Atmos. Chem. Phys. Discuss., 6, S603–S608, 2006
www.atmos-chem-phys.org/acpd/6/S603/
European Geosciences Union

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “A chemical probe technique for the determination of reactive halogen species in aqueous solution: Part 1 – bromide solutions” *by* B. M. Matthew and C. Anastasio

B. M. Matthew and C. Anastasio

Received and published: 20 April 2006

Response to Reviewers

Referee #1

General comments

We appreciate the kind words and the strong recommendation to publish the paper in ACP. We hope that the referee is correct that our paper will stimulate additional studies of halogen reactions in aqueous solution.

Specific comments

1. Page 905, re: model. As requested, we have added a few lines to give a brief description of the overall model in the text.

2. Fig. 1(a). The referee is correct that H2O2 can be a significant sink for OH at low AA concentrations. We hadn't meant to exclude consideration of H2O2 as a sink for OH, but rather we meant for the term "natural scavengers" to include H2O2 (both for OH as well as for Br*, where it can also be a significant sink). We have modified the figure caption to make this point more clearly.

3. Figure 3. We'll address these questions in reverse order. a. Rate of AA loss. The rate of OH formation under these experimental conditions is 0.43 micromolar per hour. (This is approximately a factor of two higher than that calculated by the referee because of the stoichiometry of H2O2 photolysis, i.e., each photochemical event produces two OH radicals. We have modified the footnote to this reaction in Table S1 to clarify this.) This rate of OH formation is approximately 60% of the rate of AA loss at the plateau in Figure 3 (0.69 micromolar per hour). The difference is due to the polymerization reactions that we describe in the text, i.e., reaction of an AA radical (formed from the OH + AA reaction) with a molecule of AA. We have modified the text to describe this behavior more clearly.

b. Dependence of the rate of AA loss on [AA]. As the referee points out, in this system (with only H2O2 and AA) AA is scavenging essentially all of OH at [AA] above 150 micromolar and the measured rate of loss of AA reaches a plateau after this point. The modelled rate of AA loss, however, continues to rise beyond this point. The reason for this is that the rate constants of our proposed polymerization reactions are fairly slow, which results in non-steady state concentrations for the radical intermediates (AAOHr, AAOH1, AAOH2, and AAOH3; see reactions 70 - 73 in Table S3). At lower concentrations of AA, the concentrations of the intermediates are much lower than their predicted steady-state values and the net effect is less efficient polymerization. At

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

higher concentrations of AA, the polymerization reactions are faster (since they're all first order in AA), the intermediates are closer to their steady-state concentrations, and AA destruction by polymerization is more efficient. The net effect is good agreement at the lower AA concentrations but an overestimation of AA loss at higher concentrations.

However, as we state in the text, even though our empirical polymerization reactions overestimate the rates of AA loss at higher [AA], this difference has no effect on the determination of the kinetic parameters for Br*(aq). Because of this, we have modified the text slightly to better explain the impacts of polymerization, but we have not added much additional detail.

<Minor typo comments>

We have fixed the errors.

Referee #2

General comments

1. Sample preparation. It is true that extracting and quantifying the halogenated diols (e.g., 3BPD) is rather time consuming, although none of the steps are difficult. The relatively long analysis time (79 minutes) is not an issue if the gas chromatograph is equipped with an autosampler, although running the samples from a full competition kinetics experiment can take a day or two. Based on the referee's comments, we have removed the description of the procedure as "simpler" than previous methods in the introduction (line 28, p. 901).

2. Allyl alcohol analytical method. This is a rather simple method (direct UV detection with HPLC), but since we have not described it previously we added a bit of additional description of the technique to the text. Because we did not use very low AA concentrations we did not determine a detection limit for the technique, but it worked fine in the range we required (2 - 8000 micromolar).

3. Use of method for environmental samples. We had not meant to imply that we had

already used the method on “real” samples in Part 2, only that we discuss this idea in more detail in that paper. We have modified the text to clarify this.

4. 3BPD detection limit. As we state in Part 2, we believe that our method is sensitive enough that it should work for illuminated sea-salt particles and, after some modification, with seawater. However, we won’t know if this is true until we try it. We have found that there is no significant influence of halides or other salts on the detection limit for 3BPD (or 3CPD), but it is possible that there could be other matrix components in environmental samples that would raise the detection limit.

Specific comments

5. Page 910, line 22. The polymerization reactions are overestimated at the higher AA concentrations, but they fit the experimental data nicely in the lower AA range that we more typically work in. We discuss the reasons for this in comment #3 above in our response to Referee #1. The fact that our model overpredicts allyl alcohol loss at high [AA] does not significantly affect our kinetic results for Br* or our data treatment. The referee’s point that the discrepancy between measured and modelled rates of 3BPD formation increases with the upper limit of the AA concentration range is interesting. It appears that this is not due to a consequence of model overpredictions in the rate of AA loss, but rather because it is more difficult to predict rates of 3BPD formation past the “inflection point”, where rates of 3BPD formation decrease (rather than increase) with increasing [AA]. One reason that the model’s overpredictions of AA loss at high [AA] do not appear to matter is that in this range the concentration of AA does not change much (in either the model or experimental data) compared to at the lower AA concentrations. That is, the percent change in [AA] during an experiment is significantly smaller at high [AA]. This can be seen in the plot of AA loss rates that we have added to the Supplementary Material (see point 7 below).

6. Page 934, Figure 3. The “additional” AA loss above the rate of OH production is due to the polymerization reactions of AA. This is not an artifact of the model, but a real

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

phenomenon that occurs in both the model and experiment (although the model does overestimate AA polymerization at high [AA] as we discuss above). The polymerization of AA is discussed in more detail in comment #3 in our response to Referee #1.

7. Page 936 - 40, Figs. 4-6. The rate of 3BPD formation in a given experiment is determined as the slope of a linear regression in a plot of [3BPD] versus illumination time. (The same procedure is used for 3CPD in Part 2.) The rate of loss of allyl alcohol in a given experiment (i.e., at a given initial AA concentration) was determined by first taking a linear regression of ln([AA]t/[AA]0) versus illumination time, where [AA]t is the concentration at time t and [AA]0 is the initial concentration in the experiment. The slope of this plot is the negative of the pseudo first-order rate constant for AA loss. Multiplying the slope-derived rate constant by [AA]0 produces the initial rate of AA loss. We have added a short paragraph to section 2.2.2 in the text to describe these procedures.

As requested, we have added a section to the Supplementary Material (S.13) to show plots of 3BPD formation and AA loss. These are the measurements that were used to construct Figs. 5a and 5b in the paper.

Supplementary Material

a. Reaction between OH and 3BPD. We did not include this reaction in the model (or the equivalent reaction for 3CPD) because it is unimportant under our conditions since [OH] is quite low. We checked this experimentally (see section 2.2.1) and found no decay of 3BPD in an illuminated sample containing 3BPD, 1.0 mM H2O2, and 0.80 mM Br-. In addition, even in the worst-case scenario for our conditions (i.e., with the highest [OH] and assuming a fast rate constant for 3BPD and OH), the lifetime of 3BPD with respect to OH reaction is approximately 30 hours, whereas the duration of our experiments was typically 1.5 hours or less. Under these conditions, $<$ 5% of any 3BPD present would be lost during illumination.

b. Formation of polybrominated species. We do see formation of 2,3-dibromo-1-

propanol (2,3DBP) in some of our experiments, although the concentration is quite low (a few percent of the corresponding amount of 3BPD). This does not affect our data treatment for 3BPD, as the formation of 2,3DBP (and other species) is represented in the "other products" pathway in any given set of Br* + AA reactions. For example, in the case of the reactions of Br2 with AA, reaction 83 (Br2 + AA = Br2AA2; Table S3) represents all of the channels that do not form 3BPD, including the channel that forms 2,3DBP. The 3BPD pathway (reaction 82) is independent of the identities of the products formed in reaction 83. Although 2,3DBP does not affect use of 3BPD, we hope to be able to use a combination of these two products in the future to increase the specificity of the probe technique.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 899, 2006.