Atmos. Chem. Phys. Discuss., 12, C12831–C12838, 2013
www.atmos-chem-phys-discuss.net/12/C12831/2013/

Atmospheric Chemistry and Physics Discussions

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

A. W. Birdsall et al.

matthew.elrod@oberlin.edu

Received and published: 21 February 2013

General Comment 1a: 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.

Response: Because of the NMR lock requirements (high concentrations of deuterium atoms are necessary) and the unfavorable equilibria for oligoester formation for compositions with significant water content, we were forced into a composition space with larger acid concentrations (for which deuterated species are available) and smaller 2-

MG concentrations (for which only a normal isotope species was synthesized). We have added information on this experimental constraint to Section 2.5 of the revised manuscript. However, because of the successful activity-based parameterization of both the equilibrium constant and the acid-catalyzed rate constant, we believe that our results can be extrapolated to other compositions.

General Comment 1b: 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 Esperatero 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 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 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 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.

General Comment 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 to not report control results.

Response: We have added a paragraph to the Introduction section, a paragraph to the Experimental section, and a paragraph to the Results and Discussion section, each of which deals with the possibility of self-catalyzed esterification reactions for hydroxy-acids. In the introduction, we discuss previous experimental work for lactic and glyceric acid. While there don't appear to be formal studies of the kinetics of the process for either lactic or glyceric acid, we cite information from this previous work that suggests that the self-catalysis is quite slow. More importantly, we report our own estimate of the kinetics of the process for 2-MG. We estimate that, after monitoring two largely water free 2-MG samples for six months, the pseudo-first order self-catalysis lifetime is on the order of 3600 days. We also note in the Atmospheric Implications section that this lifetime is roughly consistent with the rate constant determined from high acidity experiments and the expected pH of our 2-MG samples (assuming a similar pKa to that of lactic acid). Because the samples will likely reach an equilibrium point with some 2-MG remaining, the actual time to equilibrium is probably much less than 3600 days, but it seems clear that the self-catalysis kinetics are prohibitively slow on both the atmospheric chamber and ambient atmosphere timescales.

General Comment 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 13C NMR. However, the text also contains detailed discussions of 1H 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 13C are difficult to follow. I suggest either the authors include these missing NMR spectra in the main manuscript or move all the 1H 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.

Response: As suggested by the reviewer, we have added a new supplemental information section that contains details of the NMR analysis. In particular, we have moved most of the detailed assignment discussion to the SI section and have included all relevant spectra, including the COSY and HMBC spectra not originally included in the manuscript.

General Comment 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.

Response: We feel that the Espartero et al. labeling scheme is actually fairly useful for distinguishing between the NMR-active nuclei on the various subunits of the oligoesters. Our use of the same system will also make it easier for readers to compare the lactic acid and 2-MG NMR data. However, we have improved the naming of the C and H atoms in the NMR assignment section of the manuscript in order to make the logic of the system more clear.

General Comment 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 Keq values for those solutions.

Response: As suggested by the reviewer, we have reordered the tables so that the solution compositions are reported first.

Specific Comments

Specific Comment 1. Experimental section: For the synthetic characterization of 2-

MG, please provide a 1HNMR spectrum of the pure compound and report the separation/purification technique used.

Response: This spectrum is contained in the SI section, and the Experimental section now reports that no further purification was pursued after the dehydration step.

Specific Comment 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.

Response: We have clarified this language so that it is clear that the strong acid content was neutralized by adding the appropriate stoichiometric amount of sodium hydroxide, but that the solution remains acidic due to the acidity of 2-MG.

Specific Comment 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).

Response: This has been added to the Introduction section of the revised manuscript.

Specific Comment 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%)?

Response: We estimate that our uncertainty in these measurements is about 10%. We now report the actual yield of 2-MG as 104 $\pm$ 10% in the revised manuscript.

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

Response: As suggested, we have renamed the section.

Specific Comment 6. Sections 3.1.1-3.1.3 – The text in these sections describing 1H,

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.

Response: These spectra are now included in the SI section.

Specific Comment 7. Table 1 reports 1H shifts relative to D2O, while in the text 1H 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.

Response: We have now made it clear in the text and in all NMR spectra that the chemical shifts were calibrated relative to the solvent HDO peak for all 1H spectra, and relative to DSS for all 13C spectra.

Specific Comment 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 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.

Response: The reviewer refers to our finding, based on interpreting the correlations in a 2D HMBC NMR spectrum, that the carboxyl peak of the B unit of the 2-MG-diester is further downfield from the carboxyl (ester) peak of the C unit, whereas the Espartero et al., found the opposite relative location of these peaks for the oligoesters of lactic acid. (For both 2-MG and lactic acid, both diester peaks in the carboxylic region are upfield from the monomer peak.) Though our assignment differs from that of Espartero et al., our assignment is in agreement with textbook 13C NMR shift data, which indicates that the chemical shift of the carboxyl carbon of an ester tends to be further upfield than its corresponding carboxylic acid. (Silverstein et al., 2005) Furthermore, the C unit carboxyl carbon is located closer in the molecule to the reactive site than the B unit

carboxyl, leading to a prediction that the C unit carboxyl would have a larger change in chemical shift from the monomer 2-MG than the B unit.

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

Response: We do in fact mean that the methylene protons of the B and C units (i.e., both units of the 2-MG-diester) appear at 4-4.2 ppm. These are not anomalous chemical shift values for protons near several deshielding groups. This statement has been clarified in the revised manuscript by improving the naming of H and C atoms, as suggested in the reviewer's General Comment 3.

Specific Comment 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.

Response: As explained in our response to General Comments 1 and 5, we have added several new sections to the revised manuscript regarding the self-catalyzed esterification reaction. It is also true, however, that the equilibrium diester:2MG ratio was never measured under these conditions due to the very slow self-catalyzed esterification kinetics.

Specific Comment 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.

Response: We feel that the best comparison is an "apples-to-apples" comparison using AIOMFAC-web for modeling both the experimental solution and the strong acid-only case. In this comparison, the deviations are much smaller, and we no longer think it is an issue worth discussing. Therefore, we have removed this language from the revised manuscript.

Specific Comment 12. Page 14, lines 15-17. How much of the spread in Keq 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 Keq values are reproducible.

Response: If the Keq plot is constructed with molarities instead of activities as the independent variable, the resulting relationship is much less linear, which we take as an indication that the solution non-idealities must be taken into account. Further, since Solutions 2 and 6 were performed with near-identical (+/- 1% difference in starting 2-MG amount) compositions, and gave molarity-based Keq' values of 2.3 and 2.7, our experimental error in determing Keq seems to be much smaller than the non-ideal effects and is generally consistent with our estimate of 10% concentration errors via the NMR method.

Specific Comment 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?

Response: We have written this section to more accurately describe the previous experiments.

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

Response: We have made the suggested change.

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

Response: We have corrected the indicated typos, with the exception of "m-1." This particular quantity does in fact have inverse molality units.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 30039, 2012.