

## ***Interactive comment on “Study of the kinetics and equilibria of the oligomerization reactions of 2-methylglyceric acid” by A. W. Birdsall et al.***

**Anonymous Referee #1**

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Study of the kinetics and equilibria of the oligomerization 1 reactions of 2-methylglyceric acid A. W. Birdsall, C. A. Zentner, and M. J. Elrod

This paper reports modeling and NMR measurements of the extent of oligomerization from 2-methylglyceric acid (2-MG) due to bulk-phase Fischer esterification. The kinetics, equilibria, and structures of ester formation are described. The results of the experiments will likely be of significant interest to the atmospheric chemistry community. In particular, the finding that that nitrate/sulfate esters are formed in an acidic bulk phase in predominantly the primary position is an important insight. However, given that other hydroxyacids like lactic acid auto-esterify in aqueous solution, it is interesting that the authors conclude that Fischer esterification is too slow to produce significant oligoesters for 2MG on the timescale of a few hours. Perhaps discrepancies may be

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due to the very high acid-to-2MG ratios that may hydrolyze the product esters. Results of control experiments (evaporating only 2MG with no added acids) are not reported in the paper. Furthermore, the manuscript text is difficult to follow in places, and detailed discussion of some observations reported in the manuscript is lacking.

General comments: 1. In general, acid-catalyzed ester formation is reversible and the best way to control the outcome of the reaction is to control the reagent concentrations. In Fischer esterification procedures, the alcohol is kept in excess to push the reaction forward, which would mean in this case that [2MG] should be greater than [acid catalyst]. Yet, from Tables 5 and 7, which lists all the experiments done, it seems that the acid-to-2MG ratio is always  $> 1.5$  and sometimes higher than 10.

Interestingly, lactic acid (another hydroxyl acid that the authors themselves note behaves similarly to 2MG) even in aqueous solution spontaneously forms the oligoesters under the mild acidity provided by itself (Montgomery, 1952). The paper with which the authors compared NMR results (Espartero et al, *Macromolecules* 1995) performed NMR analyses on 90% lactic acid in water, which Espartero et al noted already contains a series of oligomers up to the tetramer without the addition of acid (Espartero et al., 1996). I expect 2MG may be able to autoesterify in the same way. Perhaps under atmospheric chamber conditions, with neutral seed aerosol or no seed aerosol, the acid-to-2MG ratio favors oligoester formation? The pH of pure isoprene SOA particles (no seed) is on the order of 6 but the experiments performed here seem to have  $\text{pH} < 2.5$  for the “neutralized” solution (although the authors did not list the pH for all the experiments performed). I understand that Table 8 reports calculated diester formation lifetimes for pH up to  $\sim 5$ , but these calculations use data extrapolated from high acid experiments. The authors need to provide experimental evidence that solutions with high 2MG, low water and low acid (or no acid so that the only acidity is from the organics) do not lead to oligoester formation? If not, the conclusions of “acid-catalyzed kinetics of the mechanism may be too slow to rationalize the 2-MG oligoester production timescales observed in the atmospheric chamber experiments” and “unrealistically

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high ambient SOA acidities would also be required for significant 2-MG oligoester content to arise from a Fischer esterification mechanism in the atmosphere” will need to be reassessed.

2. The authors achieve the main point of the NMR sections, which I believe is to identify the structures of the oligoesters, by reporting the shifts and spectra of <sup>13</sup>C NMR. However, the text also contains detailed discussions of <sup>1</sup>H NMR, COSY and HMBC. These supporting data can be very helpful if their spectra were to accompany the discussion; however, unfortunately they do not. As a result, I found discussions of NMR data besides <sup>13</sup>C are difficult to follow. I suggest either the authors include these missing NMR spectra in the main manuscript or move all the <sup>1</sup>H and 2D NMR discussion to the supplemental information section (where they should also include spectra) and refer the reader to this section in order to avoid distracting from the focus of the text.

3. I suggest labeling the carbons and protons on the structures and referring to them as, for example, “A\_H1” or “A\_C1” (for first H or C, resp., on structure A) instead of “methylene protons of the b unit of the diester” or “ester carbon of the c unit” which becomes difficult to follow after a while.

4. Section 2.4 describes the “controlled composition” experiments and early tables and figures (e.g., Table 1 and Figure 4) refer to experiments by their “solution number.” Yet, the reader must wait until Table 5 to learn of the compositions of the solutions. I suggest introducing an experiment list table, where added concentrations of acid and 2MG are reported, alongside the pH of the solution. Then later tables can report the *K<sub>eq</sub>* values for those solutions.

5. It seems that control experiments, where 2MG (which is a weak acid) is evaporated without the addition of mineral acids, were either not performed or not reported in Tables 5 and 7. It is expected that even dilute 2MG, like lactic acid, will autoesterify resulting in a series of oligomers. Please clarify and, if necessary, justify the decision

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to not report control results.

Specific comments:

1. Experimental section: For the synthetic characterization of 2-MG, please provide a <sup>1</sup>H NMR spectrum of the pure compound and report the separation/purification technique used.

2. Section 2.3. This section can be clearer. For the “neutralized” solutions, one may read that the authors added strong acid then “neutralize” only the strong acid component until pH 2.3. Please clarify if this is the case.

3. Page 3, line 7. Oligoesters from 2MG up to 8 units in length have been reported under dry conditions from isoprene photooxidation (Nguyen et al., 2011).

4. Page 3, line 31. The authors used an internal standard for NMR quantification, which enables purity estimations more exact than “near 100%.” Furthermore, typical NMR instruments may not be more precise than, say, within 5%. Can the authors give a more useful estimation of purity with actual instrument uncertainty (e.g., purity > 96%)?

5. Page 6, line 29. Should this be Results and Discussion section as there is no stand alone Discussion section?

6. Sections 3.1.1-3.1.3 – The text in these sections describing <sup>1</sup>H, COSY, and HMBC spectra was not accompanied by these spectra and therefore was difficult to follow. If manuscript length is a limitation (and it should not be with ACP), one can utilize the supporting information section to show these important aspects of the paper.

7. Table 1 reports <sup>1</sup>H shifts relative to D<sub>2</sub>O, while in the text <sup>1</sup>H shifts are seemingly reported relative to TMS (e.g., page 8, line 9). It would be clearer if the authors picked a convention and stuck with it.

8. Page 7, lines 20 – 23. The authors note that their carboxyl shifts differ from that of Espartero et al., while the rest of the observations are similar. The authors should

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comment on this discrepancy. Likewise upfield/downfield shifts of oligomer units with respect to the parent were reported in this section, but not discussed further. Considering not all readers of ACP may be experts in NMR, these trends should be explained and compared with expectations.

9. Page 8, line 9: I'm sure the authors do not mean that the  $^1\text{H}$  peaks of B and C units occur in the 4 – 4.2 ppm region. Please rephrase.

10. Page 11, lines 1-3: This sentence seems out of place. The authors should report the “diester:2MG” ratio for the control experiment (if done) which is vacuum dehydration of just 2MG here instead.

11. Page 12, line 9: “deviated significantly” is too vague – please report the actual values of the proton activities for 2MG/acid solution compared to just the acid or refer the reader to a table/graph that the information can be found.

12. Page 14, lines 15-17. How much of the spread in  $K_{eq}$  is due to “non-ideality” as the authors claim and how much due to experimental error? Have the authors done duplicates to see if some of the  $K_{eq}$  values are reproducible.

13. Page 17, line 26. While experiments in Chan et al 2010a were performed at RH 9-11%, experiments in Zhang et al 2011 and Nguyen et al 2011, as the authors pointed out prior, were performed at both dry and humid conditions and they came to similar conclusions. Why then do the authors group the Zhang study with high RH and the Nguyen study with low RH conditions?

14. Figures 4 and 5: Please replace 3a and 1a with the more conventional notations 3o and 1o.

Typos: 1. Page 11, line 21. “due” 2. Page 12, line 25 “equilibrium” 3. Page 17, line 17 “M-1” not “m-1”

References: Espartero, J. L., Rashkov, I., Li, S. M., Manolova, N., and Vert, M.: Nmr analysis of low molecular weight poly(lactic acid)s, *Macromolecules*, 29, 3535-3539, C10751

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