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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Laboratory simulation for the aqueous OH-oxidation of methyl vinyl ketone and methacrolein: significance to the in-cloud SOA production" *by* X. Zhang et al.

Anonymous Referee #2

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Overall Comments

This manuscript presents detailed chemical data obtained from aqueous-phase oxidations (by OH radical) of methacrolein (MACR) and methyl vinyl ketone (MVK). This study falls in line with many recent studies examining the role of cloud processing of gas-phase oxidation products produced from a number of VOCs emitted into the atmosphere. Owing to the fact that MACR and MVK are two important gas-phase oxidation products of isoprene, which is the most abundant non-methane hydrocarbon emitted annually into the troposphere, this study is quite relevant to the current literature. Although many improvements were made in my initial assessment of this manuscript

before publication in Atmospheric Chemistry & Physics Discussions, the authors need to fully address my specific and minor concerns outlined below before publication can be considered in Atmospheric Chemistry & Physics. One of my biggest concerns with this paper, which also applies to many previous studies by other research groups, relates to how the authors concluded that high-molecular weight products were present. Although the authors clearly state that HPLC was employed before ESI-MS detection, which is a good way to ensure that observed ions are real compounds and not artifacts of ESI, no report of retention times were made for the mass spectra shown in Figure 3a. My concern is that these likely water-soluble organic compounds all eluted at the beginning of the LC run, which meant these compounds were not retained by the reverse-phase LC column employed. Why does this matter? Well, I wonder how much of these high-mass ions are actually due to oligomeric reactions as the authors propose? Could these high-mass ions be simply adducts or clusters formed in the ESI source? There are two ways in which the authors could more fully support their claim that these high-mass ions are indeed high-molecular weight species formed by oligomeric (or accretion) reactions: (1) resolve these "possible" co-eluting compounds on a LC column that contains a more suitable stationary phase compared to that of the C18 phase they currently employ; and (2) use the capabilities of the ion trap mass spectrometer to their benefit; more specifically, isolate some of these high-mass ions and conduct CID experiments in order to produce fragment (or daughter) ions that might provide some more detailed insights into chemical structure as well as chemical formation mechanism. The reason it is important to further prove the existence of the proposed high-molecular species in their system is due to the fact that the authors argue that these compounds could explain the discrepencies in their box model.

Specific Concerns

1.) Reagents and Materials Section

The authors state that the employed concentrations of MACR, MVK, and H2O2 are $\sim$ 2 orders of magnitude higher than those in atmospheric cloud droplets. I would

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like to suggest that the authors consider discussing somewhere in the text that it is possible that certain pathways (or branches) are favored in their experiments due to these higher concentrations employed, thus, these pathways proposed in this study may not fully apply to atmospheric cloud droplets.

2.) Product Analysis Section

The authors specifically state peroxides were determined on the basis of flourescent analysis by HPLC with post-column derivation, involving the hemin-catalyzed oxidation of peroxides to a floursecent derivative using hydroxyphenylacetic acid. Does this mean the authors were also trying to measure organic peroxides? If so, why was none of this data shared in the main text? It would be interesting to know if the authors were able to resolve H2O2 from organic peroxides. If organic peroxides were detected, then this would further support the proposed mechanisms in Figures 4 and 5.

3.) Page 15604, Section 3.2

Was the detection of malonic acid verified with its authentic standard? In fact, I'm wondering if this is true with all compounds identified in this study since this wasn't explicitly stated in the experimental section. If so, then the authors need to include the sources and purity of each authentic standard in the experimental section.

Minor Concerns

1.) Page 15597, Line 19.

Change "Methyl" to "methyl"

2.) Page 15598, Line 7.

Can the authors give the readers here a range of previously observed high concentrations of MVK and MACR in atmospheric cloud droplets?

3.) Page 15599, Lines 21-22.

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The authors should change:

"The aqueous reactions were carried out as close as possible to the atmospheric clouds conditions (T = 283K, pH = 4)."

TO

"The aqueous reactions were carried out as close as possible to the conditions of atmospheric cloud droplets (T = 283K, pH = 4)."

4.) Page 15601, Lines 10-11.

Why did the authors not scan higher than 300 Da? I'm curious to know why this was selected as the upper range?

5.) Figure 1

The authors should clearly indicate what these different colored lines mean in the figure caption.

6.) Figure 2

The authors should clearly indicate in the figure caption at which retention time were these mass spectra obtained.

7.) Figure 4 and 5 captions

The authors should say that these are "Scheme for the tentatively proposed reaction pathways leading to the...." in both figure captions.

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