ACCOUNTS
of chemical research

The Effect of Freezing on Reactions with Environmental Impact

RUAIRÍ O'CONCUBHAIR AND JOHN R. SODEAU*
Department of Chemistry and Environmental Research Institute, University College Cork, Cork, Ireland

RECEIVED ON MAY 7, 2013

CONSPECTUS

Adapted with permission from *J. Phys. Chem.* **1996**, *100* (32), 13874–13884. Copyright 1996 American Chemical Society.

The knowledge that the freezing process can accelerate certain chemical reactions has been available since the 1960s, particularly in relation to the food industry. However, investigations into such effects on environmentally relevant reactions have only been carried out since the late 1980s. Some 20 years later, the field has matured and scientists have conducted research into various important processes such as the oxidation of nitrite ions to nitrates, sulfites to sulfates, and elemental mercury to inorganic mercury. Field observations mainly carried out in the polar regions have driven this work. For example, researchers have found that both ozone and mercury are removed from the troposphere completely (and almost instantaneously) at the time of Arctic polar sunrise. The monitoring activities suggested that both the phenomena were caused by involvement of bromine (and possibly iodine) chemistry. Scientists investigating the production of interhalide products (bromine and iodine producing interhalides) in frozen aqueous solutions have found that these reactions result in both rate accelerations and unexpected products. Furthermore, these scientists did this research with environmentally relevant concentrations of reagents, thereby suggesting that these reactions could occur in the polar regions. The conversion of elemental mercury to more oxidized forms has also shown that the acceleration of reactions can occur when environmentally relevant concentrations of Hg^0 and oxidants are frozen together in aqueous solutions. These observations, coupled with previous investigations into the effect of freezing on environmental reactions, lead us to conclude that this type of chemistry could potentially play a significant role in the chemical processing of a wide variety of inorganic components in polar regions. More recently, researchers have recognized the implications of these complementary field and laboratory findings toward human health and climate change. In this Account, we focus on the chemical and physical mechanisms that may promote novel chemistry and rate accelerations when water-ice is present. Future prospects will likely concentrate, once again, on the low-temperature chemistry of organic compounds, such as the humic acids, which are known cryospheric contaminants. Furthermore, data on the kinetics and thermodynamics of all types of reaction promoted by the freezing process would provide much assistance in determining their implications to environmental computer models.

Introduction and Background

Motivation for the Studies. The global impact of chemistry and physics that occurs in the polar troposphere is only just being raised due to recent advances in satellite observation, field measurement, and climate change concerns. Two phenomena of chemical origin noted for both the Arctic and Antarctic regions have been identified as being of particular importance: (i) halogen-promoted, ozone, and mercury depletion events accelerated by the effects of cooling and freezing; (ii) photochemical release mechanisms of NO_x and oxygenated volatile organic compounds (OVOC) from snow/ice surfaces.[1]

The possibility that a range of "cryo-reactions" (chemistry in/on ice) could play important roles in atmospheric chemistry began to be explored in the 1980s.[2] Subsequently a variety of cold/frozen materials dispersed throughout the Earth System such as snowpack, PSCs (Polar Stratospheric Clouds), cirrus clouds, frost flowers, freezing fogs, snowflakes,

10.1021/ar400114e

and hailstones have been put forward as potential surfaces for heterogeneous chemistry to take place on. Perhaps the most famous example is provided by the so-called Antarctic ozone "hole".[3] The phenomenon depends crucially on the role of PSCs in transforming the two chlorine sinks, hydrochloric acid and chlorine nitrate, to their ionized and solvated forms. Reactions between these surface species and incoming HCl and $ClONO_2$ molecules subsequently lead to nitric acid/nitrate ions adsorbed to the ice surface and the gas-phase release of "active" ozone-depleting species such as molecular chlorine and hypochlorous acid.[4,5] Cryo-reactions can be classified, from observation, into two groupings: Type I, in which the apparent rate of a known reaction is accelerated, and Type II, when an unexpected chemical transformation occurs as a result of cooling/freezing. Type I reactions are, to many, completely counterintuitive: conventional thinking would lead to the expectation that reactions in solution slow/stop completely upon cooling/freezing. However, this assumption has been shown not to be true because reactions have been observed, which can take place in frozen systems with faster reaction rates than in fluid solution.[6,7] Type II cryo-reactions can be thought of in two ways: (i) to be more like conventional catalytic-surface processes in which activation energies are lowered; (ii) those in which the relative rates of the chemical reactions may change. In any case, unexpected chemical pathways are indeed observed to occur and such processes often yield completely unexpected products.[8,9]

Physical Processes Associated with Ice Formation and Growth. The mechanisms currently understood to be responsible for freeze-induced accelerations and observations of unexpected chemistry are as follows:[10]

1. Freeze-concentration: Solutes in the freezing solution are rejected from the growing ice crystals and concentrate in the unfrozen liquid contained within triple junctions/micropockets.
2. Freezing potential: Not all of the solutes are rejected from the growing ice phase. In fact, some of the solutes are incorporated into the ice itself. The separation and variation in the number of anions and cations incorporated into the phases leads to the generation of an electric potential.
3. Catalytic effect of the ice surface: The surface of ice is a chemically distinct phase and contains a liquidlike layer known as the quasi-liquid layer (QLL). This liquid layer exhibits different characteristics from the bulk material because molecules or atoms residing in this layer only encounter bonding forces with other molecules from one side.[11]
4. Convection effects: The direction in which a solution is frozen affects the concentration gradient of the solution.
5. Temperature differences: The cooling of a solution under laboratory conditions can lead to temperature variations within the sample. The effect can result in differing thermodynamics and kinetics of reaction.

Early studies on the effects of freezing on chemical and biochemical systems have been well summarized in an earlier review.[12] It is made clear in the publication that the initial driving force for the research was linked to concerns about the preservation of food stuffs during frozen storage. Therefore, in this context, much of the early work was performed using frozen organic compounds although some inorganic systems were also investigated.[13,14]

It was reported, with regard to the five mechanisms outlined above, that freeze-concentration accounts for the majority of the induced acceleration effects while the other mechanisms play minor roles.[15] However, in 1991, another study[16] revealed that the freezing-potential phenomenon, which is based on the premise that different solutes can be incorporated into the growing ice-phase with differing efficiencies, could be of major importance in some systems. Therefore the freeze-concentration and freeze-potential effects are now thought to account for most reaction accelerations in freezing solutions and so these two factors are discussed in detail below. In contrast to the 1969 review on reactions in frozen systems the assessment given here focuses on the study of "Atmospheric Chemistry in the Cryosphere", a topic only perceived to be of some global importance over the last 15 years.

The Freeze-Concentration Effect. The effect of freeze-concentration is thought to be the largest contributor to the acceleration of reactions in frozen solutions. This phenomenon operates in the frozen state above the eutectic point and here both solid and liquid coexist in an environment somewhat analogous to a "sorbet". The liquid portion is distributed between the many micrometer-sized inclusions that are spread uniformly throughout the ice structure. Solutes can subsequently become concentrated in these regions (often termed "micropockets" by chemists and "triple junctions" by physicists). As the temperature is lowered, the liquid sites reduce in size thereby further concentrating the solutes. In fact, ice from the Antarctic has been shown to contain triple junctions (micropockets) with cross sectional area of 2 μm^2 at 253 K, decreasing to <1 μm^2 below 238 K.[17] This evidence clearly suggests that as the temperature is

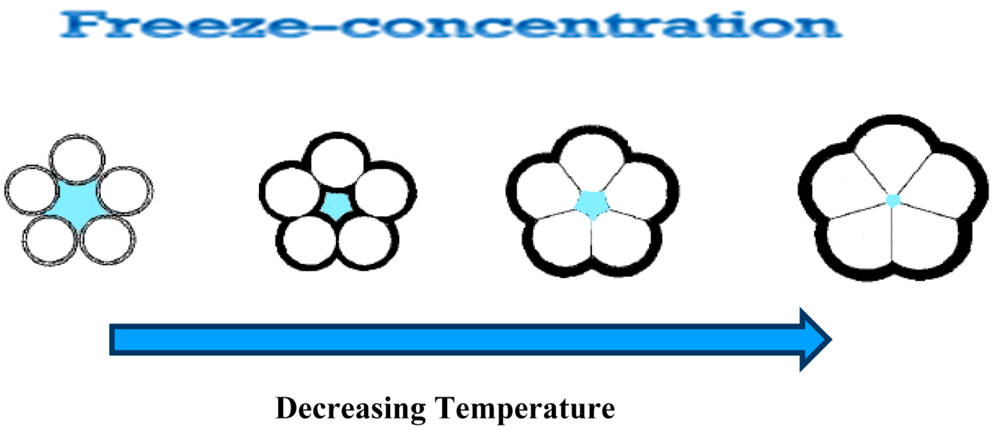

FIGURE 1. Effect of decreasing the size of "micropockets" in solution as a function of temperature. Adapted with permission from ref 6. Copyright 1996 American Chemical Society.

reduced the size of the triple junctions (micropockets) in the ice decrease. A schematic of the process is shown in Figure 1.

The rate acceleration of reactions with decreasing temperature is, to many, counterintuitive, but it has been shown in numerous experiments performed on ice systems that the freeze-concentration effect can outweigh the Arrhenius-type influence. However, not all reactions in frozen hosts are accelerated, and the specific criteria for an acceleration to occur are not only difficult to discern but the magnitude of any acceleration is not easily predicted. The origin of the effect was originally discussed in 1966. It was shown that on freezing acidified solutions containing arsenic acid and iodide, the reactants are concentrated into unfrozen solution thereby increasing the rate of the forward reaction. On the other hand, the rate of the reverse reaction, which is retarded by the presence of iodide ions and protons, was decreased.[18]

This work was subsequently expanded upon.[19] Hence, in the case of a second order reaction proceeding without molar change throughout the reaction, the rate coefficient after thawing, k', can be expressed as

$$k' = A \exp(-E_a/RT)(C_{mp}/C_T) \qquad (1)$$

where A is the Arrhenius pre-exponential factor, E_a is the activation energy, R is the gas constant, and T is the temperature. The concentrations of the solutes, A and B, in the micropockets can be expressed in terms of the sum of the concentration of all solutes in the solution (C_T) and the total concentration in the micropockets (C_{mp}) and is determined from appropriate diagrams of the equilibrium between the solution and solid ice.

From eq 1 it proved possible to determine that a reaction must satisfy the three following criteria for it to be accelerated by the freeze-concentration effect.

1. The reactions are required to be second order or higher, as first order reactions in ice are essentially equivalent to those in the solution and, therefore, are not accelerated.
2. The total initial concentrations must be low as described above.
3. A small activation energy is necessary for the reaction.

Indeed, as mentioned above, many studies have now shown that the freeze-concentration effect accelerates reactions in water-ice media.[6,7,20] However the freeze-potential effect can also be a major contributor to rate accelerations in ice as previously discussed.[16]

The Freeze-Potential Effect. In 1946, Workman and Reynolds set out to investigate a physical process that could potentially lead to the generation of electrical charges, similar to those generated in a thunderstorm. Subsequently, in 1948, they reported that an electric charge separation occurs during freezing water containing between 10^{-3} and 10^{-6} M concentrations of solutes.[21] They concluded that this effect was due to the freezing process as it began when freezing was initiated and ceased when freezing ended.

It was also reported that when very dilute solutions of particular salts (e.g., NaCl, KCl or NH_4Cl) are rapidly frozen, a strong potential difference (freezing potential) is established between the solid and liquid phases.[13] As the magnitude of the freezing potential was found to depend on the ionic composition of the solution, it was concluded that the phenomenon was due to differing incorporation of ions into the growing ice phase. Furthermore, it was found that anions such as the halides are incorporated into the growing solid phase, thus giving the ice a negative potential, with the magnitude decreasing as the size of the anion increased. The inclusion of ions into the ice structure is thought likely to be based on the size and structure of the ion so as to provide a minimum readjustment of the ice lattice.[13] As evidence of this, when solutions containing large *anions* such as SO_4^{2-}, NO_3^{2-}, or $C_2H_3O_2^{2-}$ with a small countercation, such as sodium, are frozen, large positive potentials develop. One exception to this behavior has been found, namely, the ammonium *cation*, which generates a large positive potential in solution due to its ability to readily become incorporated into the growing ice phase. This phenomenon has been attributed to the isomorphism of NH_4^+ with H_3O^+.[21]

According to theory, it is the charge distribution that determines the magnitude of the freezing potential.[16] Therefore, the size and magnitude of the potential developed is highly dependent on the identity of the anions and cations dispersed in the solution. Only small amounts of solutes are incorporated into the ice crystals but the separation of the cations and anions between ice crystals and the unfrozen solution generates an electric potential.[19] In fact, as several diverse ion constituents may become incorporated into the growing ice phase, it is the differential rates of transfer of ion species across the boundary layer of the ice that generates the electric potential. The electric potential itself is generated by the flow of H^+ and $O\bar{H}$ ions across the water/ice interface, which is dependent on the charge of the ice originating from the build-up of solute ions at the ice interface. The values of freezing potential that have been reported range from -90 to $+210$ V.[13] Hence, in a solution that contains a salt which can induce a negative freezing potential (of the ice relative to the solution), protons will migrate from the solution to the ice resulting in a pH increase of the unfrozen solution.

The theoretical framework has been verified experimentally. For example, it has been demonstrated that the pH-dependent decomposition of gallic acid can be stimulated when NaCl is added to the mixture prior to freezing.[22] The authors calculated that the initial pH of 5.6 increased by three units within the liquid micropockets, as a result of the Workman−Reynolds effect. Furthermore, in situ measurements using UV−visible spectroscopy with pH sensitive dyes[23] have also shown that a change in pH occurs when aqueous solutions of electrolytes are frozen because of charge separation.

Freezing Reactions with Environmental Impact. The cryosphere is defined as the portions of the Earth System where water is frozen in a solid form. A wide-ranging distribution of potential materials such as snowpack, cirrus cloud ices, and frost flowers is available on land, in sea, and in air, upon which freezing reactions might occur and has led to much research being performed that is related to atmospheric chemistry. The field is relatively new, although a number of wide-ranging reviews with an environmental rather than a chemical perspective are now available that outline the influence of terrestrial ice and snow on chemical releases from the polar regions.[1,24]

Hence, a significant number of studies have, by now, been conducted into the phenomenon because of the need to construct more accurate predictive computer models related to atmospheric chemical composition change and climate effects. The earlier studies, in the 1980s, focused on understanding the uptake of gases adsorbed onto ice surfaces due to the perceived, and soon proven, importance of heterogeneous chemistry catalyzed by Polar Stratospheric Clouds and the subsequent impacts on polar ozone depletion.[2] Later both ozone and mercury were shown to be removed from the troposphere completely (and almost instantaneously) at the time of Arctic polar sunrise. The monitoring activities suggested that the phenomena were caused by the involvement of halogens. However, it was not until the 1990s that the significance of chemical transformations related to the freezing of aqueous solutions containing environmentally relevant solutes located on land and in oceans or the air became more fully appreciated.

For example, a paper published in 1991 suggested that coupled oxidation−reduction reactions occur in ice crystals grown in a snow chamber.[25] It was proposed that the reactions were occurring by means of ion separation promoted by freezing (i.e., the Workman−Reynolds effect).

Subsequently, it was shown that nitrite ions were efficiently converted into nitrates upon freezing aqueous samples that had been collected from the field.[26] The reaction was found to be accelerated by as much as 10^5 times when compared to the analogous reaction at room temperature. A more detailed study was later conducted[6] based on earlier studies[12,15] as templates. All possible factors that could result in the oxidation of nitrite ions to nitrate were systematically addressed. First, the thawing process was ruled out as the cause of the oxidation by examining the rate and temperature to which the solution was heated. Then the rate of freezing was varied and it was shown that product formation was linearly dependent on the freezing rate. The conclusion was that the reaction was accelerated during the freezing of the solution. The effect of photolysis was also investigated, and the results compared with samples kept in the dark: no significant difference was observed. The catalytic effect of ice was also ruled out by adding crushed ice to the solution and maintaining the temperature at 273 K, while stirring the solution to increase the collision frequency of the reactants with the growing ice surface. Again no significant increase in nitrate ion formation was monitored. Finally, it was reported that acidic media were required for the reaction to occur, although the identity of the acid used was irrelevant.

It was suspected that a freeze-concentration effect was occurring with the nitrite ion being excluded from the growing ice phase and concentrating in the bulk solution. Therefore, a solution was frozen from the flask bottom upward, with the liquid and solid states then separated and analyzed. From the experiments, it was concluded that during the formation of polycrystalline ice the reactants were concentrated into unfrozen (micro)pockets surrounded by ice grain walls.

The unfrozen liquid (micro)pockets decrease in size as the temperature is lowered because they gradually become incorporated into the growing ice phase. Clearly, as the quantity of liquid is reduced in the (micro)pocket because of a decrease in size, the concentration of the solute(s) increases. Of course, the concentration effect and any reactions in the unfrozen pockets cease at temperatures below the eutectic point of the solution when all is solid. Thus, in order to examine the effect of temperature on the reaction, Takenaka et al.[6] froze solutions at various temperatures (from 272.8 to 77 K) and measured the concentration of nitrate formed. It was discovered that below 270 K the reaction rate was linearly dependent on the freezing rate, implying that the freezing process was the rate-determining step for nitrate formation.

The freezing potential effect was also investigated as a possible mechanism for the acceleration. The cause was deemed to be due to the freeze-concentration effect with freezing potential also playing a role by lowering the pH of the unfrozen solution within the ice structure. The overall chemistry suggested to occur for nitrite ion to nitrate ion oxidation in frozen solutions is shown in reactions 2 and 3:

$$NO_2^- + H^+ \rightleftharpoons HNO_2 \qquad (2)$$

$$2HNO_2 + O_2 \rightarrow 2H^+ + 2NO_3^- \qquad (3)$$

This mechanism in the ice is fully equivalent to that known to occur with the room temperature reaction. Finally, the likelihood of this oxidation reaction taking place in the troposphere was evaluated by freezing rainwater or fog samples. The reactions were shown to proceed below pH 6. By studying frozen fog particles generated by an ultrasonic humidifier, it was established that the nitrite concentration decreased while the nitrate concentration increased suggesting the oxidation of nitrite to nitrate could occur in freezing fogs.[27]

Later experimental support was provided for the conclusion that the autoxidation of species such as nitrite and sulfite ions could be promoted when dilute aqueous solutions were frozen.[7] It was concluded that higher dissolved oxygen concentrations yielded more product, that is, that the product yield was O_2-limited. The study was in agreement with the hypothesis[6] that the acceleration of the nitrite oxidation was likely due to the freeze-concentration mechanism.

The oxidation capacity of the atmosphere is of key relevance to predictive models for chemical compositional change. Therefore, following on from the above studies,[6] the reaction between iodide and nitrite ions was shown to be accelerated by freezing to 245−260 K with dilute aqueous solutions of the ions at levels up to pH 6.1.[10] The corresponding room temperature reaction is described as

$$2HNO_2 + 2I^- + 2H^+ \rightleftharpoons 2NO + 2I_2 + 2H_2O \qquad (4)$$

At room temperatures, reaction 4 has been found to be so slow above pH 5.5 that product formation is insignificant. By contrast, in the freezing experiments, a 7.5 mM $NaNO_2$/KI aqueous solution with pH 6.1 (using H_2SO_4 for acidification) was frozen, thawed, and analyzed using UV−vis spectroscopy. The use of HCl for acidification purposes is discussed in more detail in the next section.

The resulting spectra showed an absorption band corresponding to the tri-iodide ion, which is produced from reaction between iodine and the iodide ion. This measurement implied that the oxidation of iodide to iodine could occur at a more atmospherically relevant pH upon freezing. The conclusion was made that a freeze-concentration effect was occurring, with the number of H^+ ions increasing in the micropockets, which thereby played a significant role in the acceleration process. The presence of dissolved oxygen was found to enhance the production of the tri-iodide ion because experiments performed under anoxic conditions resulted in yields some six times lower than when dissolved oxygen was present. It can be suggested from these results that the formation and possible release of NO to the atmosphere might be enhanced by freezing nitrite ions in the presence of iodide ions. The study of the oxidation capacity of a variety of halide ions in frozen aqueous solutions have provided many new insights into potential chemistry occurring in snowpacks as will be discussed in detail below.

Atmospherically Relevant Freezing Reactions

Introduction. Monitoring studies at Summit, Greenland, performed in the late 1990s have shown significant enhancement in the concentrations of several trace gases in the snowpack pore (firn) air relative to the atmosphere.[1]

Analytical measurements have been reported for organic compounds such as formaldehyde, alkenes, halocarbons, and alkyl nitrates that are typically a factor of 2–10 higher in concentration within the firn air than in the ambient air 1–10 m above the snow. Firn air also contains elevated levels of nitrogen dioxide, and mechanisms involving nitrate ion photolysis are thought likely to be important. Indeed the effects of photolysis on frozen thin films of water-ice containing nitrogen dioxide (as its dimer, dinitrogen tetroxide) have been investigated using a combination of Fourier transform reflection–absorption infrared spectroscopy and mass spectrometry. Under these circumstances HONO, was shown to be released from the ice by a mechanism involving the nitrosonium nitrate ion ($NO^+NO_3^-$) and its solvated, protonated product H_2ONO^+ (the nitroacidium ion).[28] However, such experiments were performed under temperature conditions far removed from those encountered in the polar regions. In contrast, the chemistry of a number of reactions with potential relevance to the poles involving halides and also mercury have been performed more recently at relevant temperature and concentration conditions.

Iodochloride Interhalides. During the studies on the freezing effect of iodide on nitrite chemistry in aqueous solutions carried out,[10] a predictable product was observed in the spectrum of the nonfrozen solution when hydrochloric acid was substituted for sulfuric acid as the acidification agent. This product was determined to be the di-iodochloride interhalide ion and further investigation into the mechanism by which it formed was therefore carried out. It was shown that the $I_2\bar{Cl}$ product was produced when the pH of room temperature solutions was lowered below 3: initially because of the production of iodine. Identical samples were frozen for one hour at 243 K and the contents analyzed after thawing using a UV–vis spectrophotometer. However, these spectra displayed unexpected absorption bands at 224 and 342 nm which could be readily assigned to the ICl_2^- polyhalide species. The conclusion was that the freezing process appeared to alter the reaction pathway operative at room temperature.[29] It is well-known that acidified nitrite ions can form both nitrous acid and the nitroacidium ion and hence the formation of H_2ONO^+ as oxidant, was suggested to represent an important participant in the freezing scheme described by reactions 5 and 6 to produce the ICl_2^- interhalide.

$$I_2Cl^- + H_2ONO^+ \rightleftharpoons INO + ICl + H_2O \qquad (5)$$

$$ICl + Cl^- \rightleftharpoons ICl_2^- \qquad (6)$$

The necessity for the participation of the nitroacidium ion can explain the requirement for a pH 3 or less as described previously.[30] In support of this suggestion, it was found that the concentration of the dichloroiodide ion produced mirrored the concentration of the nitroacidium ion in solution.

In principle, the formation of ICl in the freezing process, although not at room temperature, and its subsequent airborne photolysis could lead to ozone destruction in the atmosphere because of chlorine atom formation. In fact, so-called "sudden" ozone depletion events have been monitored in the Arctic troposphere. However, the low pH required to promote the reaction from the above scheme would appear to rule out any environmental relevance in this case.

Iodobromide Interhalides. A later investigation to determine whether bromohalides exhibited similar behavior, but under more environmentally relevant conditions, was assessed.[9] Solutions prior to freezing were found to contain I_2Br^-, but following freezing analysis showed them to contain IBr_2^- as expected from prior results.[29] Again it was apparent that the freezing process altered the reaction pathways from the room temperature counterparts. The nitroacidium ion was clearly shown to be involved in the initial step of the reaction.[6] Dissolved oxygen was also observed to participate in the process.

By analogy with the iodine-chloride experiments the conversion of the diiodobromide ion to the dibromoiodide ion was proposed to occur via the iodine monobromide intermediate as shown in reaction 7.

$$I_2Br^- + Br^- \rightleftharpoons IBr_2^- + I^- \qquad (7)$$

The favored products in this equilibrium will therefore depend on the ratio of the bromide to iodide ions present in solution. It is apparent from reaction 7 that high concentrations of iodide ion will inhibit the formation of the dibromoiodide ion by shifting the equilibrium to the left and promote di-iodobromide formation. However, the presence of both acid and nitrite ions in the frozen solutions lead to the generation of HONO, a species known to oxidize iodide ions to iodine.[10] The formation of iodine is further stimulated by the presence of dissolved oxygen. The outcome of this chemistry is that iodide concentrations will be reduced thereby driving reaction 7 to the right, which favors the formation of dibromoiodide ions.

A more detailed investigation was conducted by examining product formation as a function of temperature (268–243 K). Although no temperature dependence was found, a freeze-concentration effect could not be ruled out from these results. Thus, in order to provide some evidence for the occurrence of a freeze-concentration effect, the concentrations of the bromide and iodide ions were increased by a factor of 1000 and left at room temperature. The resulting UV−vis spectra showed that the dibromoiodide ion was formed indicating that by concentrating the initial reactants by a factor of 1000 similar results to freezing the low concentration solutions were obtained. This observation provided clear evidence that a freeze-concentration effect did indeed occur in the frozen solutions including solutions that contained other oxidants than HONO. Subsequently, investigations into whether interhalide formation would occur at a bromide to iodide ratio more relevant to that found in natural environments were undertaken. Hence, the ratio of bromide to iodide was increased to 6160:1 and the resultant product was found to be the dibromoiodide ion. Interestingly, the formation of the interhalide ion required less acidic conditions to form. Indeed, the dibromoiodide ion was found to form, above the limit of detection, up to a pH of 5.3. Thus, the work suggests that the formation of the dibromoiodide ion may take place at environmentally relevant concentrations, temperatures, and pH. The formation of IBr_2^- described in the study is again relevant to tropospheric ozone destruction because it can decompose to produce IBr which may diffuse into the atmosphere and release reactive bromine and iodine atoms after photolysis.

Bromochloride Interhalides. Until recently, no studies on "freezing oxidation" relevant to the formation of bromochloride interhalides had been performed. In contrast, several studies on the reactions of hypobromous acid, HOBr, with water-ice containing chloride and bromide ions have been conducted. The results show that gaseous bromine and BrCl can be released from ices and dry surfaces containing NaBr and NaCl.[31−33] In addition, room temperature studies utilizing high concentrations of reagents have been performed and the relevant equilibrium constants have been reported.[34] It was found that temperature did affect the equilibrium constants but no temperatures below 273 K were examined. Several models have also been constructed related to the formation of interhalides at environmental concentrations of reagent.[35] The effect of temperatures below 273 K on the reactions were not taken into account with these experiments, but subsequently, the effect of freezing on the formation of the bromochloride interhalide ions has been examined.

The formation of the bromine chloride interhalides was initially observed in experiments employing relatively high concentrations (M) of reagents albeit at room temperature.[34] A further investigation was carried out later to determine whether freezing solutions containing environmentally relevant concentrations of appropriate reagents could accelerate the formation of the interhalide products.[36] Therefore, solutions containing bromate, bromide, chloride and sulfuric acid (pH ∼ 2.5) were frozen to 243 K for 1 h and compared with their nonfrozen counterparts using UV−vis spectroscopy to analyze the thawed contents. The nonfrozen solutions displayed no absorbance peaks in the spectra, but the frozen solutions did produce some new features. These bands were attributed to the presence of the $Br_2C\bar{l}$ ion in solution. In the high concentration room temperature solutions that had previously been studied, the dominant product was determined to be the $BrCl_2^-$ ion, yet in the frozen low concentration solutions the dominant product was clearly the Br_2Cl^- ion. Furthermore, an equilibrium process was established to exist between the dibromochloride and the dichlorobromide ion minor products as shown in reaction 8.

$$Br_2Cl^- + Cl^- \rightleftharpoons BrCl_2^- + Br^- \tag{8}$$

The results were subsequently probed further by investigating the effect of temperature, acidity, and reagent concentrations. It was found that, as the temperature was reduced from ∼273 to 243 K, the concentration of the dibromochloride ion increased. It was deduced from all the results that both a freeze-concentration effect and a freeze-potential effect were likely to play a role in the mechanism. Acidity again was shown to play a crucial role, most likely by protonating bromate ions to form hypobromous acid.

It was also found that both the bromate concentration and the chloride to bromide ratio influence the identity of the major interhalide product formed. Thus, as the bromate ion concentration is decreased the formation of the Br_2Cl^- ion becomes favored. It is also favored as the chloride to bromide ratio is decreased. The unusual formation of the dibromochloride product by freezing and at low concentrations of reagents is a discovery of potentially great importance as the dibromochloride product can release "active" bromine to the atmosphere to cause tropospheric ozone depletion in the polar regions.[35] Surprisingly, sudden ozone depletion events related to bromine release were also subsequently linked to the behavior of mercury in the polar troposphere.[37]

Elemental Mercury Oxidation. A substantial amount of mercury is carried into the Arctic via long-range transport by air and water currents from human sources at lower latitudes. Hence, understanding the processes by which the oxidation of elemental mercury occurs in the polar regions is of importance due to the ability of inorganic mercury to be transformed to methyl mercury, a potent neurotoxin.

Therefore, in order to determine whether oxidation of elemental mercury could be promoted by freezing, solutions initially containing relatively high concentrations of sulfuric acid or hydrogen peroxide were frozen at 243 K for 1 h in the presence of elemental mercury. The concentrations of the reagents were set to environmentally relevant concentrations, and mercury oxidation was observed in the frozen flasks. Furthermore, the oxidation of Hg^0 by sulfuric acid was found to be enhanced when dissolved oxygen was present. Additionally, the combination of environmentally relevant concentrations of sulfuric acid and hydrogen peroxide proved to be an effective mercury oxidant when frozen in the presence of Hg^0: approximately 50% of the mercury in solution was oxidized.[38]

Conclusion

Counterintuitively, the freezing of solutions containing more than one component can lead to an acceleration of certain organic and inorganic reactions. The process results in chemical processes that are deemed to be slow at room temperature becoming promoted by freezing; it can also produce unexpected chemical products. The mechanisms by which freezing can accelerate certain reactions relevant to atmospheric chemistry in the cryosphere have been described. The main importance of the physical and chemical processing driven by the ices is that products formed can diffuse into the atmosphere and, if photochemically active, can produce species capable of destroying ozone in regions such as the Arctic troposphere. Future prospects will likely concentrate, in a return to the earliest cryochemistry work related to the food industry, on the low-temperature chemistry of organic compounds, such as the humic acids, which are known snowpack contaminants. In addition, more data on the kinetics and thermodynamics of all types of reaction promoted by the freezing process would provide much assistance in determining their implications to environmental computer models.

Although the processing results related to field observations have been described in previous reviews relevant to polar regions, this report is the first to discuss the various laboratory-based findings in terms of connected chemical and physical mechanisms.

BIOGRAPHICAL INFORMATION

Professor John Sodeau is Head of Chemistry at UCC and has published extensively on atmospheric processes driven by solid surfaces especially water-ices, particulate matter, and bioaerosols.

Dr. Ruairí O'Concubhair is a Postdoctoral Fellow at UCC.

FOOTNOTES

*To whom correspondence should be addressed.
The authors declare no competing financial interest.

REFERENCES

1 Abbatt, J. P. D.; et al. Halogen activation via interactions with environmental ice and snow in the polar lower troposphere and other regions. *Atmos. Chem. Phys.* **2012**, *12* (14), 6237–6271.

2 Tolbert, M. A.; Rossi, M. J.; Golden, D. M. Antarctic Ozone Depletion Chemistry - Reactions of N_2O_5 With H_2O and HCl On Ice Surfaces. *Science* **1988**, *240* (4855), 1018–1021.

3 Solomon, S.; et al. On the Depletion of Antarctic Ozone. *Nature* **1986**, *321* (6072), 755–758.

4 Horn, A. B.; et al. Low temperature reaction of chlorine nitrate with water ice - Formation of molecular nitric acid. *J. Chem. Soc., Faraday Trans.* **1998**, *94* (12), 1721–1724.

5 Koch, T. G.; Sodeau, J. R. Photochemistry of Nitric Acid in Low-Temperature Matrices. *J. Phys. Chem.* **1995**, *99* (27), 10824–10829.

6 Takenaka, N.; et al. Acceleration mechanism of chemical reaction by freezing: The reaction of nitrous acid with dissolved oxygen. *J. Phys. Chem.* **1996**, *100* (32), 13874–13884.

7 Betterton, E. A.; Anderson, D. J. Autoxidation of N(III), S(IV), and other species in frozen solution - A possible pathway for enhanced chemical transformation in freezing systems. *J. Atmos. Chem.* **2001**, *40* (2), 171–189.

8 O'Driscoll, P.; et al. Freezing halide ion solutions and the release of interhalogens to the atmosphere. *J. Phys. Chem. A* **2006**, *110* (14), 4615–4618.

9 O'Sullivan, D.; Sodeau, J. R. Freeze-Induced Reactions: Formation of Iodine-Bromine Interhalogen Species from Aqueous Halide Ion Solutions. *J. Phys. Chem. A* **2010**, *114* (46), 12208–12215.

10 O'Driscoll, P.; et al. Release of nitric oxide and iodine to the atmosphere from the freezing of sea-salt aerosol components. *J. Phys. Chem. A* **2008**, *112* (8), 1677–1682.

11 Boxe, C. S.; Saiz-Lopez, A. Multiphase modeling of nitrate photochemistry in the quasi-liquid layer (QLL): implications for NOx release from the Arctic and coastal Antarctic snowpack. *Atmos. Chem. Phys.* **2008**, *8* (16), 4855–4864.

12 Pincock, R. E. Reactions in frozen systems. *Acc. Chem. Res.* **1969**, *2* (4), 97–103.

13 Cobb, A. W.; Gross, G. W. Interfacial electrical effects observed during the freezing of dilute electrolytes in water. *Electrochemical Science* **1969**, *116* (6), 796–804.

14 Eyal, Y.; Maydan, D.; Treinin, A. The autoxidation of I^- in ice. *Isr. J. Chem.* **1964**, *2*, 133–138.

15 Fennema, O. Reaction Kinetics in Partially Frozen Aqueous Systems. In *Water relations of foods*; Duckworth, R.G., Ed.; Academic Press: London, 1975; pp 539−556.

16 Bronshteyn, V. L.; Chernov, A. A. Freezing Potentials Arising On Solidification of Dilute Aqueous-Solutions of Electrolytes. *J. Cryst. Growth* **1991**, *112* (1), 129–145.

17 Fukazawa, H.; et al. Acid ions at triple junction of Antarctic ice observed by Raman scattering. *Geophys. Res. Lett.* **1998**, *25* (15), 2845–2848.

18 Pincock, R. E.; Kiovsky, T. E. Kinetics of Reactions in Frozen Solutions. *J. Chem. Educ.* **1966**, *43* (7), 358–360.

19 Takenaka, N.; Bandow, H. Chemical kinetics of reactions in the unfrozen solution of ice. *J. Phys. Chem. A* **2007**, *111* (36), 8780–8786.

20 Takenaka, N.; et al. Rapid reaction of sulfide with hydrogen peroxide and formation of different final products by freezing compared to those in solution. *Int. J. Chem. Kinet.* **2003**, *35* (5), 198–205.

21 Workman, E. J.; Reynolds, S. E. Electrical Phenomena Occurring during the Freezing of Dilute Aqueous Solutions and Their Possible Relationship to Thundrstorm Electricity. *Phys. Rev.* **1950**, *78* (3), 254–259.

22 Takenaka, N.; et al. Rise in the pH of an unfrozen solution in ice due to the presence of NaCl and promotion of decomposition of gallic acids owing to a change in the pH. *J. Phys. Chem. A* **2006**, *110* (36), 10628–10632.

23 Heger, D.; Klánová, J.; Klán, P. Enhanced protonation of cresol red in acidic aqueous solutions caused by freezing. *J. Phys. Chem. B* **2006**, *110* (3), 1277–1287.

24 Grannas, A. M.; et al. An overview of snow photochemistry: evidence, mechanisms and impacts. *Atmos. Chem. Phys.* **2007**, *7* (16), 4329–4373.

25 Finnegan, W. G.; Pitter, R. L.; Young, L. G. Preliminary-Study of Coupled Oxidation Reduction Reactions of Included Ions in Growing Ice Crystals. *Atmos. Environ., Part A* **1991**, *25* (11), 2531–2534.

26 Takenaka, N.; Ueda, A.; Maeda, Y. Acceleration of the Rate of Nitrite Oxidation By Freezing in Aqueous- Solution. *Nature* **1992**, *358* (6389), 736–738.

27 Takenaka, N.; et al. Fast oxidation reaction of nitrite by dissolved oxygen in the freezing process in the tropospheric aqueous phase. *J. Atmos. Chem.* **1998**, *29*, 135–150.

28 Hellebust, S.; O'Sullivan, D.; Sodeau, J. R. Protonated Nitrosamide and Its Potential Role in the Release of HONO from Snow and Ice in the Dark. *J. Phys. Chem. A* **2010**, *114* (43), 11632–11637.

29 O'Driscoll, P.; et al. Freezing Halide Ion Solutions and the Release of Interhalogens to the Atmosphere. *J. Phys. Chem. A* **2006**, *110* (14), 4615–4618.

30 Riordan, E.; et al. Spectroscopic and optimization modeling study of nitrous acid in aqueous solution. *J. Phys. Chem. A* **2005**, *109* (5), 779–786.

31 Adams, J. W.; Holmes, N. S.; Crowley, J. N. Uptake and reaction of HOBr on frozen and dry NaCl/NaBr surfaces between 253 and 233 K. *Atmos. Chem. Phys.* **2002**, *2*, 79–91.

32 Huff, A. K.; Abbatt, J. P. D. Kinetics and product yields in the heterogeneous reactions of HOBr with ice surfaces containing NaBr and NaCl. *J. Phys. Chem. A* **2002**, *106* (21), 5279–5287.

33 Abbatt, J. P. D. Heterogeneous Reaction of HOBr With HBr and HCl On Ice Surfaces At 228-K. *Geophys. Res. Lett.* **1994**, *21* (8), 665–668.

34 Liu, Q.; et al. Kinetics and mechanisms of aqueous ozone reactions with bromide, sulfite, hydrogen sulfite, iodide, and nitrite ions. *Inorg. Chem.* **2001**, *40* (17), 4436–4442.

35 Vogt, R.; et al. Some new laboratory approaches to studying tropospheric heterogeneous reactions. *Atmos. Environ.* **1996**, *30* (10−11), 1729–1737.

36 O'Concubhair, R.; Sodeau, J. R. Freeze-Induced Formation of Bromine/Chlorine Interhalogen Species from Aqueous Halide Ion Solutions. *Environ. Sci. Technol.* **2012**, *46* (19), 10589–10596.

37 Lu, J. Y.; et al. Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry. *Geophys. Res. Lett.* **2001**, *28* (17), 3219–3222.

38 O'Concubhair, R.; O'Sullivan, D.; Sodeau, J. R. Dark Oxidation of Dissolved Gaseous Mercury in Polar Ice Mimics. *Environ. Sci. Technol.* **2012**, *46* (9), 4829–4836.