**Atmospheric
Chemistry
and Physics
Discussions**

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.
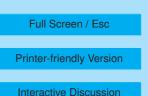
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Overall comments:

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

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first work of its kind examining MVK.

Our responses: Thanks for your effort and constructive comments. We highly appreciate your help. Here are our responses to your comments.

Specific comments:

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

(Q1). 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.

(A1). Yes, we have cited Tan et al. (2009) and added discussions with regard to the dependence of product distribution on precursor concentrations 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 MVK–OH reactions, we suggest that our experiment conditions might favor HMWs formation as opposed to a more dilute aqueous phase."

(Q2). 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

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– 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.

(A2). Yes, we have acknowledged Liu et al. (2009) in the introduction and compared our results for MACR with those of Liu in Section 3.2 in the revised manuscript. Detailed revisions are as follows.

Introduction:

". . .Liu et al. (2009) studied the photooxidation of MACR in the aqueous phase under simulated cloud droplet conditions. They proposed that the radical chemistry could explain the products observed from OH-oxidation of MACR." Discussion, Section 3.2:

"Products identified chromatographically in the OH-oxidation of MACR are formaldehyde (FA), methylglyoxal (MG), formic acid (FOA), acetic acid (AA), pyruvic acid (PA), and oxalic acid (OA). These observations are generally consistent with Liu et al. (2009), in which FA, MG, PA, and OA were identified as well."

Discussion, Section 3.4:

"The yields of formaldehyde, methylglyoxal and acetic acid after 0.2 mM MACR was fully consumed are comparable with results in Liu et al. (2009)."

"As shown in Fig. 8, the amount of OOC at longer irradiation time is much lower than the initial value, indicating that a significant portion of products were not characterized in this study. These missing products primarily include hydroxyl-containing acids and multi-functional compounds. Moreover, some compounds, like formic acid, will be completely oxidized into CO_2 and H_2O, which are difficult to measure in the aqueous phase. In Liu et al. (2009), the total carbon yields were also far from being balanced and they suggest that the non qualified oligomers could explain the lack of carbon."

(Q3). 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 con-

centrations 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).

(A3). We have rewritten this paragraph, according to the reviewer's suggestions. Detailed revisions are as follows.

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

(Q4). 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.

(A4). Yes, we have used "higher molecular weight compounds" as substitute to "oligomer" in the revised manuscript.

(Q5). Methods: Make clear to the reader that hydrogen peroxide was added as a

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source of OH radical. Some may think that this experiment was about MVK being oxidized by H2O2.

(A5). Yes, we have added this information in the Experimental Section. Detailed revisions are as follows.

"The OH radical source is the photolysis of hydrogen peroxide."

(Q6). 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.

(A6) First, according to the reviewer's suggestion, we have added corresponding experiments in Section 2.3. Detailed revisions are as follows.

"To verify the stability of known products in hydrogen peroxide, two mixed standards were prepared: (1) formaldehyde (0.1 mM) + methylglyoxal (0.1 mM) + glyoxal (0.1 mM) + H2O2 (2 mM) + H2SO4 (0.05 mM); and (2) formic acid (0.1 mM) + acetic acid (0.1 mM) + pyruvic acid (0.1 mM) + oxalic acid (0.1 mM) + H2O2 (2 mM) + H2SO4 (0.05 mM). Samples were kept in 283 K in darkness until analysis by HPLC-UV or IC. The results show that the effect of H2O2 on the stability of carbonyls is insignificant, see Fig. S3 in the supplementary material. However, rapid pyruvic acid loss occurs within 10 min and in the meantime, acetic acid concentration substantially increases, as shown in Fig. S4 in the supplementary material. The rapid transformation of pyruvic acid to acetic acid in H2O2 solution, which is consistent with previous studies (Carlton et al., 2006), can explain the unexpected loss of pyruvic acid over the course of OH

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oxidation. "

Second, we have incorporated the corresponding reactions involving pyruvic acid in our mechanism, please see (A16).

(Q7). 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.

(A7). We have used HPLC-MS to analyze the single standard sample of formaldehyde, glyoxal, methylglyoxal, formic acid, acetic acid, pyruvic acid, oxalic acid, and malonic acid (MA). None of them produced HMWs during electrospray ionization.

(Q8). 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%.

(A8). Our recovery experiments showed that the recoveries for carbonyls and organic acids determined in the present study were $95-100\%$, for example, 96% for formaldehyde and 95% for formic acid.

(Q9). The authors did not provide analytical details about the IC system they used.

(A9). We have added this in the revised manuscript. Detailed revisions are as follows.

"The organic acids were analyzed using ion chromatography (DIONEX 2650, USA) equipped with an ED50 conductivity detector. An AS11 column (4 mm) with an AG11-HC (4×50 mm) guard column and an Anion Trap column (ATC-3, 9×24mm, for 4 mm) were used for anion detection. The sampling volume was 100 mL, and the eluting solution was 0.4–6 mM NaOH (gradient) with a flow rate of 1.2 mL/min."

(Q10). 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?

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(A10). It is true that the mechanism leading to malonic acid in MVK + OH is uncertain. To the best of our knowledge, although we cannot find the corresponding rate constant of R6 (R3 in the revised manuscript), similar radical-radical reactions were reported in previous studies (Guzman et al., 2006). So in this study we propose this possible reaction pathway that could explain the presence of malonic acid.

(Q11). 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.

(A11). It is true that the scheme in Fig. 4 is similar to that in Liu et al. (2009). Actually, the radical processes in the aqueous phase have been extensively studied by Sonntag and Schuchman (1997). In this study, we incorporated this scheme into a box model to better explain the experimental results. So the merit of Fig. 4 is to provide readers detailed information in terms of the mechanism in the model.

(Q12). 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 species.

(A12). It is a good suggestion. But we cannot measure TOC at present. We have explained "OOC" in the revised manuscript. Detailed revisions are as follows.

"Based on the calculated molar yields, the observed organic carbon (OOC, defined as the sum of dissolved organic carbon molar yields) was estimated here..."

(Q13). 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

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Discussion Paper

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.

(A13). The aqueous mechanism in our box model has offered three channels to the oxalic acid formation. The first one originates from H-atom abstraction of acetic acid by OH, the second starts with glycolaldehyde via either glycolic acid or glyoxal as an intermediate, and the third begins directly from glyoxylic acid. Since the decomposition rate of acetic acid is slow, the last two channels become the major contributor to oxalic acid. In the MACR-OH reaction, oxalic acid is mainly from glyoxylic acid oxidation and in the MVK-OH reaction, oxalic acid is mainly from the glycolaldehyde oxidation. To our knowledge, radical processes that produce glyoxylic acid and glycolaldehyde (R18 and R21 in Table S1 of Supplementary materials) have not been well studied yet, so the stoichiometric coefficient for the formation of glyoxylic acid and glycolaldehyde is uncertain.

For Fig. 11, we have labeled each subplot with the experiment it refers to and included the measured oxalic acid concentrations for comparison.

(Q14). Since these experiments have been modeled, presumably the authors have some idea of what the OH radical concentrations are. They should share this information.

(A14). Yes, the modeled OH concentrations are shown in Fig. S3 in the supplementary material in the revised manuscript.

(Q15). Line 288 – the authors note that a significant portion of the products are not characterized in this study. Although not mentioned, CO_2 is one of these.

(A15). Yes, we have added this in the revised manuscript.

"Moreover, some compounds, like formic acid, will be completely oxidized into CO_2

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Discussion Paper

and H2O, which are difficult to measure in the aqueous phase."

(Q16). 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.

(A16). Thanks for the reviewer's information.

According to Tan et al. (2009), the formation of formic acid from glyoxylic acid and H2O2 competes with the formation of oxalic acid from glyoxylic acid and OH radical at higher H2O2 concentrations. So we incorporated this reaction into our box model (R36 in Table S1).

According to Carlton et al. (2006), pyruvic acid also reacts directly with H2O2 to form acetic acid. So we incorporated the following reaction into our box model (R53 in Table S1).

According to Lim et al. (2005), pyruvic acid can be photolyzed. So we incorporated the following reaction into our box model (R52 in Table S1).

As for the reactions of glycolaldehyde and OH, we have already referred to Terri et al. (2009).

We have re-simulated MACR/MVK-OH reactions based on the updated mechanisms. The comparison of modeled and measured concentrations of small products is shown in Fig. 9 and 10. It can be seen that the modeled results of pyruvic and acetic acid have improved to a certain extent.

(Q17). I continue to worry about whether or not yields reported from these types of ex-

periments 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.

(A17). First, it is true that precursor concentrations in this study are approximately two orders of magnitude higher than those at cloud-relevant conditions. But the high concentration used in this study is to better characterize the possible products.

Second, the initial concentrations of MACR in this study (0.2 mM) and Liu et al. 2009 (0.4 mM) are in the same order of magnitude. Yields of products, including formaldehyde, methylglyoxal and acetic acid, when 0.2 mM MACR was fully consumed in this study are similar to those in Liu et al (2009).

Minor Comments:

(Q1). Page 15600, line 10. Decay rates of H_2O_2 in Fig. S1 seem not statistically different among experiments. This sentence should be revised to accurately explain Fig. S1.

(A1). Yes, we have revised this sentence in the revised manuscript.

(Q2). 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?

(A2). Yes, we have updated our mechanisms based on CAPRAM 3.0.

(Q3). 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 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.

(A3). Yes, we did not include cloud physics in our simulations. The purpose of running this model is to examine whether the mechanism proposed in this study can explain the time evolution of all the products we observed in the experiment. We chose "10-min basis" and "7h" in the model to better compare with the experimental results.

(Q4). 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.

(A4). Yes, we have corrected these mistakes in the revised manuscript. The reviewer is right that the OH oxidation of glycoaldehyde also produces glycolic acid. This route has been already incorporated in the box model.

(Q5). Page 15606, line 3, in the "channel of Reaction (R6) is an important intermediate". R6 should be R5.

(A5). Yes, thanks.

(Q6). 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.

(A6). Yes, we have revised this sentence in the revised manuscript.

(Q7). 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?

(A7). We have changed (a), (b), (c), and (d) into (1), (2), (3), and (4), respectively in the revised manuscript. Sulfuric acid was used in experiment (4).

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Discussion Paper

(Q8). Some space could be saved by cutting out R2 and the text on page 189 that explains how MVK becomes crotonaldehyde.

(A8). Yes.

(Q9). What is different about the two y axes in figure3?

(A9). We have redrawn Fig. 3 in the revised manuscript.

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