

Interactive comment on “Mechanistic study of secondary organic aerosol components formed from nucleophilic addition reactions of methacrylic acid epoxide” by A. W. Birdsall et al.

Anonymous Referee #2

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This paper describes a detailed investigation of the mechanisms of reactions of methacrylic acid epoxide (MAE) in solution by NMR under conditions relevant to atmospheric aerosols. It is found that hydrolysis proceeds significantly more slowly than for the analogous SOA-forming species IEPOX, in agreement with recent computational results. This is important, as previous atmospheric modeling studies have had to make assumptions about MAE reactivity in the aqueous aerosol phase due to a lack of experimental data. In addition, important insights into MAE aerosol-phase chemistry are presented. These include a mechanistic explanation of the observed inverse dependence of oligomerization on aerosol water content, and the prediction that for-

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mation in atmospheric aerosols of long-chain oligomers from MAE is less likely than could be implied by the results of chamber studies, because of the presence of a wider variety of nucleophiles in ambient aerosol and the observed mediocre nucleophilicity of MAE. These findings are well presented, are relevant to current atmospheric research, and are within the scope of ACP. It is recommended that this manuscript be accepted for publication with consideration of some minor questions and comments that follow.

General Comments/Questions:

- 1) The authors mention in the introduction that the Fischer esterification of 2-MG could not account for observed oligomer formation in smog chamber experiments. How do the rate constant for hydrolysis of MAE presented here along with the measured relative nucleophilicities do in regards to predicting oligomer formation from MAE when compared to chamber experiments?
- 2) How long were the prepared MAE and 2-MG stored prior to use? Was there any noticeable degradation over time? This seems like something that is important to mention because of, e.g., the presence of 2-MG in the self-reaction of MAE discussed in section 3.4.
- 3) Can anything be said about the corresponding reaction to form nitrate esters based on your results and previous work exploring sulfate and nitrate ester formation from reactions of IEPOX (from, e.g., Eddingsaas et al. 2010)?

Specific comments/questions:

Page 19929, line 11. Is the second half of this sentence referring to the slow formation of 2-MG from MAE followed by reaction with sulfate, or is there some 2-MG present at the start of the reaction?

Page 19930, Section 3.3.2. I would suggest including some figures of the spectra being discussed, perhaps as SI.

Page 19930, lines 6. It's not immediately apparent what 'the 2-MG peaks' is referring

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to, and new peaks 'near' an existing peak could be more precise unless the spectra are shown.

Page 19931, line 14-18. Would the difficulty of forming a primary carbocation also suggest a more SN2-like mechanism?

Page 19932, lines 14-16. I think it would be helpful to include some quantification of the species present at the beginning of the reaction if possible. (See comment on Table 1) Given the slow hydrolysis of MAE and the conditions it is stored under, is this much 2-MG expected? (See general comment 2)

Page 19933, line 9. As per the previous comment, some estimate of the concentration of the water impurity may be useful.

Page 19934, Section 3.5 and Table 3. If possible, I would suggest that some estimate of the error associated with these values be calculated and included in the text and/or Table 3.

Page 19934, line 18. How close were the two values calculated for methanol/MAE nucleophilicity prior to averaging?

Page 19936, line 1,2. Does IEPOX reactivity also increase under more acidic conditions, so that if MAE reactivity were estimated as equal to that of IEPOX, it will now be lower even under conditions of high SOA acidity?

Page 19943, Table 1. Although it is mentioned in the main text, I think there should be a comment in the table caption or as a footnote regarding how these values were calculated, because a mole fraction for MAE of 1.000 implies that no other species were present in concentrations $> 5e-4$ mole fraction. However, as shown in Fig. 8 and discussed in section 3.4, there was a not-insignificant amount of water and 2-MG present at the beginning of experiment 4. Some indication of the important impurities present in each experiment should be made in the table. Also, an estimate of the error associated with the final measured concentrations should be included, if possible.

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Page 19953, Figure 8. It may aid the reader to have a comment in the figure caption defining the species referred to by the labels ('diester', 'triester', etc.) or referring to the figure where their structures are shown.

Minor edits:

Page 19923, line 2: 'for' should be removed from phrase in parentheses

Page 19932, line 28: missing 'the' at the end of the line

Page 19934, line 17: missing 'be' between 'can' and 'used'

Page 19936, line 13: 'this result leads' or 'these results lead'

Page 19937, line 20: missing 'the' before diester

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