequence, (1)−(14), to explain the above chemistry.

The nitroacidium ion is a powerful oxidizing agent and, so, initially oxidizes iodide ions to form nitrosyl iodide (INO).[8−11,26]

$$[H_2ONO]^+ + I^- \rightarrow INO + H_2O \tag{1}$$

Nitrosyl iodide can hydrolyze rapidly to form nitrous acid and hydriodic acid in a step analogous to that found for the hydrolysis of the other nitrosyl halides.[27,28] Hydriodic acid (HI) subsequently dissociates in aqueous solutions to form iodide ions and hydronium ions and, in the prevailing acidic solutions, nitrous acid is protonated to re-form the nitroacidium ion.

$$INO + H_2O \rightarrow HI + HONO \tag{2}$$

$$HI + H_2O \leftrightarrow I^- + H_3O^+ \tag{3}$$

$$HONO + H_3O^+ \leftrightarrow H_2ONO^+ + H_2O \tag{4}$$

Therefore, the elementary reactions 1−4 can be summarized by the following equilibrium as proposed by Ferranti et al.[8,9] and Dózsa et al.[10]

$$[H_2ONO]^+ + I^- \leftrightarrow INO + H_2O \tag{5}$$

If this was the only chemistry present, then no iodine (I_2) or nitric oxide (NO) would be observed. However, the mechanism of the formation of iodine and nitric oxide is not well understood. Both Ferranti et al.[9] and Dózsa et al.[10] postulate that one of the pathways involves the formation of an I_2^- intermediate from the reaction of INO and I^-. In a second pathway, Ferranti et al. propose the intermediacy of HN_2O_3I due to reaction of INO with HONO and Dózsa et al. suggest that iodine and nitric oxide are formed via a $H_2N_2O_3I^+$ intermediate. Also, Dózsa et al. proved that a bimolecular reaction of INO is untenable because the rate of its reaction is too slow compared to the rate of its reaction with the reactants. Regardless of which pathway is taken the products are the same, i.e., iodine and nitric oxide. The overall reaction can be written as follows:

$$2[H_2ONO]^+ + 2I^- \rightarrow 2NO + I_2 + 2H_2O \tag{6}$$

As discussed, triiodide ions produced from the addition of iodide ions to iodine were also observed. These can react with the nitroacidium ion to form nitrosyl iodide, iodine and water. Nitrosyl iodide breaks down to form the reactants as in reactions 2−4 or it can react with the reactants to form more iodine and nitric oxide.[9,10]

$$I_2 + I^- \leftrightarrow I_3^- \tag{7}$$

$$[I-I-I]^- + [H_2ONO]^+ \leftrightarrow INO + H_2O + I_2 \tag{8}$$

Because excess chloride ions are present, the following equilibrium will also be setup.[29]

$$I_2 + Cl^- \leftrightarrow [I{-}I{-}Cl]^- \quad (9)$$

In the current experiments, I_2Cl^- ions were observed at room temperature before freezing but no ICl_2^- ions were present. This observation can be readily explained if different pathways operate before freezing and during freezing. Before freezing, the nitroacidium ion reacts with I_2Cl^- ions to form nitrosyl chloride (ClNO) and molecular iodine. Reaction with the chlorine atom of the polyhalide ion rather than the iodine atom is more favorable because the most electronegative atom is more likely to dissociate from the interhalide ion[29,30] and, also, nitrosyl chloride is a more thermodynamically favorable product compared to its iodine counterpart.[31]

$$[I{-}I{-}Cl]^- + [H_2ONO]^+ \rightarrow ClNO + I_2 + H_2O \quad (10)$$

The nitrosyl chloride product then hydrolyses in the normal fashion:[27,28]

$$ClNO + H_2O \rightarrow HCl + HONO \quad (11)$$

$$HCl + H_2O \rightarrow Cl^- + H_3O^+ \quad (12)$$

Nitrous acid from step (11) can become protonated as in reaction 4 to again re-form the nitroacidium ion. Hence, from this sequence no ICl_2^- ions are formed.

However, during the cooling process, a different mechanism can take place within liquid “micropockets” due to “freeze-concentration” effects.[21] Such environments are known to be uniformly distributed throughout frozen solutions and allow both solid and liquid phases to coexist at temperatures between the initial freezing point and the eutectic point.[17] Hence, the interhalide and nitroacidium ions become very concentrated in the “micropockets” and, therefore, cannot always orientate themselves to react via the end-chlorine atom. Instead, some are forced to react through the iodine atom.

$$[I{-}I{-}Cl]^- + [H_2ONO]^+ \rightarrow INO + ICl + H_2O \quad (13)$$

Nitrosyl iodide thereby produced can be recycled via reactions 2−4 to form the reactants. It can also react with the reactants to form molecular iodine and nitric oxide, as mentioned above.[9,10] The ICl formed can then react with the chloride ions to produce the observed dichloro iodide ion:

$$ICl + Cl^- \leftrightarrow [Cl{-}I{-}Cl]^- \quad (14)$$

Possible analogous chemistry for bromide-driven processing was also investigated and shown to follow the chloride-type chemistry exactly. Hence, sodium bromide was added to nitrite/iodide solutions acidified by sulfuric acid. Before freezing, a peak due to I_2Br^- at 267 nm[16] was observed in the UV/vis spectrum, whereas after freezing, a new band was observed at 254 nm, which is assigned from a previous study to IBr_2^-.[32]

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 trihalide 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.

In terms of relating the above laboratory-based findings to field measurements, it should be noted that IO[33] and HONO[34] have both been measured in the polar atmosphere and the acidity of sulfate aerosols, as emitted from frost flower sources,[35] has been discovered to be very low.[36]

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