

## ***Interactive comment on “Unexpected high yields of carbonyl and peroxide products of aqueous isoprene ozonolysis and implications” by H. L. Wang et al.***

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Thanks for your effort and constructive comments. Here are our responses to your comments.

General comments: (Q1) Although the topic is indeed important, the manuscript is very poorly written and poorly organized. Numerous grammatical errors appear throughout the text, and the style of writing is far too informal for a proper scientific manuscript. There are too few figures to explain the author's points and too much descriptive text which could easily be in tables/figures. Also, the title of the paper is based on the author's conclusions, which are based on numerous assumptions. A better title would

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be something like: “Understanding the aqueous phase oxidation of isoprene” etc..

(A1) Yes, we have improved the writing, provided more illustrations and changed the title in the revised manuscript.

(Q2) The biggest scientific issue with this manuscript is the assertion of relevance to the ambient atmosphere. These experiments were conducted with unrealistically high concentrations of isoprene and ozone, under conditions where isoprene is in excess. None of these conditions would ever exist in the ambient atmosphere. As a result of these conditions the reactions are essentially complete in less than 5 minutes. Although this means that one can potentially determine the final yields (as the authors have done), it is unclear what would happen under conditions more relevant to the atmosphere. Although complete in 5 minutes here, the kinetics of the reactions under real conditions may be limiting the importance of such reactions to the atmosphere (ie: it may take a week for any products to form under ambient conditions). Also, it is unclear if the mechanism would be the same under low concentration conditions. These issues need to be honestly discussed by the authors. Ideally additional experiments at lower concentrations would be performed, but if not, then a realistic discussion of the limitations of these experiments needs to be included.

(A2) We agree that our experimental conditions were far from those in the ambient atmosphere. Unfortunately, due to the technique limitation, we are unable to perform the experiments under the real atmospheric conditions including the reactant concentrations and reaction time. But we simulated the pH and temperature change. In the present study, we pay close attention to two questions: (i) how isoprene produces the first generation products; (ii) what are the final products for the aqueous ozonolysis of isoprene when ozone is in excess. If ozone was in excess in the aqueous ozonolysis of isoprene, the real yields of the first generation products (MAC and MVK) couldn't be obtained, because MAC and MVK would simultaneously react with ozone. When isoprene was in excess, the rate of isoprene reaction was much higher than that of MAC/MVK reaction, then the yields of these two products can be conveniently deter-

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mined. For answering the second question, we combined the yields of MAC and MVK with the stoichiometric of MAC/MVK and ozone in the aqueous phase which was reported in our previous study (Chen et al., ACP, 2008). This combination provides us a profile of the aqueous isoprene evaluation in the ozone excess, which is similar to the real atmosphere.

It is true that the results obtained in our experiments would differ from those in the real atmosphere. We have reminded the readers to pay attention to this in the revised manuscript.

(Q3) The experiments here use isoprene from a stock solution in acetonitrile. This means that there is potentially more acetonitrile in the final solution, than there is isoprene. What affect does this have on the mechanism? Is it possible that acetonitrile is involved somehow? Perhaps it stabilizes radicals more so than water? The affect of ACN in these experiments needs to be honestly discussed.

(A3) Yes, this should be concerned. We have added a experiment for aqueous isoprene ozonolysis in absence of acetonitrile to determine if acetonitrile could affect the products formation and the kinetics. 1- $\mu$ L pure isoprene was injected directly into the 500-ml ozone solution in the reactor by a syringe and a sealed teflon stopple, and immediately the reactor was shaken for 2 min. The subsequent experimental steps are the same as those in the reaction system in the presence of acetonitrile. Under the conditions of pH=7, and T=4 °C or 10 °C, it turns out that the molar yields of MAC (48.1% at 4 °C; 50.8% at 10 °C), MVK (58.1% at 4 °C; 60.2% at 10 °C), HMHP (18.2% at 4 °C; 16.8% at 10 °C), and hydrogen peroxide (59.1% at 4 °C; 60.0% at 10 °C) are near to those in the corresponding experiments in the presence of acetonitrile, with a relative deviation of less than 10%. Moreover, no organic acids were detected. In addition, Gäb et al. (1995) also indicated that acetonitrile would not affect the product distributions in the aqueous ozonolysis of alkenes, only slowed the ozonolysis rate, although the acetonitrile concentration used in their work was higher than ours. In summary, we thought 1% acetonitrile used in the present study has little effect on the products formation.

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(Q4) The discussion of the stoichiometry is poorly organized. The authors use results from another one of their papers to define an overall yield for products of isoprene oxidation. The results are equations 1-4. What are the uncertainties on these yields? This is important if one wants to compare with the gas-phase yields. Also, although some text is devoted to comparing gas phase yields, it would be much clearer if a table of yields (gas vs aqueous) or the equivalent equations (1-4) for the gas phase were shown. There has been considerable study of the gas-phase yields, so one should be able to get a decent idea how they compare to the aqueous phase results.

(A4) We have reorganized the paragraph about the stoichiometry in the revised manuscript. The uncertainties of products yields arise from the deviation between the parallel experiments. We give a mean  $p/m$   $^2$  standard deviation for the molar yields of products in Table 1. In the revised edition, we have added a sentence to remind the readers to see the uncertainties in Table 1 in the present study and Table 1 in the reference (Chen et al., 2008). Furthermore, we have added a comparative Table 2 for the products yields in the gas phase and aqueous phase.

(Q5) The discussion of the aqueous phase mechanism is also poorly organized. It would be better to show the equivalent gas-phase mechanism as a comparison, or at least the parts that are different than the aqueous mechanism. Having said that, the proposed mechanism here is based entirely on the known gas-phase mechanism with changes to yields etc. . . There is no evidence that the liquid phase mechanism must be the same. If the authors are going to use the gas-phase mechanism as a starting point for the liquid phase mechanism then they should state this, and discuss potential issues with doing so. Also, what affect does the large amount of acetonitrile have on the mechanism?

(A5) Thanks for your suggestions. In the manuscript, we told the readers that this aqueous phase mechanism was based on the present experimental results and the available corresponding gas phase mechanism, see page 6428: line 16-17. In the revised manuscript, the gas phase mechanism (Fig. 3a) was provided to compare with

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the aqueous mechanism. Although the aqueous mechanism was based on the known gas-phase mechanism, we deduced that condensed water can stabilize the radicals leading to higher yields of relatively large molecular weight substances such as 100% methacrolein + methyl vinyl ketone. While in the gas phase, the organic radicals are easy to decompose to smaller compounds. Our additional experiments show that the acetonitrile has no obvious effect on the products formation and kinetics.

(Q6) This paper really needs a reactant and product time profile for times less than 5 minutes. The one figure shown only illustrates what happens after 5 minutes (which is nothing). If they cannot perform their analysis fast enough, then they should reduce concentrations to slow things down and allow for such an analysis.

(A6) This is a good suggestion. We have tried to do so, unfortunately found that the reaction lifetime was less than 1 second according to the kinetics. If the reactants concentration was decreased to one-hundredth, the products could not be detected by our instrument. Moreover, the longer the reaction lasted, the larger the uncertainty was for the measurement of unstable peroxides.

(Q7) The authors assert that OH radical reactions played no role in these experiments. However, by their own admission the yields of MAC and MVK from OH oxidation are quite large. It is quite easy to form OH in solution, especially when there is ozone present which oxidizes organics. This process can produce OH. It may be that the OH formed reacts with isoprene also, which would explain the 100% yield for MAC and MVK. This issue needs to be discussed and at least a lower limit to the OH effect determined.

(A7) Our previous work indicated that the molar yields of MAC and MVK formation in isoprene + OH reactions were 11% and 24% (Huang et al., 2011). The combined yield (CY) of MAC and MVK was 35% in aqueous isoprene-OH reaction and 100% in the aqueous ozonolysis of isoprene (the present study) respectively. If the isoprene consumption was due to 5% by OH and 95% by O<sub>3</sub>, the CY was estimated to be 96.8%.

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The observed CY (100%) indicated that the isoprene-OH reaction was minor (less than 5%) in our experiments.

Specific Comments:

Abstract, page 6420, lines 25-28: Very poorly worded. Its not clear how this should effect the emission of VOCs from plants

A: The last sentence in the abstract was deleted in the revised manuscript.

Pg 6421, line 4: poor grammar - "...a lot of attention..."

A: We have rewritten this sentence.

Pg 6421, line 25: remove "the" before "aqueous"

A: We have removed "the" before "aqueous".

Pg 6422, line 1: unclear what is meant by this line.

A: We know that psVOCs can't enter into the aqueous bulk but they can collide with the wet surface, we think psVOCs can react on the aqueous surface. Furthermore, the surface reaction may be important for the psVOCs sink and the modification of wet aerosols. We have rewritten this sentence.

Pg 6422, line 2: remove "typically"

A: We have removed "typically".

Pg 6423, line 10: What is "transformation of oxidants" supposed to mean?

A: The type of oxidant was transformed from ozone to peroxides and formaldehyde.

Pg 6423, line 16: Start the sentence with "A" not "The"

A: We used "A" instead of "The" in the revised manuscript.

Pg 6423, lines 21-27: Is 5ml of this isoprene solution even soluble in the ozone solution

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based on Henry's law?

A: We are not sure about this. Acetonitrile could assist isoprene to dissolve in water.

Pg 6424, line 6: poor grammar

A: We have rewritten this sentence.

Pg 6424, line 20-24: Was the acetonitrile taken into account when determining the amount over the headspace? I assume not, because Henry's law constant in mixed org/water solutions do not exist. It would be some much more relevant if they simply prepared the stock solution in water to begin with, without ACN. What was the point of adding it in the first place? If you are trying mimic the atmosphere, one should simply dissolve what can be dissolved in pure water.

A: We thought that 8.6% estimated on Henry's law was an upper limit for the aqueous isoprene loss to the gas phase, because acetonitrile could assist isoprene to dissolve in water. Because using acetonitrile stock solution of isoprene is more constant, reliable and easier to implement than using a syringe to add isoprene into water during each experiment, all the experiments discussed here were performed using acetonitrile stock solution of isoprene. We have added a paragraph about the experiment without acetonitrile and the reason of using acetonitrile stock solution of isoprene. Please see the latter part of section 2 in the revised manuscript.

Pg 6425, 22-23: Although MG is a second generation product in the gas-phase, how can you be so sure it is in the aqueous phase?

A: Thanks for your consideration. We mentioned in the manuscript that "MG was not observed when the isoprene was in large excess to ozone (e.g.,  $C_{ISO} : C_{O_3} > 10:1$ )" (page 6425: lines 21-22). So we thought MG couldn't be a 1<sup>st</sup> production. And because "a minor amount of methylglyoxal (MG) was observed when  $C_{ISO} : C_{O_3} = 2 : 1$ " (page 6425: lines 19-20). We think MG is a 2<sup>nd</sup> generation product. MG is considered to be formed by the ozonolysis of MAC and MVK, which are first-generation products in the

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aqueous isoprene-O<sub>3</sub> reaction system.

Pg 6426, lines 16-17: How was the pH changed? What inorganic salt was used? This can potentially also be involved in the mechanism. Lower pH can also result in other acid catalyzed reactions. These points need to be discussed.

A: We used H<sub>2</sub>SO<sub>4</sub> to adjust the initial pHs. We found that the pHs didn't change during the investigated reaction time and the product yields were independent on the concentrations of H<sub>2</sub>SO<sub>4</sub>. Thus, we think that the observed products were not significantly affected by the added H<sub>2</sub>SO<sub>4</sub>.

Pg 6427, 14: change to "pyruvic"

A: Yes.

Pg 6427, line 20: Of what importance is the fact that this ratio is 1 : 1?

A: Our study show a 1 : 1 ratio for isoprene reaction with ozone in the aqueous phase. Then we can use this ratio to estimate the consumed amount of isoprene in the aqueous solution by determining the consumed ozone.

Pg 6427, line 27: "...in excess in ..." relative to what? Ozone is never in excess in reality.

A: We have changed this sentence into "Taken together, these results indicated that, in the earth's atmosphere where ozone is in excess compared to isoprene...".

Pg 6429, lines 10-14: This may be true in the gas phase but cannot be extended to the aqueous phase necessarily.

A: We are not sure about such extendibility. We would like to keep these sentences to remind the readers' further thinking.

Pg 6429, lines 19-20: It is not clear where the values of 57% and 43% came from. Need to explain.

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A: We have changed this sentence into “we suggest that the yields of MAC and MVK, which were determined in this study, represent the proportions of pathways a and b, respectively; i.e., 43% for pathway a, and 57% for pathway b.”

Pg 6429, lines 21: “...expected yield of 100%.” Why is 100% expected? Based on what?

A: According to the aqueous mechanism we suggested in figure 3, the total molar yield of peroxides ( $\text{H}_2\text{O}_2 + \text{HMHP}$ ) was supposed to be 100%.  $[\text{CH}_2\text{OO}]^*$  produced from pathway a1 and b1 would be stable and react with  $\text{H}_2\text{O}$  to produce HMHP.  $[\text{CH}_2=\text{C}(\text{CH}_3)\text{CHOO}]^*$  and  $[\text{CH}_2=\text{CHC}(\text{CH}_3)\text{HOO}]^*$  would finally decompose into  $\text{H}_2\text{O}_2$  plus MAC and MVK. Thus the yield sum of the two should be 100%. However, we observed a 68% yield of peroxides. This yield is lower than the expected 100% yield deduced in the aqueous mechanism, implying that other reactive oxygenated substances (ROS) possibly form in the reaction. In Fig.3b, we used “O” to represent ROS. The “unexpectedly high” yield was inaccurately used, and we have revised this in the revised manuscript.

Pg 6431, line 9: “...but the distribution contrasted...” what does this mean? What are the authors trying to say in this paragraph?

A: One will be confused by this sentence, so we have deleted this.

Pg 6432, line 7: what effect would 10-20 times have on the results to make them different than yours? Why?

A: The peroxide yield should be independent on the initial isoprene concentration. So we have deleted the related sentences.

Pg 6433, line 1: How do you know they occur simultaneously?

A: We are not sure about this. We have changed this sentence into “...they may occur simultaneously...”

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Pg 6434, 2nd paragraph: This entire paragraph is far too speculative, and should be removed or toned down.

A: We have removed this paragraph in the revised manuscript.

Pg 6435, lines 10-11: The missing OH is in the gas phase. This very likely has nothing to do with the aqueous phase chemistry here.

A: We have deleted this sentence in the revised manuscript.

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