

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.

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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. Al-

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though 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 discrepancies in their box model.

Our response: Thanks for your effort and constructive comments. We highly appreciate your help.

We have reported of retention times for the mass spectra in Fig. 3 in the revised

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manuscript. As you suggested, we are now looking for suitable LC columns to efficiently separate the co-eluting compounds. Hopefully, this problem will be partly solved in our future work. The reviewer is right that there are many uncertainties in the identification of HMWs. In this work, we are trying to find some evidence for HMWs formation. Further study is definitely necessary to characterize these compounds in the future.

Our responses to your specific and minor comments are as follows.

Specific comments:

(Q1). Reagents and Materials Section

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

(A1). Yes, we have added some discussions in Section 3.3 in the revised manuscript. Detailed revisions are as follows.

“...This study provides evidence that the aqueous MACR/MVK oxidation produces HMWs. It should be noted the initial MACR/MVK concentration of 2 mM used in the HPLC-MS analysis is much higher than that can be expected in cloud droplets. Tan et al. (2009) have revealed a strong dependence of the oligomer formation on the initial precursor concentration in the aqueous OH-oxidation of glyoxal. Considering that glyoxal is formed with high yields in MACR/MVK-OH reactions, we suggest that our experiment conditions favor HMWs formation as opposed to a more dilute aqueous phase.”

(Q2). Product Analysis Section

The authors specifically state peroxides were determined on the basis of fluorescent C7616

analysis by HPLC with post-column derivation, involving the hemin-catalyzed oxidation of peroxides to a fluorescent 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.

(A2). Our instrument can be used for determining hydrogen peroxide (retention time: 6.2 min) and a series of organic peroxides, including methylhydroperoxide (retention time: 10.2 min), hydroxymethyl hydroperoxide (retention time: 7.1 min), ethylhydroperoxide (retention time: 20.0 min), and peroxyacetic acid (retention time: 14.3 min). However, none of these organic peroxides was detected, for the following two reasons. First, all the experimental samples had been diluted 100 times with Milli-Q water before they were detected by HPLC-fluorescent, in order to decrease the H₂O₂ concentration in experimental samples and thus to obtain valid H₂O₂ data. Second, the initial H₂O₂ concentration was 2 mM, which was several orders of magnitude higher than concentrations of hydroxymethyl hydroperoxide that was supposed to be produced from MACR/MVK – OH reactions. Considering the close retention time of these two peroxides, the hydroxymethyl hydroperoxide peak was possibly covered by the H₂O₂ peak in the HPLC spectra.

(Q3). 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.

(A3). Yes, all the carbonyls and organic acids were verified with their authentic standard. We have included the sources and purity of each authentic standard in the experimental section in the revised manuscript. Detailed revisions are as follows.

"The source and purity of each authentic standard for verifying possible products are: formaldehyde (Riedel-dehaen, 36.5% solution), glyoxal (Sigma, 40% solution), methylglyoxal (Avocado, 40% solution), formic acid (Alfa Aesar, 97%), acetic acid (Alfa Aesar, 99.9985%), pyruvic acid (Avocado, 98%), oxalic acid (Alfa Aesar, anhydrous, 98%), and malonic acid (Alfa Aesar, 99.5+%)."

Minor Concerns:

(Q1). Page 15597, Line 19. Change "Methyl" to "methyl"

(A1). Yes.

(Q2). 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?

(A2). Yes, detailed revisions are as follows.

"Indeed, both of them have been observed in cloud droplets with high concentrations (i.e. $< DL - 0.5 \mu M$ for MACR and $0.02 - 0.2 \mu M$ for MVK, van Pinxteren et al., 2005). . ."

(Q3). Page 15599, Lines 21-22. 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 ($T = 283K$, $pH = 4$)."

(A3). Yes.

(Q4). 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?

(A4). Actually, full scan mode analysis was conducted in our previous experiment and we found most ions were distributed in the m/z range of 150 – 300. So we selected the scan range of m/z 35 – 300 in the following experiments to improve the sensitivity.

(Q5). Figure 1. The authors should clearly indicate what these different colored lines

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mean in the figure caption.

(A5). Yes, detailed revisions are as follows.

"Fig. 1. Transformation of MVK in water solution. Item (1): 0.2 mM MVK in acetonitrile ($pH = 7$); Item (2): 0.2 mM MVK in ultrapure water ($pH = 7$); Item (3): 0.2 mM MVK + 2 mM H_2O_2 in ultrapure water ($pH = 7$); and Item (4): 0.2 mM MVK + 2 mM H_2O_2 in ultrapure water ($pH = 4$). (The inset figure is the HPLC-UV spectra of MVK dissolved in ultrapure water)."

(Q6). Figure 2. The authors should clearly indicate in the figure caption at which retention time were these mass spectra obtained.

(A6). Yes, detailed revisions are as follows.

"Fig. 3. Characteristics of high-molecular-weight ions (HMWs): (a) HPLC-MS spectra of HMWs (The retention time of HMWs formed from MACR–OH reactions in positive and negative mode is $\sim 3 - 5$ and $\sim 2 - 4$ min, respectively. The retention time of HMWs formed from MVK–OH reactions in positive and negative mode is $\sim 3 - 5$ and $\sim 2 - 4$ min, respectively.); and (b) Evolution of selected HMWs from MACR/MVK–OH reactions. "

(Q7). 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.

(A7). Yes.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 15595, 2010.

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