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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Photolysis of frozen iodate salts as a source of active iodine in the polar environment" *by* O. Gálvez et al.

Anonymous Referee #1

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In the manuscript "Photolysis of frozen iodate salts as a source of active iodine in the polar environment" the author describe a series of experiments and model calculations to characterize the photolysis reaction of frozen ammonium iodate samples. They conclude that the photolysis is a viable pathway for the release of iodine species in the polar atmosphere. In principle, I think, this is a very interesting contribution to the important and growing field of atmospheric halogen chemistry. However, there are a number of issues in the presentation and the conclusions that need to be addressed.

A fundamental question that needs to be addressed is why the ammonium salt of iodate was chosen for the photolysis experiments. As the authors describe in the manuscript, the ammonium ion is consumed in a 1:1 ration together with the iodate. This can be expected to at least affect which iodine species is released, and might in principle alter

the whole process in a way that it is not representative for other iodate salts.

Other general questions:

- In the Experimental Methods section it is described that the ice films are produced in a way that ions remain solvated by water molecules. However, all measured samples were subsequently subjected to higher temperatures in order to remove at least part of the water. Is any information available, whether, or for how long the ions remain segregated?

- The proposed reaction mechanism seems ill-founded. In reaction (R1) the formation of an O- ion (together with OIO) is proposed. This would be a species with extremely high energy. What is this proposal based on? Reactions (R2) and (R3) are referenced to Huang et al., 2008. However, neither of this reactions is to be found in the referred paper. Although the oxidation of ammonia to nitrate is discussed, this does not involve NH2OH as an intermediate, and requires additional oxidants. In the present system, containing only ammonium iodate and water, it is unclear what this additional oxidant could be (reaction with additional iodate would change the observed ratio). Unless any additional evidence can be provided, I recommend removing the discussion of the mechanism.

- The choice of a Gaussian function with maximum at 205 nm that is indicated to be based on the spectra in Fig. 2 is not self-evident. It might be helpful to add a plot of the function together with the corresponding spectrum to illustrate the agreement.

- Spectra/plots given in Fig. 3-6 are of different collections of samples/conditions. Fig. 3 shows the four conditions also given in Table 1; Fig. 4 shows data at 298 K that is not mentioned otherwise; Fig. 6 shows a system at 150 K that is not mentioned otherwise, and one at 100 K with a water content that differs from otherwise mentioned systems. The reason for this is not clear. It would be helpful to add a supplement containing corresponding plots at all studied conditions.

Other comments:

- p 27924, line 11: possibly give integration limits in the supplement.

- p 27924, line 17: “... stablished...” should be “... established...”

- p 27926, line 16: Referenced Figure should be Fig. 4

- p 27929, line 13-15: Is all reactive iodine assumed to be IO, or how much of it is, in the mentioned equilibration, converted into IO?

-p 27939 (Fig. 4): Are these plots referring to pure salt? Especially for the higher temperatures this can be assumed, but might be worth mentioning.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 27917, 2015.