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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A chemical probe technique for the determination of reactive halogen species in aqueous solution: Part 2 – chloride solutions and mixed bromide/chloride solutions" *by* C. Anastasio and B. M. Matthew

Anonymous Referee #2

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General:

The manuscript reports the application of the method developed first for the investigation of reactive halogen species in aqueous bromide solution (Part 1) and now applied to chloride and mixed chloride/bromide solution.

The probe technique has been validated comparing the experimental data with the results obtained from model calculation with an extended set of kinetics data which

includes 192 reactions (“Mix full model”).

A critical discussions of the reactions considered in the full model is generally missing or only restricted to the remarks to the Tables in the Supplementary material. This raises serous concern. In fact, most of the rate constants reported in Table S3, S5 and S6 are only estimated, whereas the rate constants compiled in Tables S1, S2 and S4 are obtained from the literature. The lack of reliable kinetic data represents a serious limitation to the method and it should be extensively discussed in the text.

In particular, the aqueous phase chemistry of $BrCl^{-}$ radical anion is not only very new but is still not well know. The few rate constants been published and implemented in the kinetic model are also a result of complex chemical model (Reaction 173, 176, 191, Ershov, 2004) or fit to experimental data (Reactions 189, 190, Donati, 2002). How this estimation can influence the observed model results? Has been a sensitivity test performed?

Recommendation: We can only suggest publication after major revision according to the points addressed in this review. The publication should be granted after the acceptance of the part 1 as there is no reason to publish this paper alone.

Specific:

Page 953, line 4: The kinetic model has been first validated with a set of experiments measuring the formation of reactive chloride or bromide gaseous species. However, no experimental results have been presented in the manuscript. More details on the system and the obtained results should be added.

Page 959, line 15: The authors do not present any experimental data derived from “real samples” to support the hypothesis of successful application of their method with environmental samples. If the technique should work readily with sea-salt aerosols it would be interesting to see the results from such experiment.

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Supplementary material:

Page 22, Table S5: Which “models” have been used to model the rate constants for the reaction of $BrCl^-$ radical anion with allyl alcohol?

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 941, 2006.