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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.

O. Gálvez et al.

ogalvez@iem.cfmac.csic.es

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Comment: 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 ratio 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.

Response: Ammonium iodate was chosen for several reasons: (i) It was not possible to monitor iodate signal in the presence of high water concentration since the infrared iodate band overlaps with water absorptions. The fact that the chosen salt has a cation like NH4+ that presents a band with no interference (and that it is consumed in a 1:1 ratio with iodate), allowed us to measure the photolysis of iodate indirectly as described below. (ii) The integrated IR absorption coefficient of iodate band was unknown, and in consequence, it was not possible to quantify the amount of iodate in the samples. One of the possibilities to solve this problem is to use an iodate salt for which the integrated absorption coefficient of the IR band of the counter-ion was known, like ammonium iodate. More details of these calculations are given in the next section. (iii) Moreover, ammonium iodate is expected to be one an abundant iodate salts in the atmosphere, since ammonium concentrations are high in some environments, and it could be deposited into the ice as large fluxes of iodinated compounds have been observed during glacial period (Spolaor et al., 2013), and the presence of ammonium ions in ice samples is also expected. Moreover, ammonium and iodinated compounds have been detected at the same time in melting Artic sea ice, implying that this salt could be atmospherically relevant (Assmy et al., 2013).

However, we recognize that other salts like NaIO3 or KIO3, would be probably more representative of polar environments, although, considering the arguments given above, we think that ammonium iodate should be also a good choice to study the photolysis of iodate.

This discussion has been incorporated in the new version (see the section "Experimental methods").

As referee1 comments the fact that ammonium ion is consumed in a 1:1 ratio together with the iodate could affect which iodine species is released, but from our point of view hardly would affect the rate of photolysis, which it is what we are measuring in this work, since this is not determined by secondary chemistry, only by the absorption iodate itself. However, we think as well that it would be desirable to study the photolysis of other frozen iodate salts and we have added this as proposed experiments in the future.

Comment: 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?.

Response: We do not have specific previous information about this issue, nevertheless we have carried out some text experiments in order to see if the degree of segregation of the iodate ions could affect their photolysis. As it was mentioned in the MS (page 27927) some diluted samples were also irradiated (some of these samples were not annealing in order to avoid the segregation). In these samples, it is supposed that ions are mainly solvated by water molecules, meanwhile the degree of segregation of the salt (NH4IO3) is low. In these cases, the calculated J values were only slightly higher than mean J values for the rest of samples, but this effect could be due to a larger surface/bulk ratio in these samples. So, although we do not know the degree of solvation/segregation of the ions in the samples, we think that this variable is not affecting significantly the photolysis rate in our samples. This point has also been clarified in the new version of the MS.

Comment: 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.

Response: We agree with the referee1 that to propose a mechanism with only the product information obtained in these experiments is challenging, that is the reason why in the paper we wrote: “we tentatively proposed the following mechanism for the photolysis of ammonium iodate ice”, and we do not claim that is a definitive mechanism, only a possible hypothesis to be assessed in future studies. In this proposal, we have considered reactions channels anticipated in other papers about radiolysis and photolysis of aqueous iodate salts (Klaning et al., 1981) and products information from photolysis of other ice samples (Spolaor et al., 2013). Reactions R1 (IO3- + light ïĆő OIO + O-) has been proposed in flash photolysis experiments (at 248 and 308 nm) of iodate solutions (Klaning et al., 1981) that although they used a more powerful source of light still it could be extrapolated to our case.

IO3- + light ïĆő OIO + O- (R1)

R2 (O- + H2O ïĆő OH + OH-) is a well-known reaction in aqueous solutions (Klaning et al., 1994). Formation of NH4OH in photo-enhanced radical oxidation of aqueous ammonia or ammonium in solution has been proposed in previous works (Hamilton et al., 2013; Huang et al., 2008), although the referee 1 is right, in these papers reaction R2 is not shown, although R3 is the result of several reactions in Hung et al, 2008 (NH4+ + H2O ïĆő NH3 + H3O+; NH3 +âĂćOH ïĆő âĂćNH2+H2O; NH2+âĂćOH ïĆő NH2OH). So, R3 is a set of reactions where from aqueous ammonia in the presence of radicals is converted in NH2OH and then in other more oxidized species of nitrogen like nitrite and nitrate. It is right that in both references they have an external âĂćOH source that facilitate the oxidation of ammonia, but in this case the âĂćOH source could be the photolysis of iodate (after reaction with water by R2).

We think that our mechanism is still possible so, in our opinion, it is worth to show in the paper.

Comment: - 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.

Response: In Figure 2, it can be observed that the spectrum of a solution of 9.6 x 10-4 M (blue trace) NH4IO3 has a maximum at 205 nm, and this value has been chosen for the maximum of the function to simulate the differential absorption cross section of our frozen iodate salts. However, as it was mentioned in the text (last paragraph in pag. 27927 and first paragraph in pag. 27928), the UV-Vis spectra of the different iodate salts solutions show practically null absorptions above 300 nm, so if we had to try to fix our function to this spectra we would have obtained a null value above 300 nm. According to this explanation, we cannot illustrate the agreement between the function and the UV-Vis spectrum of the solution. We would like to highlight that, as was also mentioned in the text, the photo-reactivity of our iodinated samples should be related to the low temperature effect, and mainly to the fact that iodate ions are in a frozen solution. According to this point, we have to take into account that our simulation is merely exploratory, because we do not know the shape of the absorption spectrum of the NH4IO3 frozen solution, but it looks reasonable to expect a similar shape than that in water solution, but extending the absorption range to larger wavelength. All these points have been clarified in the new version of the MS. In order to choose a function for the simulation, Gaussian or Lorentzian functions are usually selected for this task. In the figure R1, we show a comparison between both functions to simulate the UV-Vis spectrum of a solution of 9.6 x 10-4 M NH4IO3. From this data, both fitting show similar agreement, so in principle, both functions could be chosen for this particular problem. In our case, a Gaussian-type function was been finally used, but similar results are expected for a Lorentzian fitting. For the Gaussian function, the total area from 300

to 900 nm has been fixed to the calculated value of the integrated absorption cross section, but the width selected (parameter “w” in the Figure R1) is completely arbitrary, due to not previous information is available. We have chosen this value in order to encompass approx. 95 % of the cross section value below 500 nm, as can be seen in Figure 7 of the MS.

Comment: - 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.

Response: During the experiments, we generated many samples covering a wide range of temperatures (at 100, 140, 150, 200 and 298 K), different water proportions (from “dry” to much diluted samples, which show a H2O:NH4IO3 ratio of approx. 100:1) and using the two generation methods described in the text, namely hyperquenching and vapour deposition. All these samples have been irradiated and IR spectra have been taken along of this process (usually around 10-12 spectra were collected for each experiment). All the different infrared bands of the spectra were lately integrated, which allow us to compose line regression fits of the integrated bands vs photolysis time, as those shown in figure 6. In summary, a large amount of data based on the IR spectra recorded was generated. We think that, due to the large amount of spectra and data generated, including all this information in a supplementary section would not result useful to clarify any additional point to the future reader. The spectra and data included in the figures 3-6 are basically selected examples of the different conditions mentioned above. Nevertheless, we agree with the referee 1 that probably all the conditions studied and the reason for what the spectra shown in figures were chosen was not clearly described in our previous version of the MS. According to the referee’s suggestion, more details of these conditions have been included in the new version (in the “experimental method” section) to clarify this point.

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

Response: In order to integrate the bands, different criteria were considered. First, the atmospheric water and CO2 absorptions was removed from the spectra. The choice of fixed integrations limits introduced significant errors in the integration of the IR bands, due to the presence of different amounts of water in the samples considerably varied the baseline of the spectra, especially for the case of the iodate band which also overlaps with the libration water band. In addition, the different methods for the generation of the samples also introduced different baselines in the spectra which complicate the use of fixed limits in the integration process. It is worthy to highlight that the smallest variations are in the integration of the ïĄő4 (NH4+), band finally selected to derived the “J value”, due to this band is not affected by water absorptions. For these reasons, as a general procedure, the integration limits chosen were different for the different samples in order to minimize the errors in the integrations process. We would like to remark that we have paid special attention in this step to be consistent and to minimize the errors in the integration process. Typically, the stretching bands of NH4+ and H2O were integrated from 3660 to 2500 cm-1, the ïĄő4 (NH4+) from 1530 to 1330 cm-1, and the iodate and libration water mode from 870 and 650 cm-1. Although, as was mentioned above, these limits were flexible. All this information has been added in the new version of the MS.

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

Response: The word “stablished” has been changed by “formed” in the text.

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

Response: Change done.

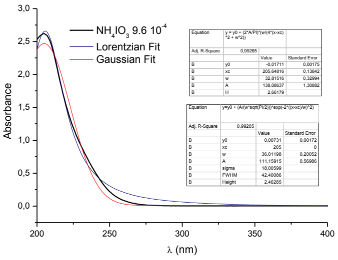
Comment: - p 27929, line 13-15: Is all reactive iodine assumed to be IO, or how much of it is, in the mentioned equilibration, converted into IO?.

Response: We assume the resulting photofragment to contain all the reactive iodine in the form of IO. Nevertheless, considering the fast I + O3 oxidation reaction, if the photofragment was to be atomic iodine the modelled IO levels would not change significantly, at the ozone levels measured under typical Antarctic boundary layer conditions.

Comment: -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.

Response: “Pure Salt” was included in the caption of the figure.

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



Equation	y = y0 + (2*A/PI)*(w/(4*(x-xc)^2 + w^2))		
Adj. R-Square	0,99265		
		Value	Standard Error
B	y0	-0,01711	0,00175
B	xc	205,64816	0,13842
B	w	32,81516	0,32994
B	A	138,08637	1,30882
B	H	2,66179	

Equation	y=y0 + (A/(w*sqrt(PI/2)))*exp(-2*((x-xc)/w)^2)		
Adj. R-Square	0,99205		
		Value	Standard Error
B	y0	0,00731	0,00172
B	xc	205	0
B	w	36,01198	0,20052
B	A	111,15915	0,56986
B	sigma	18,00599	
B	FWHM	42,40086	
B	Height	2,46285	

Figure R1. UV-Vis absorption spectra from 200 to 400 nm for NH_4IO_3 at 9.6 x 10^{-4} M. Gaussian and Lorentzian functions fitting the spectrum curve are also showed.

Fig. 1.

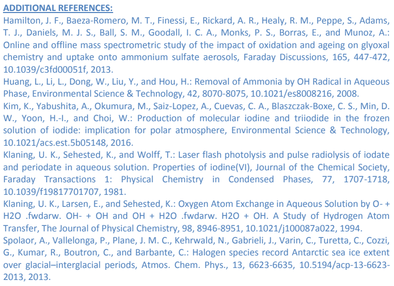


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Fig. 2.