

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.

X. Zhang et al.

zmchen@pku.edu.cn

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General comments:

Comment on X. Zhang et al. The authors present an interesting study that extends previous laboratory experiments on SOA formation in the aqueous phase. I have a few comments the authors might want to consider in order to tie their study better into the context of other studies on cloud chemistry and aqueous phase SOA production. Our responses: Thanks for your effort and constructive comments. We highly appreciate your help. Here are our responses to your comments.

Specific comments:

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(Q1) The concentrations of MVK and MACR used in the experiments are much higher than it can be expected in cloud droplets due to the small Henry's Law constants of MACR and MVK. While I understand that these conditions have been chosen due to detection limits in the experiments, the authors should try to justify the applicability to atmospheric conditions by including findings from recent studies:

Recent studies on glyoxal oxidation in the aqueous phase have revealed a strong dependence of the product distribution on the initial precursor concentration (Tan et al., 2009). In these experiments it has been shown that with increasing glyoxal concentration (0.03 mM to 3 mM) the formation of oligomers becomes more likely. In the current study, initial MACR and MVK concentration of 0.2 mM are used. Assuming that glyoxal and related compounds are formed with high yields from these compounds in the aqueous phase, the experiments resemble the intermediate conditions used by Tan et al. (2009) and thus favor oligomers formation as opposed to a more dilute aqueous phase.

It has been discussed in previous studies that carbonyl compounds might oligomerize in the aqueous phase at high concentrations (e.g., (Ervens and Volkamer, 2010) and references therein) and thus shift the partitioning equilibrium of organic species towards the aqueous phase. Is there any evidence that MVK and MACR oligomerize at high concentrations?

Recently it has been suggested that not only oligomer formation but also interactions of organics with solute ions (as present in ambient aqueous aerosol particles) might lead to an enhanced uptake of organics (Lim et al., 2010). Thus, higher MACR and MVK concentrations might be rather encountered in aqueous particles where strong ion-carbonyl interactions could be expected.

In summary, I think that the authors should point out that (i) the applied experimental conditions favor oligomers formation due to the higher concentrations but (ii) the suggested chemical pathways might (also) occur in concentrated aqueous particles that

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exist in the atmosphere for much longer times than cloud droplets.

(A1) First, we have added discussions on the oligomer formation in atmospheric clouds and cited Tan et al. (2010) in Section 3.3 in our revised manuscript.

“...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 MVK-OH reactions, we suggest that our experiment conditions might favor HMWs formation as opposed to a more dilute aqueous phase.”

Second, we do observe a high molecular weight ion with m/z 181 in the positive mode in the HPLC-MS spectra of the mixture of MVK (2 mM) and H₂O₂ (20 mM). We suppose that MVK might oligomerize at concentrations ten times higher than those we used in HPLC and IC analysis. But we cannot identify this ion.

Third, we have added discussions in terms of the aqueous chemistry in wet aerosols in the Conclusions and Implications Sections in the revised manuscript.

“This work adds to the increasing body of literatures that cloud processing contributes to the SOA formation in the atmosphere. In addition, the chemical pathways proposed in this study are mostly applicable to aqueous particles. Considering the higher concentrations of dissolved particle constituents and longer lifetime of aqueous particles (Ervens and Volkamer, 2010), the aqueous MACR/MVK oxidation should play a more important role in atmospheric chemistry than expected before.”

(Q2) The authors conclude that the observed SOA yields represent a lower limit since (among other reasons) dicarboxylic acid concentrations still increase after 7 h and thus in longer-lived clouds, SOA yields would be higher.

Two issues in this section should be clarified:

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While a cloud might indeed live several hours, the lifetime of an individual cloud droplet is usually restricted to a few minutes until evaporates. Thus, cloud chemistry will not occur on the time scale of several hours but it will be interrupted by evaporation (not only water but also organics) and new droplet formation. However, since I think that the chemical pathways suggested here are (mostly) applicable to aqueous, deliquesced particles, I suggest clarifying the differences in the aqueous phases - cloud droplets vs aqueous particles - not only in terms of their concentrations (as suggested above) but also in terms of their life time.

My second point addresses the life time of dicarboxylic acids in the aqueous phase. All dicarboxylic acids react further with OH to form smaller acids and finally OH. Thus, a long reaction time will finally lead to a decrease of the total SOA mass and thus reduce SOA yields (cf (Ervens et al., 2008)).

(A2) First, as you suggested, we have added the corresponding discussions on cloud droplets vs aqueous particles in the Conclusions and Implications Sections.

Second, we have revised discussions on the lifetime of dicarboxylic acids in Section 3.5.

“Both MACR-OH and MVK-OH reactions generate dicarboxylic acids, which are recognized as precursors of SOA. The SOA yield, defined as the ratio of the mass concentration of aerosol formed to that of MACR/MVK reacted, increases significantly with the reaction time. The maximum values are 8.8% from MACR-OH and 23.8% from MVK-OH after 7 h reaction, if the partition efficiency of both oxalic and malonic acid was estimated as 100%. It should be noted that the estimated SOA yield in this study cannot be completely applied to atmospheric clouds conditions, for the following three reasons. (i) The observed HMWs were not considered in the calculation. (ii) All dicarboxylic acids react further with OH to form smaller acids (Ervens, et al., 2008), resulting in a decrease of the total SOA mass. (iii) SOA production will be interrupted by evapo-condensation cycles, considering that the lifetime of an individual cloud droplet is only

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a few minutes. However, these SOA formation pathways might continue during water evaporation (El Haddad, et al., 2009). ”

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