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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 #1

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Review of Zhang et al "Laboratory Simulation for the Aqueous. . .MVK and MACR"

In this paper laboratory experiments simulating the formation of products from aqueous OH oxidation of methyl vinyl ketone (MVK) and methacrolein (MACR) are presented and the significance of this chemistry to secondary organic aerosol (SOA) formation is discussed. This work is important in the context of a larger body of research examining the degree to which SOA forms from reactions occurring in clouds. Similar work has been previously published for MACR (Liu ACP 2009), but to my knowledge this is the first work of its kind examining MVK.

The following are major limitations of this work and must be addressed:

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1. All these experiments were conducted at 0.2 mM which is two orders of magnitude higher than cloud-relevant concentrations. The work by Tan et al (EST 2009) was not cited by this paper, and it is important here because Tan et al (2009) demonstrates that the precursor concentration can affect the composition and yield of products. Thus, it is doubtful that the yields obtained are relevant to clouds. However, during cloud droplet evaporation, concentrations will increase and presumably reactions will continue at these higher concentrations and will also take place in aerosols. The likely dependence of yields on precursor concentrations needs to be explicitly addressed in the discussion.

2. The MACR oxidation paper by Liu et al (ACP, 2009) is cited in this paper, appropriately. However, in the introduction, the authors need to acknowledge the Liu paper – what are its contributions and what, if anything, does the current paper contribute to the MACR story? In the discussion, the authors should compare their results for MACR with those of Liu.

3. One major conclusions of this work is about SOA yields from aqueous phase oxidation of MVK and MACR. The authors calculated these yields using product concentrations after 7 hours of reaction time. Since a typical cloud cycle is only ∼10 minutes and an air parcel can undergo several cloud cycles (Ervens et al., 2004), it will be more reasonable to calculate the theoretical SOA yields at earlier time points. It is appropriate that the authors remind the reader that additional chemistry during droplet evaporation might also affect their reported yields (e.g. Haddad).

4. The authors should use the term "higher molecular weight compounds" rather than oligomers, since the presence of oligomers has not been proven. The regular pattern of mass differences (12, 14, 16amu) in the ESI-MS does not necessarily indicate oligomer formation.

5. Methods: Make clear to the reader that hydrogen peroxide was added as a source of OH radical. Some may think that this experiment was about MVK being oxidized by

H2O2.

6. Control experiments: Importantly, the authors need to check the stability of known products in hydrogen peroxide. Why is pyruvic acid concentration so low? Is it lost in samples awaiting analysis? Tan et al (EST 2009) found that glyoxylic acid reacts with H2O2 while awaiting sample analysis forming formic acid. Perhaps pyruvic acid is similarly lost. Dark reactions should also be included in the kinetic modeling, as these reactions might change the predicted time profile of products. This might well explain descrepancies for pyruvic acid, formic acid and acetic acid. The papers by Guzman and Hoffman (2006?) about pyruvic acid photolysis and by Carlton (2006?) about pyruvic acid + OH radical probably provide some insights about these issues.

7, does a standard mix of expected products form high molecular weight products during electrospray ionization? This potential artifact needs to be ruled out. Control experiment results should be provided as supporting information.

8. The authors should present some recovery data to validate their quantification. Some observed products, such as formaldehyde and formic acid, are relatively volatile. Quantification might be biased if their recoveries are quite different from 100%.

9.The authors did not provide analytical details about the IC system they used.

10. The chemical mechanism leading to malonic acid (R6) in MVK + OH is uncertain. How will this reaction compete with the reaction between acetic acid radical and dissolved oxygen?

11. What is the merit of Fig. 4? Liu et al. (2009) have already proposed a very detailed chemical mechanism regarding MACR + OH. Fig. 4 is not different from Liu's mechanism.

12. The physical meaning of OOC (R7 and Fig 8) is not at all clear and needs to be explained. It would be much more helpful to see measured total dissolved organic carbon as a function of time and to know how much of this is accounted for by measured

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species.

13. Fig. 11 and Page 15610, lines 8-25. What does "the branching ratios for the formation of glycolaldehyde and glyoxylic acid" referring to? These compounds are simultaneously produced via Russell mechanism from acetic acid radicals as indicated in Fig. 5. I guess the authors are talking about the branching ratios for the formation of glycolic and glyoxylic acids from glycoaldehyde. Does the ratio mean glycolic acid divided by glycoaldehyde or glyoxylic acid divided by glycoaldehyde? Please specify the meaning. Fig. 11 also lacks explanations. Label each subplot with the experiment it refers to. It is better to include observed oxalic acid concentrations in Fig. 11 for comparison.

14. Since these experiments have been modeled, presumably the authors have some idea of what the OH radical concentrations are. They should share this information.

15. Line 288 – the authors note that a significant portion of the products are not characterized in this study. Although not mentioned, CO2 is one of these.

16. Modeling – Carlton 2007 is discussed in the context of this work. The authors need to read Tan EST 2009 (same research group) to get their updated thoughts on these topics. Likewise, the poor agreement for acetic and pyruvic acids might have to do with pyruvic acid reactions with H2O2 (see Carlton GRL 2006). The authors should investigate the potential for H2O2 reactions with all major products. There is also a paper by Perri (atmospheric environment 2009?) that covers glycolaldehyde + OH radical. This should also inform the discussion in the modeling section. Perhaps Ervens ACPD 2010 and Lim ACPD 2010 are also helpful.

17. I continue to worry about whether or not yields reported from these types of experiments mean anything in the atmosphere. I am much happier when the chemistry itself is used, with atmospherically relevant input concentrations, to predict SOA formation, or to obtain yields from cloud parcel models (e.g., Ervens GRL 2008). How can the yields for the various published experiments be compared in a meaningful way?

Experiments with different compounds are generally conducted at different OH radical and precursor concentrations. Some yields are reported for 10 min, others 40 min, others for 7 hours after initialization.

Minor Comments: 1. Page 15600, line 10. Decay rates of H2O2 in Fig. S1 seem not statistically different among experiments. This sentence should be revised to accurately explain Fig. S1. 2. Page 15601, line 14. The latest version of CAPRAM is 3.0 (Herrmann et al., 2005). CAPRAM 3.0 has additional reactions and would predict somewhat different time profiles of products. Can the authors try to use CAPRAM 3.0? 3. Page 15601, line 19. I think the authors use reactions from CAPRAM 2.3 model to simulate kinetics in the reactor. Why the authors mention "The simulation was carried out on a 10-min basis and preceded 20 for 7 h"? The "10 min" is typical for cloud contact time, but it seems that the authors did not include cloud physics in their simulations. 4. Mistakes and omissions in Fig. 5. P122 should produce CH2OH radical rather than CH2O radical. Why the oxidation of glycoaldehyde (formed via P121) just involves H-atom abstraction from the alcoholic carbon? The OH radical would also abstract H atom on the carbonyl carbon and produce glycolic acid. An arrow pointing to glycolic acid should be added. 5. Page 15606, line 3, in the "channel of Reaction (R6) is an important intermediate". R6 should be R5. 6. Page 15607, line 7. Oxalic acid is a "later" generation product rather a "second" generation product. Second generation means oxalic acid is directly produced from methylglyoxal or other first generation products, which is not true. Glyoxylic acid, an important intermediate, is not observed possibly because of its fast reaction with H2O2. 7. Section 3.1 discusses Figure 1. What do (a) – (d) refer to in Figure 1? This section also mentions sulfuric acid. Was this included in the experiments? 8. Some space could be saved by cutting out R2 and the text on page 189 that explains how MVK becomes crotonaldehyde. 9. What is different about the two y axes in figure 3?

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