**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

Anonymous Referee #1

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$<$General comments$>$

Matthew and Anastasio developed a new method of detecting photo-chemically formed reactive Br species in the solution and validated their technique by using a computer calculation with known and estimated reaction rates. Authors' techniques are unique, the results are interesting, and the materials are presented in a well-organized manner. The study is very important to understanding complex halogen cycles in the troposphere, which affects various atmospheric aspects. Studies of reactive halogen

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species are intensively conducted in the gas-phase but aqueous-phase formation and concentrations are not well-understood. The paper will stimulate studies of reactive halogen species in the liquid-phase. I strongly recommend publishing this report in Atmospheric Chemistry and Physics.

<Specific comments>

1. Page 905, about the model. Even though supplemental material provides detailed derivations of the equations, a few lines of description (e.g. # of chemical reactions included) of the model would be helpful to understand what follows it.

2. Fig. 1. (a). Although reaction rate constant of H2O2 and OH radical is not fast (2.7x107 M-1 sec-1) compared with Br-, allyl alcohol, and probably natural scavengers, scavenging by H2O2 had better be included in the figure since when AA concentrations are low, 1.0 mM H2O2 would be the major OH scavenger. Including H2O2 reaction in the figure would also help understanding Fig. 3, especially when AA concentrations are low.

3. Fig. 3. Two questions for this figure. First is about the increasing rate of AA loss predicted by the model. Since the illuminated solution only contained AA and H2O2, photo-formed OH radial reacts with AA, H2O2 and OH radical itself, depending on their concentrations and reaction rate constants. When the concentration of AA is increased, almost all the OH radical is scavenged by AA and steady-state is quickly reached, i.e. formation rate of OH = rate of AA loss. Experimental data clearly show the trend to me. Based on bimolecular rate constant and 150 microM AA, 95.4% of OH would react with AA and rate of AA loss should reach plateau after [AA] > 150 microM. I wonder why the model predicts increasing rate of AA loss. Second is about the rate of AA loss. Based on supplemental data, photolysis rate constant of H2O2 for the illumination condition used is 3.1x10-6 sec-1. If 1.0 mM H2O2 is used, OH radical formation rate is calculated to be 0.19 micro M min-1, which should be the maximum AA loss rate, unless there are some kinds of chain reactions. But, the experimental data show that the rate of

AA loss reached plateau at 0.7 microM min-1. I am wondering why the AA loss rate is faster than the calculated OH formation rate.

<Minor typo comments>

1. Page 903, 15th line, 18.2 ohm-cm needs to be 18.2 M ohm-cm.

2. Page 917, 27th line, "while values of RF are are within", needs to omit extra are.

3. Tables S1 and S2 in the supplemental material, CO3 -2 should be CO3 2-.

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

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