

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 #2

Received and published: 19 January 2013

Overall Comment and Recommendation:

Although SOA formation from the photooxidation (or OH-initiated oxidation) of isoprene under high-NO_x conditions has been previously observed in smog chamber studies, the exact chemical mechanism leading to this SOA remains uncertain. What is currently known about the detailed mechanism is that the photooxidation of MACR (one of isoprene's first-generation oxidation products) (Kroll et al., 2006, ES&T; Surratt et al., 2006, JPCA) and MPAN (one of isoprene's second-generation oxidation products) (Surratt et al., 2010, PNAS; Chan et al., 2010, ACP) under high-NO_x conditions produces similar SOA constituents as if one would start their smog chamber experiment with isoprene; this result strongly indicates the need for forming MPAN and subsequently oxidizing it to form SOA from isoprene. Further evidence for the need of MPAN

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was found by Chan et al. (2010, ACP), where increasing NO₂/NO ratios when oxidizing MACR yielded more SOA constituents (and thus mass). Of these SOA constituents, 2-methylglyceric acid (2-MG) has been observed in both laboratory-generated and ambient SOA samples collected from many locations (Hallquist et al., 2009, and references therein). In smog chamber studies, it was tentatively proposed that once 2-MG formed in the aerosol, it would likely oligomerize through acid-catalyzed esterification (or Fisher esterification) (Surratt et al., 2006, JPCA; Szmigielski et al., 2007, J. Mass Spectrom.). Recent work examining the effect of RH on isoprene SOA formed under high-NO_x conditions has shown that SOA mass and these oligoesters formed from 2-MG are enhanced under dry conditions (Nguyen et al., 2011, ACP; Zhang et al., 2011, ACP; Zhang et al., 2012, Environmental Chemistry). These recent RH studies are consistent with the possible role of condensation reactions, like esterification, in yielding these oligoester species. The big question remaining though is how do we even get 2-MG? This question could reveal how we also get the oligoesters, organosulfates, and organic nitrates in SOA from isoprene photooxidation under high-NO_x conditions.

The present manuscript builds on these previous studies by examining the potential role of 2-MG undergoing further esterification reactions in aerosol with H₂O, sulfate, nitrate, and another 2-MG molecule. Specifically, NMR techniques were used to study the bulk phase acid-catalyzed aqueous reactions (i.e., esterification) of 2-MG. Although this study doesn't use aerosol to study this process, these bulk solution studies are very insightful in understanding if esterification is even possible at chamber and atmospheric conditions. This study is well conducted, described, and the data clearly support the conclusions made by the authors. The authors synthesize 2-MG and then make NMR measurements of the kinetics and equilibrium of the solution-phase acid-catalyzed 2-MG oligomerization reactions. The overall conclusion of this work is that the present results suggest that other, more kinetically facile, esterification mechanisms may be necessary to rationalize the existence of 2-MG oligomers in atmospheric chamber-generated and ambient SOA. This study will clearly help guide future chamber and field investigations of isoprene SOA formation under high-NO_x conditions. This pa-

per is a significant contribution to this research area of atmospheric chemistry and should be accepted for publication in Atmospheric Chemistry and Physics with minor revisions/suggested noted below:

1.) 2-MG formation: The authors should be clear in their introduction, discussion, and conclusions sections that it remains unclear how even 2-MG forms from MPAN + OH. Although I can't state here recent results from my own group (since it is currently under review and not fully published), the results presented here clearly argue against fisher esterification as a source of oligoester, sulfate ester, and nitrate ester derivatives of 2-MG. Just to prevent confusion for the readers of your article, I would be clear that the formation mechanism of monomeric 2-MG remains unknown. I strongly believe that unlocking the mystery of 2-MG formation might provide the mechanism that explains the oligoesters, sulfates, and nitrates of 2-MG. Clearly, the results shown here argue against 2-MG undergoing fisher esterification reactions in the aerosol phase. Their conclusion is important and strongly supported by the chemical data presented.

2.) The authors don't describe any uncertainties that might be applicable to their study, especially when translating their findings from bulk solutions to aerosols. For example, does the Kelvin effect become an issue? What could these uncertainties be and how might they affect the current conclusions? The only problem aerosol scientists (who are not chemists) might have with the current approach is that you are using bulk solution studies to infer aerosol-phase processes. I encourage the authors to describe any uncertainties or potential pitfalls with their current approach in the discussions or conclusions.

3.) Page 30042, Line 2: I would make sure to cite Surratt et al. (2010, PNAS) for this sentence, especially since this study showed that MPAN + OH produces 2-MG and its oligoesters like that of MACR and isoprene oxidation under high-NO_x conditions. Chan et al. (2010, ACP) didn't use MPAN in that study, although they explored the importance of NO₂/NO ratios.

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