

Interactive comment on “Hydroxyl radical reactivity at the air-ice interface” by T. F. Kahan et al.

T. F. Kahan et al.

jdonalds@chem.utoronto.ca

Received and published: 1 January 2010

We thank the reviewer for encouraging us to discuss more thoroughly the potential influence of temperature on our results. Below we address the points individually.

Comment 1: "One of the key issues to explain the results obtained in the present work is that the ice bulk or the liquid pockets contained in the bulk is different than the quasi-liquid layer at the surface. Interestingly, similar results were obtained in the ice bulk and in the aqueous solution, and both systems differed significantly from the ice surface. It is remarkable that temperature seems not to affect the studied reactions to a significant extent. Note that the aqueous solution was studied at room temperature, ice at -16 C , and a temperature difference of about 40 C can be expected between the two systems. Accordingly, if the reaction rates were dependent on the temperature this should ap-

C9126

pear in the experimental data. The results suggest that the reaction(s) chosen by the authors were temperature-independent. If the choice of the reaction(s) to be studied we done on purpose, this should be said because a temperature-independent reaction is the best tool to compare liquid water, bulk ice and the ice surface."

The reviewer is correct that addition reactions, such as those of OH with aromatics in solution, are not expected to show a large T-dependence in their rate coefficients (at least, over the temperature range explored here). We have included the following discussion in Section 4: "We also suggest that a temperature dependence is not responsible for the lack of reactivity on ice, as the temperature dependences of OH formation from H₂O₂, NO₃(-), and NO₂(-) (Chu and Anastasio 2003, 2005, 2007) are minor. In previous work (Kahan and Donaldson 2007), we have seen no evidence of a temperature dependence to the degradation rate of anthracene due to reaction with OH formed from H₂O₂ photolysis at liquid water surfaces. Although reaction pathways in ice (specifically phenol formation vs. dimerization) have been shown to be temperature dependent (Klanova et al. 2003a), this can not explain our results: We measure similar phenol formation rates in aqueous solution and in low surface-area ice cubes, which are at very different temperatures, but measure different kinetics at air-ice interfaces and in high surface-area ice granules, which are at the same temperature as the ice cubes. This strongly suggests that temperature changes are not responsible for our observations."

Comment 2: "From page 20883, line 18 to page 20884, line 9, the authors report literature comparisons of reactions in water and ice. The present work is intended to see if the differences and the contradictions in the literature results are due to the variable reactivity of different ice compartments (typically, bulk and surface). However, differences could also be due to the reactions being temperature-dependent. In the case of the monochlorophenols (Klanova et al., 2003), a check on the original reference should be made to look for a possible dependence on temperature. Such an alternative hypothesis Should be discussed in the Introduction. This is important because the

variable behaviour of ice is expected to play a more important role on the reactions that do not depend on the temperature. In strongly temperature-dependent reactions, the temperature effect could be the main issue in the comparison between water and ice."

We have added a reference to the temperature dependence observed by Klanova et al. (see above). We explain that temperature is not responsible for the lack of reactivity observed in ice granules and at air-ice interfaces, since the experiments in these media were performed at the same temperature as experiments in ice cubes, where phenol formation rates were the same as in aqueous solution.

Comment 3: "At the beginning of the Discussion (section 4), the authors discuss and exclude the possibility that different diffusion coefficients between ice surface and water could explain the different results in the two environments. The hypothesis would imply a temperature-dependence of the reaction, and examples of similar but different temperature-independent reactions are reported. The formation of OH in the studied systems is very likely to be temperature-independent, because for instance Figure 3 reports similar formation of OH in water and bulk ice. Accordingly, it is possible that the present paper provides evidence of the temperature independence of the studied reactions, that is more direct than the examples discussed by the authors and could be brought as an additional evidence to the discussion."

We have reworded our argument about diffusion rates. The relevant paragraph in Section 4 now reads: "Since the addition of hydroxyl radicals to aromatics occurs at near diffusion-limited rates, a decrease in diffusion rates on ice could lead to slower reaction rates there. Diffusion rates are expected to decrease with decreasing temperature; however, the fact that phenol formation rates in ice cubes (at -16 C) occurs at similar rates as in aqueous solution (at 20 C) indicates that any temperature dependence to the reaction (or to diffusion rates) is minimal. Further, diffusion in the QLL is expected to be quite rapid (Lee et al. 2007), so it seems unlikely that a reduction in diffusion rates is responsible for the lack of reactivity at air-ice interfaces."

C9128

Comment 4: "Section 3.1. The differences between ice cubes and ice granules could be due to different surface-areas vs. bulk volume ratios. However, it is also possible that the two systems behave in a different way toward illumination. Is the incident light intensity expected to be the same in the two cases? Can a different extent of radiation reflection, for instance, alter the results? This issue should be discussed in section 3.1."

We have added the following to the Discussion, stating that changes in effective photon fluxes cannot likely explain our observations: "Differences in the effective photon fluxes in the various sample types could affect measured reaction rates. However, it is unlikely that photon fluxes are reduced at air-ice interfaces and in ice granules compared to in aqueous solution or in ice cubes. If anything, we might expect enhanced photon fluxes in the ice granules due to increased internal reflection. Therefore, we do not believe that changes in effective photon fluxes are responsible for the lack of reaction at air-ice interfaces."

Comment 5 - Minor issues: "Page 20886, top. "In aqueous solution" is repeated twice." This has been corrected in the manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 20881, 2009.

C9129