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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Understanding the formation of biogenic secondary organic aerosol from α-pinene in smog chamber studies: role of organic peroxy radicals" *by* B. Bonn et al.

Anonymous Referee #3

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First, I must agree with Anonymous Reviewer #4 that the incorrect English grammar and phrasing throughout the text significantly degrades the overall quality of the manuscript. Interpreting the authors' intended meaning required a great deal of effort, which if not corrected will discourage many readers and thus minimize the impact of the interesting ideas presented in the study. The authors are strongly encouraged to proofread the revised manuscript language specifically for sentence structure.

Ultimately though, the language issues are minor compared to the severe lack of organization of the manuscript's central argument, and to the lack of rigor in the analysis. At its core, the study presents two interesting hypotheses to explain the observations

associated with new particle formation in smog chamber ozonolysis studies. Both of these hypotheses are then "tested" using a detailed aerosol dynamics model. The manuscript is deeply flawed both in its presentation of the hypotheses and in their evaluation. The failings are so severe that the manuscript is not acceptable unless major revisions are incorporated into the manuscript.

The first hypothesis is a complicated mechanism which the authors suggest is a plausible pathway for the nucleation process. The description of the mechanism is spread over roughly half of the manuscript, with the discussion of its implementation in the model interspersed throughout. The description would be greatly enhanced by a graphic representation of the entire partway from the monoterpene precursor to the final nucleus. This would make the complexity of the process easier for the reader to follow. Coupled with a diagram of the mechanism should be a table summarizing the parameters used in the simulations, and their source. Such a table is necessary because there are many, many assumptions incorporated into the model, many of which seem to have only minimal justification. No single assumption is obviously wrong (though the categorical statement that there is no sulphuric acid in the system is suspect), but the shear number of them and the thin justifications for them make it difficult to view the results as a fair test of the hypothesis. This doubt could be reduced through a more organized presentation of what assumptions are made and why they are justified.

The second hypothesis is tied to the nucleation mechanism, and is proposed to explain why there is frequently an observed gap at the smallest sizes in the smog chamber data during new particle formation events. This is an interesting idea, but is so bold that it must be initially viewed with considerable skepticism. As noted by Anonymous Reviewer #4, there are other likely mechanisms that could lead to the absence of particles at such small sizes. In addition to the diffusional losses and charging inefficiencies noted by that author, there also exists the possibility that the counting efficiency functions of the condensation particle counters are different from their expected values.

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The authors do not address these possibilities, instead proposing that the particles are unstable are “destroyed” in the measurement process. What do they mean by “destroyed”? What mechanism would cause the complete disintegration of the particle once it has grown to 10 nm? By that time it has “activated” according to nano-Köhler theory, so it would not evaporate if a part of the initial cluster broke up. And, as Reviewer #4 has noted, anything less than total disintegration would leave behind a still-detectable particle. Also left unaddressed is the question of whether the charging process imparts enough energy on the unstable particle to cause its breakup. And if the butanol condensation in particle counter instead caused the particle loss, it seems just as likely to create multiple detectable droplets rather than none.

The chief evidence for both of these hypotheses is presented in the form of a comparison of the model results to a single a-pinene ozonolysis experiment. The authors are correct that the alignment between the measured and modeled particle formation events are visually persuasive. However, it is only one experiment- surely more were available for a more systematic comparison? More importantly, there were numerous parameters involved in the simulations, some of which had uncertainties spanning several orders of magnitude. Yet the authors perform no systematic sensitivity calculations to determine how robust their result is. They indicate that such analyses will be conducted in the future, yet they expect their readers to accept the validity of their results now. Given the numerous assumptions involved, this is simply too much to ask. It would really be best if publication were delayed until a more complete evaluation of the model can be included.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 3901, 2007.

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Interactive Comment