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Atmospheric Chemistry and Physics Discussions

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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.

K. Toyota, et al.

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General Comments

First of all, we would like to apologize to our two referees and editor about the great delay of the revision.

Both of the two referees strongly recommended reducing the manuscript length to improve the readability. They also suggested that we should perform additional model runs to investigate sensitivities of the results on NOx concentrations etc. Hence our basic strategy for the revision is as follows:

- As suggested by Referees (and Editor), the description of minor details in the reaction scheme is moved to the electronic supplement in order to reduce the manuscript length

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- As suggested by Referee #1 (and Editor), Introduction is shortened a little by relying more on the literature such as Sander et al. (2004) and Boucher et al. (2003)

- As suggested by Referee #1, the Results and Discussion sections are polished to refine lengthy descriptions.

- As suggested by Referees, the sensitivity of results on NOx mixing ratio is explored by performing Run 7d (as called in the revised manuscript). Unfortunately, increasing the number of sensitivity runs is likely to contradict our basic strategy of reducing the manuscript length. Therefore, we give up to include sensitivity studies other than that.

- As suggested by Referee #2, the Conclusion section is significantly updated to state some new thoughts

We have also performed some significant updates other than these points as follows:

- Section 3.4: It was confused by Authors that the rate constant of Cl^- + PAA had been taken from the literature. Actually, the rate constant had been just estimated based on the rate constants of analogous reactions. We now state this point correctly.

- Section 5.3, the last paragraph: The context of referring to the heterogenous reaction HCOBr → HBr + CO is changed.

- Reassembling of model runs: "Run 4" (as was formerly called) is deleted and Run 7d is newly performed. Accordingly, the model run IDs are changed as follows:

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old no.	new no.
4	-
5	4
6	5
7a	6a
7b	6b
7c	6c
7d	6d
8a	7a
8b	7b
8c	7c
-	7d

- Fig. 2: The time evolutions of Br^- (g) mixing ratio and excess Cl^- (e) are added (as suggested by Editor)

- Unit "kcal": The obsolete unit "kcal" is converted to "kJ" (as suggested by Editor)

Response to specific comments by Referee #1

1. Section 3 is shortened significantly by moving detailed descriptions unnecessary for the focus of the present work to the supplement; the C_2H_4 and C_3H_6 sections are merged to the alkene section while some of the details are moved to Sects. S2 and S3 in the supplement, and most of the details in the C_2H_2 section and the sections formerly numbered as 3.5-3.6 (describing a protocol for estimating rate constants for alkoxy, peroxy radicals, and intermediates) are entirely moved to the supplement. We also polished sentences in Sect. 5 to make it a little more concise.

2. Concerning the reactions involving nitrogen oxides, some of the details that could be included are neglected in the present work. This is one of the reasons why we restrict our scope to the clean MBL chemistry. For instance, only PAN-type compounds (i.e.

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PBrAN and i-BrAcetPAN) are included in our reaction scheme. The formation of peroxy haloalkyl nitrates ($\mathrm{ROONO_2}$) via $\mathrm{RO_2}$ + $\mathrm{NO_2}$ was confirmed experimentally at very low temperatures under high-NOx conditions; $\mathrm{ClCH_2OONO_2}$ or $\mathrm{BrCH_2OONO_2}$, along with PAN-type compounds in the degradation of haloacetaldehydes were identified by Chen et al. (1996), and $\mathrm{BrCH_2OONO_2}$ was also identified in the degradation of $\mathrm{CH_3Br}$ by Chen et al. (1995). Due to the reverse reactions to give $\mathrm{RO_2}$ + $\mathrm{NO_2}$ expected to occur rapidly under the mid-latitude MBL conditions, however, this type of products are very unlikely to be important for MBL halogen chemistry. On the other hand, the formation of haloalkyl nitrates ($\mathrm{RONO_2}$) via $\mathrm{RO_2}$ + NO is also feasible, by analogy with the reactions of non-halogenated compounds. Unfortunately, there is currently no experimental evidence for the formation of halogenated $\mathrm{RONO_2}$-type compounds via $\mathrm{RO_2}$ + NO. Although we speculate that $\mathrm{RONO_2}$-type compounds are of less significance than PAN-type compounds, the feasibility of such reactions should be investigated experimentally. Since the yields of $\mathrm{RONO_2}$-type compounds via $\mathrm{RO_2}$ + NO are likely to be greater as the carbon number of $\mathrm{RO_2}$ increases (Atkinson, 1990; Lightfoot et al., 1992), this class of reactions can be important when the reactions of higher molecular weight hydrocarbons ($> \mathrm{C_4}$) are considered. We added some statement about this point in Sect. S9 in the revised version of supplement.

3. We agree with Referee in that sulfate aerosols are very important for the recycling of inorganic halogen species. Unfortunately our model is still not capable of handling sulfate aerosols properly. But, by increasing the the mass accommodation coefficient of HBr by a factor of 10 (from 0.024 to 0.24), we can mimic the additional contribution from sulfate aerosols to the halogen recycling. Halogen chemistry is activated more in this situation, but our conclusion in Sect. 5.2 still holds in that $\mathrm{CH_3CHO}$ mixing ratio is an important factor for determining inorganic bromine mixing ratio (see discussion below in our response to minor comment #6 by Referee #2). To avoid making the manuscript longer, however, we gave up mentioning this issue in the revised manuscript.

4. Taking into account the referee's comment, we have slightly changed the statement

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in Abstract and Section 5.6 concerning the importance of PAA for MBL halogen chemistry. We now state in Section 5.6 as follows: "The oxidation of halide ions by PAA during the nighttime can be an important, although not major, initiator for the autocatalytic cycle shortly after sunrise." The basically same statement is made in Abstract.

5. Increasing the number of sensitivity runs, although interesting and useful to understand more about the role of VOCs in halogen activation, contradicts the demand for downsizing the manuscript. Among the sensitivity runs suggested by the referee, however, we add the results of NOx sensitivity runs in Sect. 5.4, since the benefit of including this issue was also indicated by another referee.

Response to technical comments by Referee #1

Page and line numbers below refer to those in the ACPD manuscript.

p. 4552, line 20: The recent review paper by Sander et al. (2003) has been added to cited articles.

p. 4556, line 9: We indeed refer to hydration constant, not Henry's law constant. We now add parenthetic statement to make this point clearer as follows: "since the hydration constant of HCHO is three orders of magnitude greater than that of $\mathrm{CH_3CHO}$ (whereas their intrinsic Henry's law constants are on the same order, see Zhou and Mopper, 1997, and references therein), HCHO formed in the surface microlayer will diffuse downward ..."

p. 4556, lines 18/19: We have changed the expression from "..., which would be less susceptible to anthropogenic influences than atmospheric concentrations" to "..., which would be less influenced by long-range transport of anthropogenic and/or terrestrial sources than atmospheric concentrations".

p. 4560, Reaction 21: The stoichiometry of oxygen was wrong, as suggested by Referee. We have also found the same kind of errors in Reactions (26), (53), and (72). The formation of molecular oxygen ($\mathrm{O_2}$) is now correctly accounted for in these reactions.

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p. 4567, line 14: Jenkin et al. (1997) is now cited as a reference for MCM.

p. 4587, line 28: We now change the expression from "by a factor of three or less" to "by a factor of 2-3".

p. 4596, line 5: We have dropped "halogen" once, as suggested by Referee.

Table 3: The mixing ratio of $\mathrm{C_2H_2}$ is fixed in each model run and the baseline mixing ratio of $\mathrm{C_2H_2}$ is 35 pmol/mol, as noted in Sect. 4. For clarity, however, we added more information on the rows of describing Runs 1h-i in Table 3. Furthermore, in order to give a complete list of the initial or fixed (where fixed constant) mixing ratios of chemical species in our model runs, we have added a new table, Table S1, in the supplement.

Response to major comments by Referee #2

1. In order to reduce the manuscript length, Section 3 is updated significantly by moving minor details to the electronic supplement (for details, see above in our response to specific comment #1 by Referee #1).

2. A sensitivity study to examine a sensitivity of o-Brx/i-Brx ratio to NOx mixing ratio is newly performed, presented and discussed in Sect. 5.4.

3. We add a brief statement in Conclusion regarding artifact problems in $\mathrm{CH_3CHO}$ (and also alkenes) measurements in the Conclusion section.

Response to minor comments by Referee #2

1. Section 3.4 is shortened significantly and details are moved to the supplement.

2. $\mathrm{RO_2}$-$\mathrm{RO_2}$ reactions: Referee wanted to know if the rate constants for the self-reactions of halogenated organic peroxy radicals used in the present work were consistent with the recommendation in Kirchner and Stockwell (1996) (hereafter KS96). Then we examined this issue briefly to find that agreement between the two is fair regarding $\mathrm{XCH_2CH_2OO}$ (well within a factor of 3), but poor regarding $\mathrm{XCH_2OO}$ (the KS96-based rate constant is 5- to 17-fold greater than experimentally determined values on which

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the present work is based) and $\mathrm{CH_3C(OO)CH_2X}$ (the KS96-based rate constant is 6-fold smaller than Villenave and coworkers' recommendation) where X is either Cl or Br. These comparisons suggest that the KS96 recommendation does not necessarily work well for halogenated organic peroxy radicals formed from up to C3-hydrocarbons, and thereby justify taking the rate constants of cross-reactions simply from the generic value in MCM (Saunders et al., 2003). We added some statement about these points at the end of Sect. S9 in the electronic supplement. Besides, as indicated by the referee, the self-reactions of organic halogenated reactions are definitely unimportant in the ambient air, which is now stated in Sect. S9 as well.

3. Figure 2 in the ACPD manuscript has been moved to the electronic supplement, as the section containing the figure has also been moved there. It should be noted that the absorption cross sections of $\mathrm{ClCH_2CH_2OOH}$ recently reported by Chakir et al. (2003) are newly included in Fig. S1c (formerly called as "Fig. 2c") as a further support to our idea.

4. The expression "near-explicit" comes from MCM papers (Jenkin et al., 1997; Saunders et al., 2003). The use of this expression seems to be appropriate in that our reaction scheme and MCM both attempt to describe reaction pathways without introducing surrogate compounds to represent a series of chemical species (i.e. the lumping method). Although we believe that our methodology is an appropriate way to better describe chemical interactions between VOCs and halogens, it still appears a little far from complete due to the dearth of supporting experimental data. Based on this standpoint, we prefer to use the expression "near-explicit" for the present reaction scheme. We also want to use the same expression as the MCM papers to demonstrate that our methodology is quite similar to that of MCM's.

5. Referee stated that reporting the simulated mixing ratios of species to tenths of a ppt is unnecessary in the context of the present work. Therefore we have reduced precision in the reported mixing ratios unless necessary.

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6. In addition to the point (i.e. the impact of sulfate aerosols on inorganic halogen recycling) raised by another referee, Referee might also want to know how sensitive our results are to the choice of the mass accommodation coefficient (α) of HBr. In our model runs we use the value of α(HBr) (= 0.024, at 293 K) determined on aqueous water surfaces based on droplet train technique (Schweitzer et al., 2000). We have briefly tested the α-sensitivity issue by increasing α(HBr) from 0.024 to 0.24 in Run 7a. Halogen chemistry is activated more in this case, but our conclusion still holds - i-Brx decreases from 21 to 3 pmol/mol by increasing $\mathrm{CH_3CHO}$ mixing ratio from 0 to 250 pmol/mol (cf. Fig. 7a). Actually, Morita and coworkers recently pointed out a potential flaw in the commonly used formula for describing the gas-phase diffusion resistance to derive α (or γ) from the net uptake rates measured in the experimental system of droplet train technique and indicated that the true values of α should have been significantly greater than reported for a variety of compounds (Morita, 2003; Morita et al., 2003). Therefore it will be useful to get more information about the mass accommodation coefficient of HBr on the surfaces of various media by a variety of experimental techniques. This topic is actually beyond the scope of the present work and, besides, there is a need to avoid making the manuscript longer. Therefore we gave up mentioning this issue in the revised manuscript.

7. The Conclusions are updated significantly by dropping the simple summaries of the results obtained and by including some new thoughts that derive from them.

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