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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

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Response to Reviewers

Referee #1

General comments

We continue to appreciate the kind words and also the strong recommendation to publish this paper in ACP.

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Specific comments

1. Page 946, line 27. We've modified this portion of the text to describe why Data Treatment A can't be used in the mixed halide solutions.

2. Fig. 5. We don't believe that the formation of reactive chlorine is negligible compared to reactive bromine formation, although it is true that the rates of 3BPD formation are much greater than those of 3CPD in mixed halide solutions. But a large part of both of these products are formed from reactive mixed-halogen species, either BrCl- or (at low pH) BrCl. The differences in the amounts of chlorinated and brominated products from these intermediates are due to the fact that the yield of 3CPD is much lower than the yield of 3BPD. These yields will likely be different for different probe molecules (i.e., something other than allyl alcohol), which would produce a different ratio of chlorinated to brominated products.

Referee #2

General comments

1. Critical discussion of the reactions in the full model. As the referee points out, a number of the reactions in the model are either estimated or were determined from fitting our model output to our experimental results. For reactions between allyl alcohol and the reactive bromine, chlorine, or mixed bromine/chlorine species, we describe the constraints and modelling that we used to determine the corresponding rate constants in the Supplementary Material (Tables S3, S5, and S6). We also point out in these tables the cases in which the constraints are weak and where we have only a rough estimate of the rate constant (e.g., in cases where a given reaction is only a small source of 3BPD or 3CPD). Based on the fact that we have performed experiments over a wide range of experimental conditions, we feel comfortable that our estimated reactions and rate constants are reasonable. We have added a paragraph at the end of section 2.2 to discuss these issues.

ACPD

6, S609–S612, 2006

2. BrCl- reactions. We are currently working on a manuscript that describes the mixed halide reactions and the formation of BrCl- in more detail. As we will describe in this BrCl- manuscript, when we started our research on allyl alcohol as a chemical probe for reactive halogens, the Donati and Ershov data were not available and we did not have any of the "proposed" mixed halogen radical reactions in our model. The resulting model did not fit our 3BPD or 3CPD experimental results in mixed halide solutions, even though the model performed very well for these species in solutions containing only bromide or chloride. We then started to devise a set of mixed halide reactions, building it up from our experimental results performed under the different experimental conditions of pH, halide concentration, and AA concentration. The resulting model fit did a good job of fitting our experimental data in mixed halide solution.

At that point we found the recently published Donati and Ershov data. There was, in general, good agreement between the mixed halide reactions (and their rate constants) that we had in our model and the results of Donati and Ershov, although there were several (relatively unimportant) reactions that we did not have in our original model. We then revised our Mix Full Model to include the Donati and Ershov data, tweaking some of our mixed halide reaction rate constants to better fit our experimental data. Certainly the model could (and will) be improved by additional independent measurements of mixed halide reactions made in the future. But, as far as we are aware, our Mix Full Model is currently the most comprehensive and accurate description of halide chemistry in aqueous solution. We have added a discussion of this issue, and the fact that it is a limitation of our technique, in the new paragraph at the end of section 2.2 (Kinetic models) and also at the end of section 3.7 (Applications and limitations of the probe technique).

Specific comments

3. Page 953, line 4. We described the technique to measure gaseous, reactive halogens from illuminated solutions in a previous paper (Matthew et al., 2003). We cite this paper in both Part 1 and Part 2 when we discuss these experiments. We did not give

ACPD

6, S609–S612, 2006

much detail on the Br*(g) results in Part 1 because these are included in the Matthew et al. paper. We have changed the wording in section 3.3 in Part 1 to make it clearer that a description of the technique and the results for the bromide experiments are presented in Matthew et al. (2003). We have not changed the relatively brief description of the Cl*(g) results in Part 2 because these are negative results (i.e., no Cl*(g) was found), in agreement with our model predictions.

4. Page 959, line 15. We have modified the text in both Parts 1 and 2 to make it clear that we have not yet applied the method to environmental samples.

Supplementary Material

5. Page 22, Table S5. We used the Mix Full Model to determine rate constants for the BrCl- and BrCl reactions with allyl alcohol. We have modified the footnote of this table to make this clearer.

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