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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 #1

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General comments

This article explores the nucleation and growth of secondary organic aerosols generated by the reaction of alpha-pinene with ozone. The authors identify issues that are not yet well understood, and provide insight into the chemical mechanisms leading to the inception and growth of ultrafine particles. In particular, they discuss the role of secondary ozonides, hydroperoxide, organic peroxides and other labile compounds in the nucleation and growth of particles, vis-à-vis mechanisms comprising exclusively homogeneous condensation of non-volatile stable oxidation products. The topic is relevant and the work described is original. However, several aspects should be clarified

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Discussion Paper

prior to publication. I recommend a major revision of this manuscript, considering the following issues:

Major concerns:

1) The authors present results from a modeling calculation, which are compared to experimental data from one single experiment carried out at the EUPHORE smog chamber on 3/15/01. The reference provided for that experiment (Hoffmann, 2002) does not correspond to a peer-reviewed journal article, but to a final report submitted to the EU. Since there is no easy on-line access to a more complete description of that experiment, and particularly to its results, I suggest that the authors include a more complete description of the experiment and its results in a revised version. For example, in section 2.2 (Experimental) it is stated that, after introduction of ozone, “its concentration was monitored as for other gases like alpha-pinene, Ĕ”. It would very much improve the article if the authors showed experimental data corresponding to time-resolved chamber concentrations of ozone, alpha-pinene and nitrogen oxides. That experimental information would provide a more complete picture and contribute to a better understanding of the aerosol dynamics.

2) In the conditions of the EUPHORE experiment, alpha-pinene is the limiting reactant and ozone is in excess, at least in the first injection of alpha-pinene (110 ppbv ozone vs 9 ppbv alpha-pinene). For that reason, reactions of residual ozone with the constituents of aerosol particles cannot be neglected. However, the authors do not mention those reactions in their analysis. There is no reference to ozone chamber levels during the course of the reaction (experimental or modeled values). It is reasonable to expect that aerosol particles will be reactive towards residual ozone, which would have the effect of further depleting chamber ozone levels over the course of the nucleation and condensation events considered. Also, the chemical composition of particles could change as a function of time due to ozonation. For these reasons, it would be very important to know what the ozone chamber concentration was at the moment of the second injection of alpha-pinene. Was ozone still in excess at that time?

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3) It would be also interesting to see comparisons between alpha-pinene chamber levels (experimental values) and modeled concentrations as a function of time. That analysis would provide an additional tool to evaluate the predictive ability of the model.

4) One of the most interesting results of this study is the characterization of constituents of aerosol particles in “stable” or “labile” organics. In the discussion presented in section 4.2 (Figure 4), the “stable” fraction of organic matter is shown to be at most ˜35% for particles larger than 10 nm, and less than that value for smaller particles. Does the remaining mass (up to a 65%) correspond exclusively to “labile” organics? How much of the aerosol mass (%) can be attributed to water? Unless the contribution of water was negligible, perhaps it would it be useful to present the data as stable/unstable organic fraction, rather than total mass %. The discussion would benefit from a more complete description of mass balance (unstable organics/stable organics/water) as a function of particle size.

Minor concerns:

TABLE 2: the formulas in the first reaction include C1079O2 and C96O2.

Figures 2 and 3: the plots have no units in the x axis (time) nor in the color-coded scale on the right (particle number concentration)

Figure 5: “In the lower plot, the initial injection of alpha-pinene is increased to 11.4 ppbv and the simulated total number concentration is divided by 6”. - This procedure should be better explained in the body of the text.

Page 2 (Methods, section 2.1.1): “it might be around 0.95 nm in mass diameter” - Is it mass or diameter?

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