Review of “Different photolysis kinetics at the surface of frozen freshwater vs. frozen salt solutions”
by T. F. Kahan et al.
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First, I would like to apologize to the editor and to the authors for the lateness of my review.

Second, here is my review:

The authors present a few results examining the photolysis rate constant of harmine, a beta-carboline alkaloid, in salt solutions and in ice. They find that the rate constant on “pure ice”, i.e., ice made from water with no added salt, is approximately a factor of 4-5 faster than the rate constant in an NaCl solution. Rate constants on ice made from NaCl solutions are either intermediate between these two values (for lower salt concentrations) or the same as the aqueous value (for higher salt concentrations).

As described below, while the results are the beginning of an interesting story, there are too many holes in the work for me to recommend publication in its current, rather cursory form.

Major Comments

1. My main problem with the manuscript is that the authors present relatively few pieces of data, with no substantial exploration of the chemistry.
(a) Yes, the rate constant for harmine photolysis decreases with increasing salt content, but there is no examination of the reason(s) for this. For example, is it due to changes in the QLL concentration of harmine? The authors indicate (p. 12068, line 14) that "...faster photolysis [of harmine] on ice cannot be completely explained by a red-shift in its absorbance spectrum." What quantitative evidence is there for this? What fraction of the increased photolysis rate could be attributed to a red-shift? Have the authors tested whether aqueous solutions with high concentrations of harmine (similar to those expected in the QLL) undergo photolysis at rates seen on their "pure ice"?
(b) The authors discount the possibility that differences in photon fluxes could be responsible for the rate constant differences between aqueous and “pure ice” samples (p. 12068, line 18), but their evidence for this is that lamp power had no effect on PAH photolysis rates on ice in a prior study. The authors should have examined whether this same (very surprising) effect occurs for harmine.
(c) Fig. 1 is the same as Fig. 6b of Kahan et al., J. Phys. Chem. A 2007, 111, 11006-11012. It should be deleted here as it doesn’t add to the discussion, but rather seems to be filler. Without reading the Kahan et al. (2007) paper, the reader cannot interpret the figure. (Even if this figure shows different spectra from those shown previously (i.e., not exactly the same data points), the conditions, results, and conclusion (of reduced H-bonding in the presence of 0.01 M NaCl) are not meaningfully different from that presented in the past work.)
(d) In addition to (a) and (b) above, there are a number of avenues that could be explored to more rigorously explore the chemistry. For example: extending the ice experiments (and Raman spectra) to much lower salt concentrations; measuring rate constants for the disappearance of “bulk” (i.e., total) harmine in the entire sample along with the surface rate constant

measurements presented here; adding a quantitative treatment of the data, such as done previously by Grannas et al. (2007).

2. The authors have a very binary interpretation of their data: either the chemistry is occurring in a quasi-liquid layer (QLL) existing at the air-ice interface (for “pure ice” samples) or it is occurring in a liquid brine layer on the ice (for samples made from NaCl solutions). Yet, the data is more consistent with a continuum of QLL reactivity, ranging from higher rate constants under conditions with no added salt, to lower rate constants with increasing salt content. Indeed, the “pure ice” in the current work certainly contains solutes, including the 0.1 micromolar harmine as well as probably micromolar concentrations of impurities in the water. The results in Fig. 3 are consistent with this view: the rate constant for the “pure ice” conditions lies along the (noisy) line that is formed from the NaCl-containing ices. This latter interpretation is in agreement with the system examined by Grannas et al. (2007).

Other Comments

3. p. 12064, lines 24 – 26. The authors need to be more specific about their reservoir terms. For example, the term "bulk ice" suggests that the solutes are trapped in the bulk ice matrix rather than being in quasi-liquid layers at grain boundaries and the air-ice interface. Past work (e.g., Grannas et al., 2007; Chu and Anastasio, 2003, 2005, 2007) suggests that solute photochemistry in frozen samples is occurring in QLLs, not in the bulk ice matrix, in contrast to how this is presented in the introduction. Also, the authors have defined the QLL to exist only at the air-ice interface, but it is broader than this, also including areas at grain boundaries for example.

4. p. 12068, lines 13+. "Changing the temperature does not affect the photolysis kinetics of harmine on a pure ice surface, but the photolysis rate on frozen 0.1 M NaCl at 243 K is clearly faster than that seen at 253 K."

I’m not convinced about the first claim and I disagree with second claim since these comparisons of rate constants ignore the large uncertainties on any individual value. For example, with 0.1 M NaCl, the rate constant at 243 K is not clearly faster than the value at 253 K: in fact, given the large error bars on each point, these values appear to be statistically indistinguishable. All comparison statements in the manuscript should be made statistically rigorous (e.g., with p values).

5. p.12069, line 21. “It is possible that something resembling a QLL exists at the surface of frozen salt solutions below the eutectic temperature.” There is previous good evidence for this, as shown, for example, in the work of Grannas et al. (2007).

6. Abstract, lines 10- 13: “These results suggest that the brine excluded to the surfaces of frozen salt solutions is a true aqueous solution…”. This is overreaching since harmine disappearance is too insensitive to distinguish between a very “thick” QLL and a “true aqueous solution”: there is only a factor of 4-5 difference in photolysis rate constants between "pure ice" (with no added salt) to ice with high salt concentrations, and the relative standard deviation on any given value is quite large.

7. Table 1 should be made more quantitative. For example, instead of just indicating "faster", the range of values should be given (e.g., 2 - 4 times faster). If I remember correctly, in most cases the surface values are only modestly higher than "bulk" values (e.g., in the current work).

Recommendation

I am sorry to say that I do not recommend publication. The topic is interesting, but the manuscript falls below a reasonable threshold for “minimum publishable unit”. This is especially true if one compares it to the rather similar, previous work of Grannas et al. (2007), which explored the chemistry of a different actinometer on ice under a much broader range of conditions, with many more control experiments, and with a very nice quantitative exploration of the data using a freezing-point-depression model of QLL chemistry. There are a number of ways in which the authors could extend the manuscript to more