

## ***Interactive comment on “Modeling iodide – iodate speciation in atmospheric aerosol” by S. Pechtl et al.***

### **Anonymous Referee #2**

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Interactive comment on: Modeling iodide-iodate speciation in atmospheric aerosol by Pechtl, S. et al.

This paper presents a model scheme of the iodate-iodide speciation system in marine aerosols. In particular the article addresses the divergence between previous models, which predict negligible iodide and high iodate concentrations in aerosols, and field measurements that show that iodate and iodide concentrations are approximately equal, but depend on aerosol size. The article is well written and is presented in a clear and concise manner. It is, to the best of our knowledge, the first modeled attempt to both 1) reconcile the difference between I-/IO<sub>3</sub><sup>-</sup> ratios predicted by model calculations and those observed in field studies and 2) incorporate the growing awareness that organically bound iodine plays a role in atmospheric chemistry. It also introduces an

elegant diffusion limiting interaction term to limit the rate of some of the fastest iodide oxidizing reactions, although, as discussed, this alone cannot account for the excess iodide concentrations and low iodate levels in aerosols. I believe this article is worthy to be published in 'atmospheric chemistry and physics' after consideration of the points raised below.

General: there are very few general problems with the paper. I believe some additional information is needed in the model description (such more thorough treatment of diffusion-controlled limitations on rate constants; see below) and it would also be useful to briefly discuss at the end of the paper what implications the study has for atmospheric iodine cycling on a larger scale. Indeed, the ability to integrate a large amount of reactions and processes is one of the strong points of models and thus can help us learn more about the system as a whole. See CLAW hypothesis for a nice example. The interactions with organic iodine are one of the most interesting points in this paper and I believe that it would be appropriate to include something to this nature in the title.

#### Specific

1. the authors have employed the classic Dushman reaction in an attempt to find an inorganic sink for iodate and a source of iodide. What seems strange to me is that reduced sulfur species, which are relatively abundant in the marine atmosphere due to emissions of dimethyl sulfide and its oxidation products are not also considered as possible reducing agents. Reduction of iodate by sulfite, for example, is known as the 'Landolt reaction', where iodate is first reduced to  $I_2$  and then subsequently to  $I^-$ . In classical chemistry the initial reaction is slowed down by adding concentrated sulfuric acid, and is the rate-limiting step, whereafter the faster Dushman reaction becomes the more important reaction (with the abundant  $H^+$  this last reaction very fast indeed). However, in aerosols, concentrated sulfuric acid (as employed by chemists) is unlikely and therefore the reaction is more likely to exert a stronger influence on iodine speciation; especially as the rate of this reaction should increase with increasing pH. More-

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over, the size discrepancy in the iodate/iodide ratios can be overcome by this reaction mechanism, as reduced sulfur species derived from dimethyl sulfide will be more concentrated in the sub-micron particle size due to larger surface area for sorption and gas-to-particle phase conversion of dimethyl sulfide oxidation products. Therefore I suggest that this mechanism is incorporated into the model or at least explored for its overall effects on iodine speciation. Other evidence for iodate reduction by sulfite is that addition of sulfite is commonly applied in analytical methods that can only quantify iodide species. For example, in cathodic stripping square wave voltammetry (Luther et al., 1988) iodide is first quantified then iodate is reduced after acidification of the sample and the iodide is remeasured. The difference between the values is assumed to be the iodate. Another reference that may be of interest is (Ojo et al., 2004)

2. More references are needed of for the existence of organically bound iodine. So far the authors have only listed the work of Baker et al. and would benefit in particular by looking at the studies of (Seto and Duce, 1972; Murphy et al., 1997; Middlebrook et al., 1998). It would also be beneficial to add that the existence of organic compounds universal and appear to be relatively abundant. Works such as (Cavalli et al., 2004; O'Dowd et al., 2004) should also be reference and can perhaps be used to confine the amount of organics typically found in marine aerosols (although these samples are taken from a coastal location, it seems better to base the concentrations on something than producing totally arbitrary levels).

3. The authors mention that in the work of (McFiggans et al., 2000) iodine activation from the aerosol is required to reproduce observed IO levels in the marine boundary layer. Are these levels still reproduced despite the lower halogen activation caused by using diffusion limited rate constants? In addition to this, a more thorough description of the diffusion limited rate constants is needed. For example, what are the equations and where have the authors found them. Do they account for ionic shielding, which would also limit the interaction of elements in solutions with high ionic strength such as aerosol? I think that diffusion limited rate constants is a good idea but just needs to be

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explained a little further.

4. Can aqueous phase diffusion limit the transfer between the aqueous phase and the gas phase? Obviously the iodine is activated to a volatile form it will have to migrate from somewhere within the hydrated droplet to the surface before reentering the gas phase. This should only occur in the aqueous phase. It is a little confusing in the manuscript if the authors are exclusively focusing on the particulate phase or also on the deliquesced aerosols, as they often refer to, for example 'coupling between gas and aqueous phase' (pp10968 paragraph 15) but the main study is focused on speciation in aerosols.

5. What is the initial pH of the aerosol size fractions?

6. what time did the reaction sequence begin. I guess that it is 00h UHT time but this is not pointed out in the model. It would also be a great improvement if the nighttime hours could be highlighted in the graphs. This would make it much easier to distinguish the difference between solar activated chemistry and nighttime cycles in the figures. This could easily be done by shading the night portion of the graph a translucent gray colour.

7. The dominant direct of the reactions given in table 1 should be given. In some cases (eg. I15+) the backwards reaction is faster than the forwards reaction but this is not apparent to the reader on studying the table alone. Perhaps a 'f' or 'b' can be added to the reaction number.

8. What is the possibility of iodine being associated with organics BEFORE aerosol formation (eg. from the ocean surface microlayer) and subsequently decaying (being oxidized) in the atmosphere to release more iodide. The work of (Seto and Duce, 1972) is quite convincing that organic iodine released during algae decomposing in the oceans is transferred to the atmosphere during bubble bursting and work from in your own group (Smoydzin and von Glasow, 2006) suggests that total oxidation of organics is quite fast under ambient conditions. Such a mechanism has also been suggested in the ocean to account, in part, for the higher iodide levels then predicted

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by thermodynamics (Wong and Cheng, 2001).

9. On page 10964 paragraph 15 the authors state 'we included the reaction of I<sup>-</sup> with ICl and IBr (I8, I9), which tend to reduce iodide to molecular iodine' This is not in fact a reduction but an oxidation as iodide goes from I<sup>-</sup> to I<sub>0</sub> ie loss of one electron. Do the authors mean reduction iodate or in fact oxidation of iodide?

10. the Dushman reaction is catalyzed by iodide, I was wondering where the initial iodide comes from for this reaction to commence as there does not appear to be any other iodate reducing mechanism in the reaction table.

11. None of the hypothesized reactions with organic matter are listed in the reaction sequences. Despite the limited knowledge your assumed reactions should appear there. For example, one question that arises is 'is the organic matter oxidized during reactions with iodine species?.'

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