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Atmospheric
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Discussions

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

S. Pechtl et al.

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Response to Anonymous Referee 1

The referee is missing a discussion about the implications the aqueous phase iodine chemistry mechanism has upon gas phase iodine chemistry and the exchange between aerosol and gas phase (e.g. the release of interhalogen species from the aerosol). Our model simulations already include a detailed treatment of the gas phase as well as the exchange between the gas and aerosol phase, but we agree that this does not become clear enough in the present version of our manuscript. In the revised version, we will clarify this point and will add a discussion (to Section 3.2) about the impacts of our changes in aqueous phase iodine chemistry on the exchange with the gas phase and on concentrations of important gas phase iodine species such as IO and OIO.

Regarding the large uncertainties in atmospheric iodine (and esp. OIO) chemistry pointed out by the referee, we have already mentioned it in the manuscript to point out the resulting uncertainties in uptake of iodine species from the gas phase (esp. HIO_3, see e.g. Section 3, page 10967, lines 16-18, Section 4, page 10975, lines17-19). A comprehensive discussion of the uncertainties in gas phase iodine chemistry is, however, beyond the scope of this paper (which has its main focus on aqueous phase iodine chemistry) and has been done elsewhere (e.g. Pechtl et al., 2006, Stutz et al. submitted).

Response to Anonymous Referee 2

We especially want to thank Referee 2 for his thorough review, which certainly helps to improve our manuscript. Following the general comments of the referee, we will add details about the treatment of the diffusion-controlled limitations on the rate constants (see below). We will also mention possible implications of our findings for the atmospheric iodine budget on a larger scale in our Conclusions (Section 4). According to the suggestion of the referee, we mention organic iodine chemistry in the title (changed title: “Modelling iodide - iodate speciation in atmospheric aerosol: Contributions of inorganic and organic iodine chemistry”).

In the following, the specific comments are addressed.

Specific comments:

1. We do not consider the reduction of iodate with reduced sulfur species such as sulfite, because we have checked the effect of the reduction of iodate by sulfite in our model and found it negligible. We will explain this in the Model Description (Section2) revised manuscript as follows: “Beside the reduction of iodate by iodide, we have also considered its reduction by sulfite. Gaspar and Showalter (1987) have adopted the simple rate law $r(IO_3^- + HSO_3^-) = k [IO_3^-][HSO_3^-]$ with $k = 0.25$ $M^{-1}s^{-1}$. Edblom et al. (1987) and Luo and Epstein (1989) have used the same rate law with $k = 0.30$ $M^{-1}s^{-1}$. This value was corrected later to $k = 0.42$ $M^{-1}s^{-1}$ (Luo and Epstein, 1989).

With these values, the reduction of iodate by sulfite has no significant consequence on our results, even for the almost neutral aerosols. The use of the more complicated rate law adopted by Rabai and Beck (1988) and by Rabai et al. (1995) would not change this conclusion. As the rate of this reaction is uncertain but negligible, we have not included it in the final reaction mechanism."

Gaspar,V. and Showalter,K.: The Oscillatory Landolt Reaction. Empirical Rate Law Model and Detailed Mechanism, J. Am. Chem. Soc., 109, 4869-4876, 1987.

Edblom,E.C., Györgyi,L., Orban,M. and Epstein,I.R.: A Mechanism for Dynamical Behavior in the Landolt Reaction with Ferrocyanide, J. Am. Chem. Soc., 109, 4876-4880, 1987.

Luo,Y and Epstein,I.R.: Alternative Feedback in the Mixed Landolt Chemical Oscillator, J. Phys. Chem. 93, 1398-1401, 1989, corrected in J. Phys. Chem. 93, 6882, 1989.

Rabai,G. and Beck,M.T.: High-Amplitude Hydrogen Ion Concentration Oscillation in the Iodate-Thiosulfate-Sulfite System under Closed Conditions, J. Phys. Chem. 92, 4831-4835, 1988.

Rabai,G., Kaminaga,A. and Hanazaki,I.: The Role of the Dushman Reaction and the Ferricyanide Ion in the Oscillatory IO_3^- - SO_3^{2-} - $Fe(CN)_6^{4-}$ Reaction, J. Phys. Chem., 99, 9795-9800, 1995.

2. As suggested by the referee, we will add some sentences and references that are related to the abundant existence of organic matter in marine aerosol as well as to the correlation of iodine with organic material in aerosol (Section 3.2). Most of the references provided by the referee will be cited in the revised manuscript.

3. IO levels in the gas phase are not diminished in our model despite the use of diffusion-limited rate constants for halogen activation because of the larger iodide concentration in the aerosol. Further, we will replace the present description of the diffusion-controlled limitations on the rate constants (Section 2) by a more detailed ver-

sion: “ the encounter frequency between HOI and I^- is only about 5×10^9 $M^{-1}s^{-1}$ which is an approximate value for diffusion-controlled rate constants. The mechanism and rate laws of reaction I1 at different acidities are discussed in details in Schmitz (2004). In acidic or slightly acidic solutions, the rate law can be written:

(existing equation)

The rate constants in the forward and backward directions, k_+ and k_-, are related to the equilibrium constant K_{eq} by $k_+/k_- = K_{eq}$ and α is such that $k_+/\alpha = k_{diff}$ is the rate constant of a diffusion controlled reaction. At low [H^+], the rate law of the forward reaction converges to the accepted 3rd order rate law while at high [H^+] it converges to the highest possible value k_{diff}[HOX][Y^-]. For the theory of diffusion-controlled reactions we refer the reader to general text books of chemical kinetics, e.g. Espenson (1995). We have used the same formulation for the reactions in Table 1 noted "upper limit: yes" and also for not listed reactions that do not involve iodine species (X, Y = Br, Cl). The experimental values of k_{diff} are usually unknown and we have used the accepted approximate value for this kind of reactions involving at least one uncharged specie in water, $k_{diff} = 5 \times 10^9$ $M^{-1}s^{-1}$. "

4. The referee suggests to not only focus on aqueous phase iodine chemistry (as was done in the present manuscript), but also discuss its coupling to gas phase. We agree that such a discussion will improve the manuscript and will add respective information to Section 3.2 of the revised version (see also our answer to Referee 1). Also the reviewer seems to have misunderstood our use of the term “particulate phase” this does not imply solid particles. Rather all aerosol particles are deliquesced as the relative humidty remains above the crystallisation humidity of both sea salt and sulphate in the model runs at all times. Will will mention this explicitely in the revised manuscript (Section 2).

5. As mentioned in the text (Section 3.1), the pH of the model’s aerosol size fractions are about 6 (seasalt aerosol) and about 0.5 (sulfate aerosol). Sea salt aerosol is ini-

tialized with surface ocean water pH, which we will mention in the revised manuscript (Section 2).

6. The simulations start at midnight. This is pointed out in the Caption of Figure 2. According to the referee's suggestion, we will add a grey shading to the nighttime hours in our Figures 2, 3 and 6.

7. We deliberately do not give the dominant directions of the reactions listed in Table 1 as these depend on the specific ambient conditions. However, for the conditions of our model studies, the dominant directions are indicated (where possible) in our Figure 1. We make this more clear in the revised version of the Caption of Figure 1.

8. As described in our Section 2 (p. 10965, lines 11-16) organic iodine species (CH_3I, CH_2ClI, CH_2I_2, originating from macro- and micro-algae in the open ocean) are considered (together with I_2) as the source of gas phase iodine in our model. Of course it is conceivable that organic surfactants might contain iodine compounds as well but we are not aware of any data with this regard and therefore did not want to speculate about this. Clearly this should be addressed in future field and model studies.

9. The referee is right, iodide is not reduced, but oxidised to molecular iodine. This will be corrected in the revised manuscript. Thanks for pointing out this mistake.

10. The Dushman reaction is not catalysed by iodide since iodide acts as a true reactant (reduction of iodate by iodide giving HOI and I_2). The initial iodide is coming from the gas phase via uptake of HI which is formed during the iodine reaction cycles occuring in the gas phase. We will add a precision in the revised manuscript (4th par., Section 3.): “The introduced upper limits of the reaction rates for I1-I5 increases the modeled I- concentrations by about two orders of magnitudes. The iodide taken up from the gas phase is oxidized more slowly through these reactions which increases the rate of the Dushman reaction. The IO_3^- concentrations are almost stabilized"

11. In the revised manuscript, we will include the reaction HOI + DOM in Table 1.

The reaction is also shown in our Figure 1. As HOI is reduced to iodide by reaction with DOM, organic matter is oxidised by this process. The true nature of this oxidation process is, however, still unclear, very exciting but far beyond the scope of the present paper.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 10959, 2006.