Review of Zhao et al, “Secondary Organic Aerosol formation from hydroxyl radical oxidation and ozonolysis of monoterpenes.”

General Comments

In this manuscript, the authors report SOA formation from the photochemical oxidation of monoterpenes in a large outdoor smog chamber. They directly measure OH radical concentrations and the OH reactivity of organics and utilize this data, together with measurements of the particles size distributions, mass loading, and chemical composition, to infer conclusions about the relative importance of fragmentation and functionalization of the precursor oxidation products as the reaction proceeds. Particle growth rates are examined and compared to the growth rates for SOA production from ozonolysis reactions. The topic of SOA formation from photooxidation of monoterpenes is certainly relevant and of interest to the readers of ACP. There are fewer studies of SOA formation from the photoxidation of monoterpenes than from ozonolysis, though it is somewhat difficult to discern what new information this manuscript adds to the literature. The authors claim that their manuscript is the first to link particle growth to the reaction of OH with organics and that this new metric was used to examine the role of functionalization and fragmentation as the reaction progresses. I have some concerns regarding these two claims below, but if these concerns can be addresses satisfactorily, the manuscript could be published in ACP.

Major Comments

My primary concern with this article is the derivation of the particle growth rate and the conclusions that are derived from the growth rate. I am not an expert on particle growth physics, but a simple inspection of the equations the authors use suggest the equations are, at the very least, oversimplified. It seems that the equations do not consider mass transfer at all. For example, comparison of equation 22 in the text with a standard equation for particle growth rates available in text books (for example Equation 13.3 in Seinfeld and Pandis) show that the authors are neglecting several terms (diffusion, surface accommodation, noncontinuum effects, etc.) (Seinfeld and Pandis, 1998). In addition, several recent papers have shown suggested that particles may be exist in a viscous state (e.g., (Vaden et al., 2011;Virtanen et al., 2010;Renbaum-Wolff et al., 2013) and many others), which further complicates the particle growth dynamics and impacts size dependent growth rates and potentially the mass growth rates (Shiraiwa et al., 2013). It is difficult for me as a reviewer to assess what effect these factors will have on the conclusions drawn by the manuscript because an accurate assessment would require a relatively detailed model and information about the experiments that is not available. In any case, the authors should at a minimum state the limitation and assumptions of their kinetic modeling. I also encourage the authors to discuss potential impacts on their conclusions if the particles are not in equilibrium with the gas phase and/or they are not liquids.

I’m not completely convinced by the authors’ interpretation of the role of functionalization and fragmentation through the use of their growth efficiency metric. Fundamentally, their argument is that the particle growth stops while there is still OH available in the chamber to oxidize reactions products; therefore, fragmentation must dominate. It seem like this is an oversimplification that will be extremely sensitive to accurately determining both the particle wall loss rate and the gas wall loss rate. In fact, from Figure 2, the particles only shrink in one of the experiments and are in fact still growing rapidly at the end of another experiment. Have the authors done any sensitivity studies to determine how errors in the particle wall loss rates would affect their conclusions? How can the authors rule out that higher generation oxidation products are not simply lost to the chamber walls (Matsunaga and Ziemann, 2010) or simply too volatile to condense? Can the authors provide any additional evidence to demonstrate that fragmentation dominated over functionalization when they say it did? The authors have a PTR-MS attached to the chamber. Do they see any evidence for the increased formation of lighter VOC's from the PTR-MS data as the reaction proceeds? Related to the issue of functionalization vs fragmentation, the O:C and H:C of the particles remain largely unchanged once a sufficient amount of SOA is present in the chamber for the measurements to be significant. Wouldn't one expect to see some evolution in O:C and H:C in time if later generation oxidation products were contributing to the aerosol growth?

P 12597, lines 23 – 30. P 12599, lines 4-11. Please clarify whether an OH radical generator such as HONO or H2O2 was added to the chamber. The manuscript seems to indicate that no OH radical generator was added. The authors state that photolysis of HONO generated most of the OH radicals and the OH radical concentrations are quite high; however, they also state that NOx was below 1ppbv. I'm having trouble reconciling these observations. Photolysis of HONO produces NOx and a sizeable amount of NOx must have photolyzed in order to supply OH concentrations of 6 x 10^6 and oxidize multiple generations of the 4ppbv concentrations of VOCs. The authors should explain how the high OH radical concentrations can be generated and sustained in their experiments without NOx exceeding 1 ppbv or ozone exceeding 20 ppbv.

All figures are extremely small and hard to read in the printed version. Figures 3, 4, and 5 are particularly difficult to read. I could not distinguish the traces at all in Figure 5 in the printed versions. The H:C trace is almost invisible in Figure 3. I strongly suggest resizing the figures so they are legible before publication.

Specific Comments and Technical Corrections

The growth rates in Figure 4, particularly in panels A, B E, and F look to be either very noisy or have a very complicated non-monotonic dependence in time. It is difficult to imagine any processes (other than noise) creating such "jagged" growth rates. Can the authors comment on this?

How reproducible are the growth rates in the experiment? Only one experiment was carried out for each condition. Since no seed particles were used, particles had to nucleate. I can imagine the growth rates being very dependent on the nucleation conditions, which it typically very hard to reproduce in a chamber, particularly in one as large as this one.

Many experiments appear to start with relatively large particles present in the chamber. See for example Figure 5 in the a-pinene experiment appears to start with 40 nm particles in the chamber. The number concentrations are impossible to read, though I imagine from the mass loading that the numbers are relatively low. Please correct the scale on the number concentration on these figures and comment on the source of the relatively large particles.

P12594 lines 26-29. In chamber studies, it is very likely that oxidation products of VOC are indeed the nucleating agents because they dominate the gas-phase in these experiments and SO2 is low in clean chambers. So this line should be corrected. Whether they are involved in nucleation in the atmosphere is a different question.

Can the authors show the measured decay rate of the parent VOC's from the PTR-MS data? How does the observed lifetime of the parent hydrocarbon compare to the lifetime inferred from the OH measurements? Is the data shown in Figure 1 calculated from the measured decay of the VOC precursor or from the decay rate that would be calculate from the rate constant and the measured OH concentration?

P12595, line 18 "of whole the reaction system" is a typo.

P12596, line 16 and 17 – missing "the" before light and louvre

P12597, line25. The OH reactivity measurements should also be briefly described since they are a key part of the manuscript.

P12600 Equation 1 and throughout. The superscripts are sometimes written with a capital P and sometimes with a lower case p.

References

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