

Interactive
Comment

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.

B. Ervens

barbara.ervens@noaa.gov

Received and published: 10 July 2010

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.

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

2) 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.

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

[Discussion Paper](#)



Two issues in this section should be clarified:

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)).

Ervens, B., Carlton, A. G., Turpin, B. J., Altieri, K. E., Kreidenweis, S. M., and Feingold, G.: Secondary organic aerosol yields from cloud-processing of isoprene oxidation products, *Geophys. Res. Lett.*, 35, 2, L02816, 10.1029/2007gl031828, 2008.

Ervens, B., and Volkamer, R.: Glyoxal processing in aqueous particles: towards a kinetic modeling framework of SOA formation outside clouds, *Atmos. Chem. Phys. Discuss.*, 10, 12371-12431, 2010.

Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Aqueous chemistry and its role in secondary organic aerosol (SOA) formation, *Atmos. Chem. Phys. Discuss.*, 10, 6, 14161-14207, 2010.

Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Effects of precursor concentration and acidic sulfate in aqueous glyoxal-OH radical oxidation and implications for secondary organic aerosol, *Environ. Sci. Technol.*, 43, 8105-8112, 2009.

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

C5088

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

[Discussion Paper](#)

