

## ***Interactive comment on “Hydroxyl Radical in/on Illuminated Polar Snow: Formation Rates, Lifetimes, and Steady-State Concentrations” by Zeyuan Chen et al.***

### **Anonymous Referee #2**

Received and published: 21 April 2016

The manuscript describes a detailed kinetic study on the photochemistry of OH in ice. The manuscript is very clear and shows that experiments were very carefully done and evaluated. The data are sound and conclusions well justified. This and relevance of the hydroxyl radical in atmospheric chemistry of polar areas clearly grants publication after a minor addition. In particular, I was impressed by the comparison of OH and O<sub>2</sub> nicely discussing the freeze-concentration effect and how it differs for different reaction systems.

General comment on freeze-concentration effect and Liquid-Like-Regions: The term freeze-concentration effect was, to the best of my knowledge, first used to describe increasing reaction rates with the shrinking volume of the liquid fraction in a binary ice-

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solution system. As soon as the system was completely frozen, i.e. below the eutectic, reactivity ceased. (Takenaka, N., Ueda, A., Daimon, T., Bandow, H., Dohmaru, T., and Maeda, Y. "Acceleration Mechanism of Chemical Reaction by Freezing: the Reaction of Nitrous Acid with Dissolved Oxygen" *The Journal of Physical Chemistry* 100, no. 32 (1996): 13874–13884. doi:10.1021/jp9525806; Takenaka, N., Ueda, A., and Maeda, Y. "Acceleration of the Rate of Nitrite Oxidation by Freezing in Aqueous-Solution" *Nature* 358, no. 6389 (1992): 736–738. doi:10.1038/358736a0). I recommend to stick to this terminology which implies that one either has a freeze-concentration effect AND a liquid fraction in a frozen (binary) system or a (potentially high) reactivity in a completely frozen system that might take place in LLR/in a qll/in a liquid-like brine/or on the surface. More general, I'd appreciate a discussion on the phase behaviour of your samples. As the composition is not known, this is agreeable difficult. Nevertheless, maybe reactivity is similar in ice and liquid, because the ice is actually a mixture of ice and a reactant solution. For example, if H<sub>2</sub>O<sub>2</sub> would be the origin of OH, one might expect liquid well down to -50 °C (Foley, W. T. and Giguère, P. A. "Hydrogen Peroxide and Its Analogues: II. Phase Equilibrium in the System Hydrogen Peroxide-Water" *Canadian Journal of Chemistry-Revue Canadienne De Chimie* 29, no. 2 (1951): 123–132.) May I therefore suggest to include a short discussion on the possibility of the presence of liquid as reaction medium in your samples, both in the introduction and when comparing the results.

Specific comments:

P1 - 12ff: Laboratory studies show that . . . Does the contrast to other oxidant refer to both OH kinetics and concentration? Or only to the concentration? Could you reword.

P 3 - 15: While it has not been measured experimentally, the freeze-concentration effect might also alter . . . This is certainly a very valid hypothesis. I would suggest to underline it further by stating a few examples where reactivity was observed to change, referring to Klan and/or Donaldson earlier work (Bartels-Rausch, T., Jacobi, H.-W., Kahan, T. F., Thomas, J. L., Thomson, E. S., Abbatt, J. P. D., Ammann, M., Blackford, J.

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R., Bluhm, H., Boxe, C., Dominé, F., Frey, M. M., Gladich, I., Guzman, M. I., Heger, D., Huthwelker, T., Klán, P., Kuhs, W. F., Kuo, M. H., Maus, S., Moussa, S. G., McNeill, V. F., Newberg, J. T., Pettersson, J. B. C., Roeselova, M., and Sodeau, J. R. “A Review of Air–Ice Chemical and Physical Interactions (AICI): Liquids, Quasi-Liquids, and Solids in Snow” *Atmospheric Chemistry and Physics* 14, no. 3 (2014): 1587–1633. doi:10.5194/acp-14-1587-2014)

P 8 - 10: This is surprising as the apparent rate constant of OH towards organics spans several orders of magnitude (Schwarzenbach, R. P., Gschwend, P. M., and Imboden, D. M. “Environmental Organic Chemistry” (2005): doi:10.1002/0471649643). Would this imply that reactivity of DOC is dominated by one class of organics? Could you comment (or further support) that statement in the manuscript.

P 11 - 6: “if the blank samples. . .contamination Milli-Q. . .”. This is a reasonable assumption. Could you further support it by stating the type of Milli-Q used, does it use UV and does it maybe not filter the organics efficiently? Then one might expect high peroxide concentrations.

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