

Interactive comment on “Newly observed peroxides and the water effect on the formation and removal of hydroxyalkyl hydroperoxides in the ozonolysis of isoprene” by D. Huang et al.

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To Reviewer 2

General comments:

This manuscript presents experiments to determine the yields of hydroxyalkyl hydroperoxides in the ozonolysis of isoprene. This process has important implications for atmospheric chemistry because organic peroxides can act as oxidants or radical reservoirs and can contribute to the growth of secondary organic aerosol. There have been relatively few laboratory studies of this reaction, and, of the hydroxyalkyl hydroperoxides (HAHPs) that may be formed, only the smallest have been identified previously. The

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authors have conducted a series of careful and thorough experiments to identify several unknown hydroperoxides and characterize the role relative humidity in the reaction mechanism. Evidence of the formation of larger HAHPs from the ozonolysis of isoprene is a significant result and merits publication.

A: We thank you for your effort and constructive comments. Here are our responses to your specific comments.

Below are several specific comments and a number of suggested technical corrections.

P 5290, Section 3.3.3: There's no mention made of the relative humidity used in the experiment in which the reaction time was varied. Based on Figure 7, it appears to be 5%, is that correct? Please note this in the text and figure caption.

A: Yes, you are right. We have added this information in the text and the captions of Figures 5 and 7.

P 5294, lines 7-8: "...indicating the possibility of the formation of alpha-acyloxy hydroperoxides and peroxyhemiacetals." Are the authors suggesting that these species could be produced in the gas phase or in the collection solution? Please clarify. Also note the typo: hydroperoxides should be hydroperoxides.

A: We think that the alpha-acyloxy hydroperoxides and peroxyhemiacetals possibly form on the reactor wall and/or in the collection solution.

Yes, "hydroperoxides" should be "hydroperoxides".

P 5295, lines 7-11: "Subsequently, the unimolecular decomposition for HAHPs is unlikely to occur in the gas phase; only the water-assisted decomposition of HAHPs is efficient in the gas phase, and it generates carbonyls plus H₂O₂ or organic acids plus H₂O." Scheme 1 shows only the unimolecular decomposition channels (R4a11 and R4a12). The water-assisted channels should be indicated also. It would also be helpful to refer to Scheme 1 and cite the reaction numbers when discussing the mechanism.

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A: Yes, we have added the water-assisted decomposition channels to Scheme 1 and cited the reaction number in the text in the revised manuscript.

P 5295, line 21 – P 5296, line 12: The authors investigate the effect of varying the HAHP decomposition rate on the time and RH dependence of the concentrations of the unknown peroxides. However, the formation rates of the HAHPs are likely to have significant uncertainty as well. Were any tests done on the effect of varying the formation rate? Can the same general shape be obtained by adjusting both the formation and loss rates?

A: Yes, we also tested the effect of varying the formation rate of HAHPs on the time and RH dependence of the concentrations of several HAHPs. However, the model result suggests that the formation rate constant would have little effect. Because the formation rate constant is at least 3 orders of magnitude higher than the decomposition rate constant. The decomposition is the rate-limiting step for the production of HAHPs. About the second question, we think that adjusting both the formation and loss rates can result in the same general profile. As mentioned above, however, the profile shape is decided by the loss rate.

P 5296, line 27 – P 5297, line 8: In this section, the authors suggest that the difference between the observed and modeled humidity dependence of HMHP might be explained by the chemistry of BHMP. To shed light on this question, it would be useful to add a figure showing the measured concentrations (or yields) of HMHP and BHMP together with the model result (PO1). This would allow the reader to more easily compare the magnitudes and shapes of the measured and modeled curves. Given the relative amount of BHMP shown in Figure 3 and the shape of its RH dependence, the argument that BHMP hydrolysis could be a source of HMHP at high RH does not seem entirely convincing. Since HMHP is believed to undergo water-assisted decomposition, the HMHP yield would be expected to decrease at high RH unless its rate of production from BHMP increases by a greater amount, but BHMP concentration also decreases at high RH (although water of course increases). It seems as though it should be possible

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to estimate the rate of BHMP hydrolysis that would be required to maintain a constant HMHP concentration as RH increases, and to determine whether the result is realistic, given the amount of BHMP measured. I would suggest the authors attempt such an analysis.

A: Your suggestion is important. We added a figure showing the RH dependence profiles of measured molar yields of HMHP, BHMP and the modeled PO1 together with the corresponding linear fitting equations (Fig.1, i.e. Fig.9 in the revised manuscript). It is noticed that the modeled HMHP, i.e. PO1, is far less than the measured HMHP. Moreover, as RH increases, the decrement of BHMP due to its hydrolysis ($\Delta Y_{BHMP}/\Delta RH = 5.36 \times 10^{-4}$) can only account for about half the increment of HMHP ($\Delta Y_{HMHP}/\Delta RH = 1.26 \times 10^{-3}$). There are two possible reasons to explain this result as follows: (i) there is other source of HMHP, and (ii) it is more difficult for HMHP to hydrolyze at high RH than that for the HAHPs containing more carbons. Unfortunately, we currently cannot give a definite interpretation about the discrepancy between the modeled and observed HMHP. We have added this analysis in the revised manuscript.

Technical corrections:

P 5282, Line 25: “. . .of minutes to several hours of reaction time due to. . .” Add comma after time.

A: Yes.

P 5289, line 6: “. . .obtained their yields upper limits.” “upper limits of their yields” would be better.

A: Yes.

P 5293, line 14: “. . .are much more stable than hydroxyalkyl hydroperoxide.” Change to “hydroperoxides.”

A: Yes.

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P 5293, lines 21-26: I would suggest the following changes to plural/singular form, verb tenses, and punctuation in this sentence: “we speculate that unknown1 is a hydroxyl- or a carbonyl-group-containing C2 hydroperoxide, or both hydroxyl- and carbonyl group-containing C3 hydroperoxide. Unknown2 and unknown3 are hydroxyl-group containing C3 hydroperoxides or peroxy organic acids or hydroxyl- and/or carbonylgroup-containing C4 hydroperoxides.”

A: Yes.

P 5294, line 9: “Thus, we added a pair of carboxylic acid and aldehyde. . .” should be “Thus, we added pairs of carboxylic acids and aldehydes. . .”

A: Yes.

P 5298, line 3: “The modeled HAHPs profiles. . .” suggest “HAHP profiles.”

A: Yes.

P 5298, line 10: “. . .via the formation of hydroxyalkyl hydroperoxide.” Suggest “hydroperoxides.”

A: Yes.

Figure 3: The abbreviation BHMHP is used in the panel A legend to refer to bis hydroxymethyl hydroperoxide, whereas in the text, BHMP is used.

A: Yes, we have changed “BHMHP” into “BHMP”.

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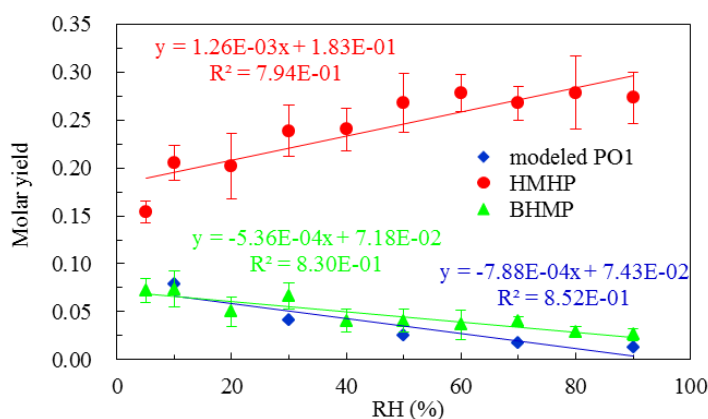


Fig. 1. Comparison of RH dependence profiles of measured HMHP, BHMP and modeled PO1 (i.e. HMHP).

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