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Different photolysis kinetics at the surface of frozen freshwater vs. frozen salt solutions

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Abstract

The presence of solutes such as sodium halide salts can greatly alter the physical nature of air-ice interfaces. In this work, we studied the effects of sodium chloride and sodium bromide on the photolysis kinetics of harmine, an aromatic organic compound, in aqueous solution and at the surface of frozen salt solutions. Harmine photolysis is much faster on pure ice surfaces than in aqueous solution, but the presence of NaCl or NaBr – which does not affect photolysis kinetics in solution – reduces the photolysis rate on ice. The rate decreases monotonically with increasing salt concentration; at the concentrations found in seawater, harmine photolysis at the surface of frozen salt solutions proceeds at the same rate as in aqueous solution. These results suggest that the brine excluded to the surfaces of frozen salt solutions is a true aqueous solution, and so it may be possible to use aqueous-phase kinetics to predict photolysis rates on sea ice. This is in marked contrast to the result at the surface of pure ice samples, where reaction kinetics are often not well-described by aqueous-phase processes.

1 Introduction

Chemical reactions in snow and ice can affect pollutant fate and atmospheric composition (Domine and Shepson, 2002; Grannas et al., 2007) in urban and remote centres. Various aspects of snowpack chemistry have been investigated through field, laboratory, and theoretical studies (ibid). However, we do not yet have a fundamental understanding of the role of snow and ice as reaction media; thus, accurately predicting the chemical fate of species in snow and ice remains an elusive goal.

Ice is a heterogeneous and complex reaction medium. During freezing, compounds can be excluded into liquid inclusions such as veins, pockets, and grain boundaries within bulk ice (Eicken et al., 2001); reaction kinetics in bulk ice have been reported to be similar to those in aqueous solution (Chu and Anastasio, 2003, 2005, 2007; Annor et al., 2006; Grannas et al., 2007; Ram and Anastasio, 2009; Kahan et al., 2010a, b).

Reagents can also reside in the disordered region at the air-ice interface known as the quasi-liquid layer (QLL) due to exclusion during freezing or gas-phase deposition. The physical properties of the QLL are distinct from both bulk ice and liquid water (Wei et al., 2001; Kahan et al., 2007); some recent laboratory studies (Sumner et al., 2004; Grannas et al., 2007; Kahan and Donaldson, 2007; Matykiewiczova et al., 2007; Kahan and Donaldson, 2008, 2010; Kahan et al., 2010a, b) suggest that reaction kinetics in the QLL can differ dramatically from those in aqueous solution.

We have recently (Kahan et al., 2010a, b) compared reaction kinetics in bulk ice and at air-ice interfaces, and have found that kinetics can differ greatly in the two regions. Direct photolysis of the polycyclic aromatic hydrocarbon (PAH) anthracene proceeds at the same rate in bulk ice as in aqueous solution, but is much faster at ice surfaces (Kahan et al., 2010b). Hydroxyl radicals react quickly with aromatic compounds both in aqueous solution and in bulk ice, but at ice surfaces no reaction is observed (Kahan et al., 2010a). These results suggest that liquid inclusions in bulk ice present similar reaction environments to liquid water, but that the QLL presents a unique reaction environment.

It is clear that the physical properties of ice surfaces can greatly affect chemical reactions that occur there. However, few studies have investigated these properties under environmentally relevant conditions; most investigations of QLL properties have used single-crystalline ice in pristine conditions in the absence of solutes. In the environment, ice is generally polycrystalline, and it is rarely pristine. Common solutes such as halide salts can significantly alter the molecular structure at air-ice interfaces, and possibly affect reaction kinetics there.

During freezing, ionic compounds such as halide salts are excluded from the ice matrix. Below the eutectic temperature, a solid solution of ice and salt is formed. Atomic force microscopy (AFM) measurements (Doppenschmidt and Butt, 2000) indicate that the salt precipitates in clumps at the ice surface at these temperatures, rather than forming a uniform layer. Above the eutectic temperature, halide exclusion results in the formation of concentrated brines in veins and pockets within bulk ice, as well as at the air-ice interface (Schondorf and Herrmann, 1987; Massom et al., 2001; Carignano et al., 2007). Glancing-angle Raman spectra acquired in this laboratory (Kahan et al., 2007), shown in Fig. 1, suggest that water molecules at the surface of frozen salt solutions are less strongly hydrogen-bonded than those at the surface of pure ice. This could indicate disruption of the QLL structure by the halide ions, or it could indicate the formation of a true liquid brine at the sample surface. This is an important distinction because, as discussed previously, reaction kinetics in QLLs can be very different from kinetics in aqueous solution. If a disrupted QLL exists at the surface of frozen salt solutions, then we might expect reactions on sea ice surfaces to occur at similar rates as on pure ice surfaces. However, if a concentrated liquid brine exists at the surface of frozen salt solutions, then we might expect the reaction kinetics to be similar to those in aqueous solution. In fact, we have recently measured heterogeneous ozonation kinetics at the surface of frozen NaBr and NaI solutions (Wren et al., 2010); the kinetics are consistent with the reaction occurring in aqueous solution. In this study, we measure photolysis kinetics of an organic probe molecule in aqueous solution and at the surfaces of pure ice and frozen salt solutions to determine whether the reaction environment at the surface of frozen salt solutions is more similar to a QLL or to aqueous solution.

2 Experimental

The aromatic compound harmine (7-methoxy-1-methyl-9H-pyrido[3,4-b]indole) was chosen as a molecular probe because its fluorescence is not strongly quenched in high ionic strength environments (Clifford et al., 2007). Solutions containing 1×10^{-7} mol L^{-1} harmine (Aldrich, 98%) and a known concentration of either NaCl or NaBr (both ACP Chemicals, 99%) were prepared daily in 18 M$\Omega\cdot$cm deionized water. Samples were irradiated by the output of a 75 W xenon arc lamp which passed through a 295 nm longpass cutoff filter. A first-surface mirror with maximum reflectivity at 355 nm directed the lamp's output downward onto the sample at an angle of approximately 45°.

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Liquid-phase samples were photolyzed in quartz cuvettes at room temperature. Ice samples were contained in a reaction chamber which has been described previously (Kahan and Donaldson, 2007). Briefly, the chamber consists of a Teflon box with cooling tubes running beneath the copper floor of the chamber. Approximately 1 mL of solution was pipetted onto a small copper plate on the chamber floor and allowed to freeze. The ice samples resembled small pancakes with diameters of approximately 1.5 cm and heights of 1–2 mm. The chamber floor was maintained at either ∼253 K or ∼243 K for experiments on ice.

Kinetics were determined by monitoring harmine fluorescence intensity during irradiation. Fluorescence was induced by the unfocussed 337 nm output of a nitrogen laser, and collected by a liquid light guide (LLG) positioned approximately 7 mm from the sample. For aqueous samples in cuvettes, the LLG was positioned to the side of the cuvette, perpendicular to the laser beam. For experiments on ice, the laser beam entered the reaction chamber through a quartz window at a shallow angle (>85° from the surface normal), such that it impinged upon the ice surface. The LLG was positioned above the ice sample. This geometry affords us surface sensitivity (Kahan et al., 2007), and allows us to measure kinetics at air-ice interfaces (Kahan and Donaldson, 2007, 2008, 2010; Kahan et al., 2010a, b; Wren et al., 2010).

The emission collected by the LLG passed through a monochromator set to 430 nm, where harmine emits strongly, then was detected by a photomultiplier tube and imaged on a digital oscilloscope. The fluorescence decay was averaged over 64 laser shots; a 500 ns slice of the decay was captured and stored for analysis. Fluorescence intensity was measured in the dark for several minutes at the beginning of each experiment to ensure that no dark loss was occurring. The sample was then irradiated for up to 4 h, with fluorescence intensity acquired at known time intervals ranging from 1–10 min. The xenon arc lamp was blocked during data acquisition.

3 Results and discussion

Figure 2 shows representative results of the decay of harmine fluorescence intensity observed during irradiation in aqueous solution and at an air-ice interface, plotted semi-logarithmically. The linearity of the data indicates that the decays are first order in harmine at the concentrations used here. The photolysis rate is approximately 4 times greater on ice than in aqueous solution. We have previously observed higher photolysis rates on ice than in aqueous solution, or at the air-water interface for other aromatic species as well, including anthracene, naphthalene, and benzene (Kahan and Donaldson 2007, 2010; Kahan et al., 2010b). We have previously measured increased absorbance of light at wavelengths above 295 nm by aromatics at the ice surface (Kahan and Donaldson, 2010; Kahan et al., 2010b). This is likely caused by their self-association there (Kahan and Donaldson, 2007, 2010; Ardura et al., 2009; Kahan et al., 2010b), and may explain the faster photolysis rates of benzene and naphthalene. However, since harmine absorbs primarily to the red of 295 nm both in aqueous solution (Dias et al., 1996; Clifford et al., 2007) and at ice surfaces (Wren et al., 2010), its faster photolysis on ice cannot be completely explained by a red-shift in its absorbance spectrum.

At the photon fluxes used in this experiment ($\sim 3\times10^{13}$ photon cm^{-2} s^{-1}), the photolysis kinetics of aromatic compounds such as anthracene, naphthalene, and benzene are insensitive to changes in lamp power (Kahan and Donaldson, 2010; Kahan et al., 2010b). Thus, the enhanced photolysis rates observed for harmine on ice are likely due to differences in the physical properties of the QLL and liquid water, rather than to differences in the photon flux in aqueous solution and at air-ice interfaces.

Figure 3 shows the rate constants obtained from the slopes of plots like those shown in Fig. 2 for harmine photolysis in aqueous solution and at air-ice interfaces under a range of salt concentrations and at different temperatures. The presence of salt does not affect harmine photolysis kinetics in aqueous solution up to 1 mol L^{-1} NaCl, which roughly corresponds to seawater concentrations. At air-ice interfaces, however, increasing the salt concentration of the solution prior to freezing decreases the photolysis rate until the observed rate at the ice surface is identical to that in aqueous solution. Harmine photolysis rates at the surface of frozen salt solutions are the same as those in aqueous solution when NaCl concentrations exceed ∼0.2 mol L^{-1}.

The eutectic temperature for NaCl-water is 251 K, which means that at equilibrium, frozen solutions at temperatures below this point are composed of solid NaCl+solid ice phases. The red symbols in Fig. 3 represent experiments performed using frozen solutions of aqueous NaCl at 253 K. Based on the phase diagram for NaCl-water (Akinfiev et al., 2001), these experiments interrogated the ice surface under conditions where one would expect co-existence of solid ice and a brine having [NaCl] ∼4.5 mol L^{-1} (excluded both to the surface and to liquid regions within the bulk). Experiments, illustrated by the grey points in Fig. 3, were also performed at 243 K which lies eight degrees below the eutectic temperature. Only ice and solid NaCl should be present. Changing the temperature does not affect the photolysis kinetics of harmine on a pure ice surface, but the photolysis rate on frozen 0.1 mol L^{-1} NaCl at 243 K is clearly faster than that seen at 253 K. This result is consistent with our expectation that the rate should be higher for harmine present at the ice surface (with its attendant QLL) than in a true solution, as represented by a brine layer. Lowering the temperature of frozen NaCl solutions to below the eutectic temperature has also been reported to increase the rate of the photochemically-initiated bimolecular reaction between pyridine and *p*-nitroanisole in frozen salt solutions (Grannas et al., 2007). It is possible that something resembling a QLL exists at the surface of frozen salt solutions below the eutectic temperature: NMR studies (Schondorf and Herrmann, 1987) indicate the presence of a liquid-like layer at temperatures at least 20 K below the eutectic. This "quasi-brine layer" (QBL) is likely not a true liquid; rather, it may be analogous to the QLL which exists at pure ice surfaces. Apart from the AFM images discussed previously, to our knowledge the physical properties of this QBL have not been investigated.

In order to further explore the influence of brine on the photolysis of harmine on ice, experiments were also performed on frozen solutions of NaBr at 253 K having initial [NaBr] of 0.05 and 0.1 mol L^{-1}, as indicated by the green symbols in Fig. 3. Under these conditions, the NaBr-water phase diagram (Tang et al., 2003) predicts that there should be two phases present at equilibrium: Ice and a liquid brine with [NaBr] ~3.8 mol L^{-1}. Therefore, one would expect that the kinetics should reflect the presence of a brine layer, and be slower than on the pure ice surface. Indeed, sodium bromide suppresses the photolysis rate on ice more than NaCl at the same temperature and initial concentration in solution. Inspection of the respective phase diagrams (Akinfiev et al., 2001; Tang et al., 2003) shows that the brine concentrations of NaBr and NaCl at 253 K should be ~3.8 and 4.5 mol L^{-1} respectively. Thus, starting from the same initial salt concentration, the concentration of the brine associated with frozen NaBr is less than that of the corresponding frozen NaCl solution; mass conservation thus demands that the volume of the brine is greater for the NaBr. A thicker brine layer (and therefore an environment which more resembles aqueous solution) could explain the slower photolysis rates in the presence of NaBr compared to NaCl.

The results of this study expand our understanding of environmental ice surfaces as reaction substrates. The observed harmine photolysis kinetics suggest that the liquid brine formed at the surface of frozen seawater has physical properties more similar to liquid water than to the QLL at air-ice interfaces. Halide concentrations in remote inland polar regions are orders of magnitude lower than those in seawater (Grannas et al., 2007), and should not form liquid brines. In urban snows, however, chloride concentrations of ~0.02 mol L^{-1} have been reported (Tatarniuk et al., 2009), due primarily to road salt. At this concentration, reaction kinetics may differ from those at pure ice surfaces.

To conclude, we present a summary (shown in Table 1) of the photochemical transformation behaviour observed for aromatic compounds in and on ice in this study and others (Kahan and Donaldson, 2007, 2010; Ram and Anastasio, 2009; Kahan et al., 2010b). It is clear that in order to accurately predict the fate of species in snowpacks, we must understand both the composition of the ice and the partitioning of the reagents (i.e. sequestered within the bulk versus present at the air-ice interface).

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Table 1. Predicted photochemical behaviour of aromatic compounds in and at the surface of liquid and frozen aqueous media, relative to those in bulk liquid water.

Medium	Bulk	Surface
Liquid water	n/a	Same as bulk liquid water (Kahan and Donaldson, 2007)
Liquid brine (up to 1 mol L^{-1} NaCl)	Same as liquid water (this work)	Not studied
Frozen freshwater (ice)	Same as liquid water (Ram and Anastasio, 2009; Kahan et al., 2010b)	Faster than liquid water (Kahan and Donaldson, 2007, 2010; Kahan et al., 2010b; this work)
Frozen brine ($\leq$0.2 mol L^{-1} NaCl in solution)	Not studied	Faster than liquid water, but decreases with increasing [NaCl] (this work)
Frozen brine ($>$0.2 mol L^{-1} NaCl in solution)	Not studied	Same as liquid water up to 1 mol L^{-1} (this work)

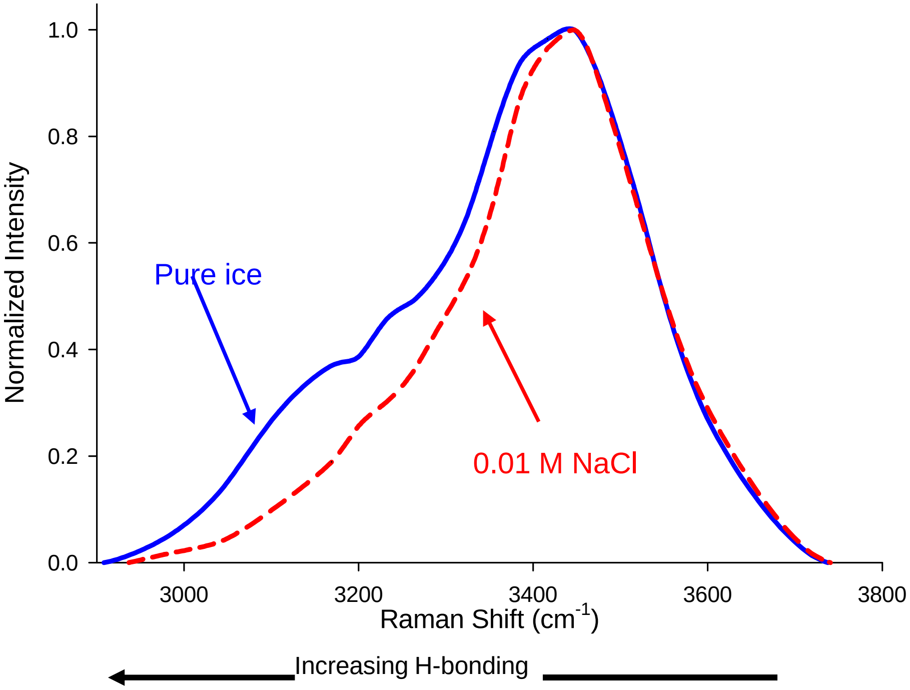

Fig. 1. Intensity-normalized glancing-angle Raman spectra of the surface of pure ice and of a frozen 0.01 mol L^{-1} NaCl solution. The lower relative intensity at lower wavenumbers for the frozen salt solution is indicative of reduced hydrogen bonding there.

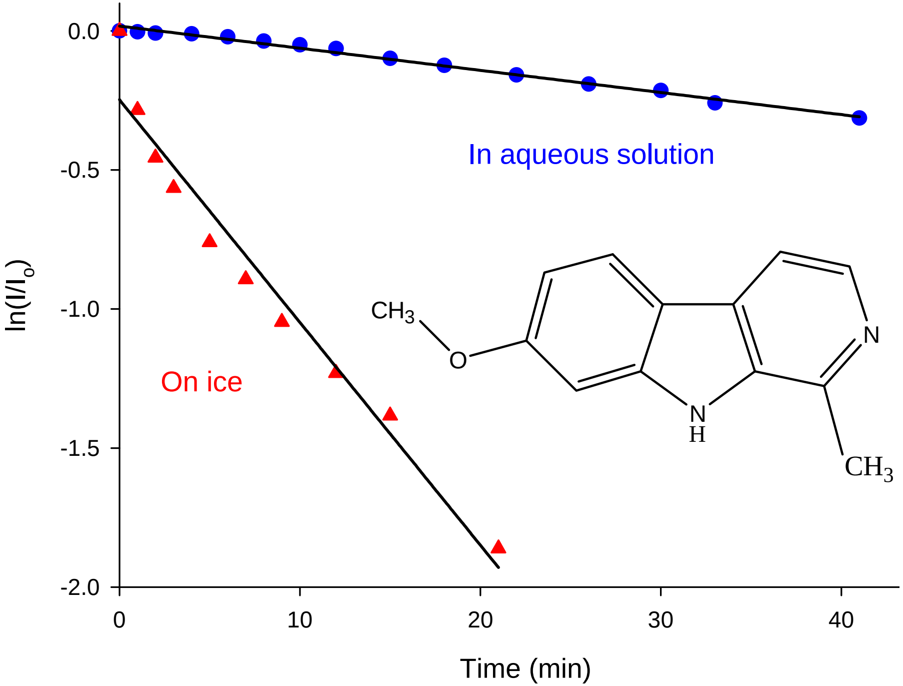

Fig. 2. Loss of harmine emission intensity as a function of irradiation time in aqueous solution and at an air-ice interface shown as semi-log plots. The solid traces are linear fits to the data. The inset displays the chemical structure of harmine.

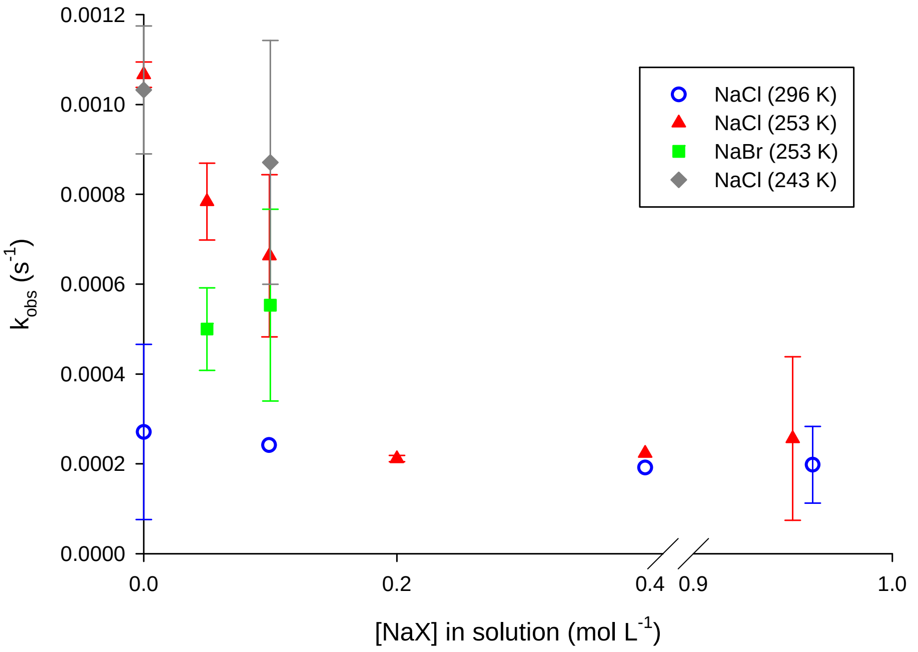

Fig. 3. Observed rate constants for harmine photolysis as a function of salt concentration: In aqueous solution at room temperature; at the surface of frozen aqueous NaCl solutions at 253 K; at the surface of frozen aqueous NaCl solutions at 243 K; and at the surface of frozen aqueous NaBr solutions at 253 K. Error bars represent the uncertainty about the mean for at least three trials.