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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Different photolysis kinetics at the surface of frozen freshwater vs. frozen salt solutions" *by* T. F. Kahan et al.

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This paper reports delicate experiments on the rate of photolysis of harmine in aqueous solution, on ice, and in frozen halide solutions. The main purpose of this study is to determine whether photolysis in frozen halide solutions takes place in a medium that is more ice-like (in fact in the quasi-liquid layer) or in a liquid brine. From their results, the authors conclude that above the eutectic, harmine photolysis takes place in a liquid brine.

Understanding snow photochemistry is a difficult problem and, as stated by this group in previous publications, the temptation to treat ice and in particular the quasi-liquid layer (QLL) present at its surface as liquid water, although convenient, does not stand up to recent data. An understanding of the properties of the actual reaction medium in which reactions take place in snow is therefore necessary. This paper makes a useful contribution to this goal and the results should be made available to the community. However, I wish to suggest some improvements to enhance the impact of this paper. I also think that the points made by the authors, although reasonable, would be better supported by a few more data points.

1-Stating the problem more clearly

I am not sure all readers will understand all the implications of the term "bulk ice" used in the introduction. As used by this group here and in previous publications, "bulk ice" is a convenient term to conceal our inadequate understanding of the medium of interest. When a solution freezes, non-equilibrium processes take place, resulting in the segregation of brines either as bubbles embedded within a crystal, or as fairly continuous network at triple junctions between grains. The actual state of the medium depends on many variables, and in particular on the freezing rate. One important point is that in such non-equilibrium solutions, the concentration of the brine cannot be predicted by the equilibrium phase diagram. In fact kinetic phase diagrams are often better suited to that purpose, and it is found that metastable brines can exist for extended durations below the eutectic.

I believe that, in the general interest of the community, the authors should expand a bit on the subject and I even recommend not using the vague and misleading term "bulk ice". In "bulk ice", we do not expect reactions to take place in anything that resembles ice, but rather in a concentrated liquid solution, so that the reaction medium would be better described as "liquid" than "ice".

These issues have been described at length in the past, and some of the aspects relevant to atmospheric problems have been detailed in Thibert and Domine (1997), JPC B, 101, 3554. This paper also describes possible errors caused by improper sample characterization, and how these errors affected the understanding of some atmospheric issues.

To sum up this point, I recommend that the authors explain the difference between laboratory samples made by freezing solutions, and which contain actual liquid media (brines) and natural samples, made mostly by the co-condensation of water vapor and impurities, and which are less likely to contain liquid media. Part of the problem is therefore to determine the applicability of laboratory experiments to the natural environment, and this requires the understanding of the role of the reaction medium on the reaction rate and mechanism.

2-Improving the data set

First of all, I fully realize that once a project is completed within the limited time available, it is not always possible to obtain additional data. However, if at all possible, I strongly recommend that here, more data be obtained. I also recommend that the authors modify somewhat some aspects of their interpretation.

The final conclusions are largely based on Figure 3. According to the authors, Figure 3 shows that (i) on ice, harmine photolysis is faster than in aqueous solutions. (ii) above the eutectic, the photolysis rate decreases monotonically as the salt solution is increases. (iii) below the eutectic, no liquid solution is expected to be formed and the photolysis rate, for a given salt concentration, is faster than above the eutectic where a liquid is present.

However, conclusion (ii) is largely based on 2 data points for salt concentrations of about 0.05 and 0.1 mol/L. The error bars on both points is large enough that the monotonic decrease is not all that obvious. Conclusion (iii) is based on just one data point obtained at 243 K for a NaCl concentration of 0.1 mol/L. The error bar is such that, in my opinion, no firm conclusion can be reached. It could be argued that the rate is the same as on pure ice, and it could also be argued that the rate is the same as when a liquid brine is present.

I believe that part of the problem is due to the fact that the freezing conditions are not very reproducible, and take place in out of equilibrium conditions; a different distribution of concentrations is present in the different brine pockets formed and the reaction medium therefore varies between one sample and another. To narrow the range of variations, I suggest attempting to freeze the solutions as slowly as possible by lowering slowly the temperature of the copper plate. Supercooling will probably cause problems. The authors may then attempt to freeze the solution at a very low temperature and then warm it up slowly to the temperature of interest. Thermal cycling of each sample may also reduce the scatter in the data.

It is possible (in fact likely) that in some of their 243 K experiments, a supercooled brine was still present. One way to solve this problem may be to cool the solution to a very low temperature, then warm it up to the experimental temperature.

To sum up this point, I believe that non-equilibrium processes took place during freezing, resulting in a poor reproducibility. Data probably cannot be interpreted in terms of equilibrium phase diagrams. The authors should either perform additional experiments to limit sample variability or modify their interpretation to include non-equilibrium processes.

Minor points :

Would this paper benefit from a brief discussion of Cho et al. (2002) JPC B, 106, 11226 ?

p. 12064, line 25. Annor et al., 2006 not in ref list.

Abstract: Mention that the conclusion applies at T above the eutectic.

p. 12066. Can the authors speculate as to what happens when a sea salt particle makes contact with the surface of a snow crystal ?

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 12063, 2010.