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

Anonymous Referee #2

Received and published: 26 April 2012

This paper describes a set of laboratory experiments performed on bulk solutions of isoprene and ozone to elucidate the mechanism of aqueous phase oxidation. This topic is potentially highly relevant to cloud droplet chemistry, and could prove to be very useful to the modeling community if ultimately verified. It should eventually be published in ACP. However, there are some important issues which need to be addressed before publication.

General comments:

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

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

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.

The experiments here use isoprene from a stock solution in acetonitrile. This means that's 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.

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

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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

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?

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.

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.

Specific Comments:

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

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

Pg 6421, line 25: remove “the” before “aqueous”

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

Pg 6422, line 2: remove “typically”

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

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

Pg 6423, lines 21-27: Is 5ml of this isoprene solution even soluble in the ozone solution based on Henry’s law?

Pg 6424, line 6: poor grammar

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.

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?

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.

Pg 6427, 14: change to “pyruvic”

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

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

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

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

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

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

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

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

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

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.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 12, 6419, 2012.

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