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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A box model study on photochemical interactions between VOCs and reactive halogen species in the marine boundary layer" *by* K. Toyota, et al.

Anonymous Referee #2

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The paper by Toyota et al., #ACP2003-089ÿ presents a very clear and impressively thorough box model study of interactions between halogen atom and radical chemistry, and reactive VOCs that are emitted from the ocean surface. This paper was very professionally prepared and is interesting and significant. I found it quite insightful, and the model runs of focus were well chosen. In particular, the paper clearly describes the importance of CH3CHO and C3H6 as halogen atom sinks, and the role that halogen atom reactions with these VOCs plays in determining the partitioning between inorganic and organic bromine and chlorine, as well as the distribution of halo-organic reaction products. The conclusions about the PAA-impact on halogen activation is also important. It certainly should be published, and I mostly only have editorial concerns. However, they are significant in that my only complaint about the paper is that its exceptional length

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will detract from its readability, and detract from focus and attention being paid to the important points. In particular, the model description sections, while quite thorough, read a bit like a project report, rather than a paper addressing some specific questions about MBL halogen atom-VOC interactions. Thus the authors must endeavor to move as much of the model description as possible into the supplement, and summarize as much as possible the points that donŠt need so much detail.

I have only two significant technical comments. One is that the paper hardly mentions the sensitivity of the model results vis-à-vis organic-Br/inorganic-Br and the distribution and concentrations of halogen species on the model NOx, and how model NOx compares to appropriate NOx measurements. This will clearly be important in a number of areas, e.g. the distribution of hydroperoxide vs. carbonyl-type Br atom-C3H6 addition products. I think the paper should discuss some model-measurement comparison for NOx, and the sensitivity of the model output to NOx. A very interesting and important point made in the paper is the role of CH3CHO in sequestering Br, and thus impacting bromine activation. In this regard, I think a bit more discussion is appropriate regarding the importance of MBL CH3CHO measurements, and the great uncertainty in the existing data, particularly in light of recent reports on problems associated with artifact aldehyde production in inlet systems.

More minor comments are as follows:

1. The paper makes it clear that C2H2 chemistry is unimportant. Thus I think section 3.4 can be deleted, and discussed instead in a sentence or two, perhaps referring to more detail in the Supplement.

2. In light of the importance of this type of reaction, I am wondering if the RO2-RO2 rate constants are consistent with or could be/should be also compared with the recommendations in Kirchner and Stockwell, 1996? On page 23 I think it is useful to comment that the RO2-radical self reactions referred to are probably unimportant compared to cross-reactions with CH3OO and CH3C(O)OO, and HO2, if indeed this is the case.

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3. Since Figure 2 is strictly from the literature, I think it can be deleted, and simply discussed in the text.

4. Section 4 Ű A very minor point, but to me, the word Şexplicit Ť is not very meaningful. All mechanisms comprised of elementary reaction sequences are explicit, arenŠt they? I recommend saying something like Şnear-complete Ť. A mechanism can be explicit, yet incomplete and perhaps inaccurate.

5. Section 5 Ű I donŠt think it is appropriate to report simulated species concentrations to tenths of a ppt. You donŠt mean to convey that sort of precision or certainty in the model, I think.

6. Section 5.2 Ű How much do the quoted simulated HBr mixing ratios depend on the range of realistic particle uptake rates for HBr?

7. There is no need to summarize anything in the Conclusions. The Conclusions should either state new thoughts that derive from the text, or they can be deleted.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 4549, 2003.