Atmos. Chem. Phys. Discuss., 13, C185–C187, 2013
www.atmos-chem-phys-discuss.net/13/C185/2013/

Atmospheric
Chemistry
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Discussions

Interactive comment on “Radical mechanisms of methyl vinyl ketone oligomerization through aqueous phase OH-oxidation: on the paradoxical role of dissolved molecular oxygen” *by* P. Renard et al.

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Received and published: 19 February 2013

This interesting work confirmed the importance of O_2 in aqueous phase chemistry. I agree with the first reviewer that oxygen depletion might not be atmospherically relevant in cloud droplets or liquid-phase particles. It is difficult to extrapolate current aqueous phase experiments to solid phase particles. Using MVK to represent the whole WSOC family also seems adventurous to me.

The depletion of O_2 could also alter radical reaction pathways. For example, acetic acid oxidation could form succinic acid under O_2 depleted conditions (Wang et al., 2001), while the same reaction is unlikely to happen in the atmosphere (Tan et al., 2012). This raises questions on pathway 7a in Figure 10. I would imagine the oligomerization of the unsaturated MVK* radical is more important under O_2 depleted or very high MVK concentration conditions. Fig 7 indicates that ratio between m/z+ 407.20 (S174) and m/z+ 419.24 (S138) became much lower in lower concentration experiments. I will take this as an evidence of my argument. Now the question is - will this pathway matter at all in the atmosphere where MVK is low and O_2 is abundant? The authors should also point out that H-abstraction on primary carbon (pathway 1b) should be more difficult compared to OH additon on C-C double bond (pathway 1a). H-abstraction accounts for <5% of the overall OH reaction of typical alkenes in the gas phase (Seinfeld and Pandis, 2006), and it might be true in the aqueous phase as well.

Specific Comment:

Pg 2918 line 24: Although the effect of precursor initial concentrations was discussed in Tan et al. (2010), the focus of that paper was on the aqueous phase oxidation products of methylglyoxal. A previous publication (Tan et al., 2009) is a more relevant reference.

References

Seinfeld, J. H., and Pandis, S. N.: Atmospheric chemistry and physics - from air pollution to climate change (2nd edition), John Wiley and Sons, Inc., New York, 2006.

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, Environmental Science Technology, 43, 8105-8112, 10.1021/es901742f, 2009.

Tan, Y., Lim, Y. B., Altieri, K. E., Seitzinger, S. P., and Turpin, B. J.: Mechanisms leading to oligomers and soa through aqueous photooxidation: Insights from oh radical oxidation of acetic acid and methylglyoxal, Atmos. Chem. Phys., 12, 801-813, 10.5194/acp-12-801-2012, 2012.

Wang, W.-F., Schuchmann, M. N., Schuchmann, H.-P., and Sonntag, C. v.: The importance of mesomerism in the termination of a-carboxymethyl radicals from aqueous malonic and acetic acids, Chemistry - A European Journal, 7, 791-795, 2001.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 2913, 2013.