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Comment

## ***Interactive comment on* “Understanding the formation of biogenic secondary organic aerosol from $\alpha$ -pinene in smog chamber studies: role of organic peroxy radicals” by B. Bonn et al.**

**B. Bonn et al.**

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### **Reply to comments given by reviewer #3**

#### **General comments**

Reviewer #3 seems to have spent a lot of time in order to follow our arguments and assumptions given. He or she is as sceptic about the present study as reviewer #4, whom we will reply in a separate comment to prevent confusion. In any case we would like to thank him or her for the detailed criticism, will try to comment his/her remarks to allow a better understanding and we will include the comments in the revised manuscript for

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improvement.

1. Reviewer #3 is very displeased with the current English and sentence structure of the manuscript. With respect to the used English and sentence structure we agree and will modify the manuscript to make it as clear as possible and to eliminate the mistakes in the used English.
2. He/she is also displeased because of the organisation of the manuscript. This is more difficult than the previous point. This study focuses on an explanation of an experiment conducted at the EUPHORE facility in Valencia, Spain. Therefore, the model used to apply the assumptions made to the case of interest is the major tool. This is why start with describing the model before explaining the experimental details, because the model itself needs to be independent of the experiment performed. We can certainly switch the order, i.e. starting with the experiment and trying several simulation solutions as it is usually done (tuning of the model). In our case this was opposite: We have developed a detailed description of the processes of aerosol formation in terpene ozone reactions and applied it to several (different) experiments including both  $\alpha$ - and  $\beta$ -pinene. But in order not to confuse any possible reader we aimed to use a single experiment and describe the process in more detail. A usage of all investigated experiments would have resulted in a list with the only advantage of a good agreement, but not insight. If all experiments would have been stated the manuscript would have at least doubled in length. However, we agree after reading the individual comments of all reviewers that a major check on the clarity of our arguments and assumptions is needed to allow the reader to follow and accept or prove them. This will be done for the revised version.
3. The third comment made by reviewer #3 concerns the 'complicated mechanism' for describing nucleation, 'which the authors suggest is a plausible path-

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way for the nucleation process'. It seems that we could not convince him or her with the statement and references given. This mechanism is not complicated, but refers simply to kinetics, which are described in that way. A single compounds resolution, although wished by most scientists, does not work in this case. No sampled organic oxidation product is able to exceed its saturation vapour pressure, which is a necessary criteria to start homogeneous nucleation. One common 'trick' is to apply a certain concentration of sulphur dioxide and thus sulphuric acid to be used as nuclei. In this case no one would expect nucleation to occur in the presence of an OH scavenger. But nucleation is observed. Why is there a negative impact of water vapour on nucleation [[Bonn et al.\(2002\)](#), [Bonn and Moortgat\(2002\)](#), [Bonn and Moortgat\(2003\)](#)]? For any acids acting as nuclei this is expected vice versa. But we agree that the entire approach and the assumptions are certainly easier to understand with a scheme and a table as suggested by the reviewer, which will be inserted both and briefly described.

5. The second assumption, which is the major one of this study, causes the most disagreement. There are always other theoretical possible explanations such as diffusion losses. However, the instrument was calibrated and tested to start reliable measurements at a particle diameter of 3 nm. However, the maximum in number density appears at about 25 nm. This observation is a common feature in secondary organic aerosol formation studies. The faster the growth the worse the situation. We will emphasize this in the revised text. The second and most critical point is the loss of particles and the compounds associated with 'unstable' or 'labile'. Here there is a need to consider the organic particle in J. Pankow's [[Pankow\(1994a\)](#), [Pankow\(1994b\)](#)] or J. Odum's [[Odum et al.\(1996\)](#)] way: The partitioning of an organic compound between gas and aerosol phase relies on the present organic aerosol mass. If a fraction of this gets destroyed, the organic mass will be reduced too. This causes a shift in the equilibrium

between gas and aerosol-phase, since this equilibrium is fragile and the bonding of a compound to the organic matter isn't that strong. It occurs much below the compounds saturation vapour pressure and hence a vaporisation is relatively easy. Except for the largest dicarboxylic acid formed, i.e. pinic acid, no compound yet identified by available techniques exceeds its saturation vapour pressure at least within the first experiment time (until second terpene injection). And even pinic acid will reach saturation level [Bilde and Pandis(2001)] not before 7 min after the first injection, assuming it to be formed in the gas phase and assuming the first reaction of  $\alpha$ -pinene with ozone to be the limiting step [Koch et al.(2000), Winterhalter et al.(2000)].

With respect to the 'unstable' or 'fragile' compounds considered, we mean hydroperoxides, peroxides, ethers, esters, hemiacetals, i.e. compounds with a weak O-O bonding, which get commonly destroyed for example in mass spectrometric analysis. At which point of the measurement process this occurs is a reasonable question and we like to thank the reviewer for pointing this out. Calculations have shown that forming a critical cluster in the CPCs with water or butanol as condensing material is likely to destroy about 25 of these bondings. About the magnitude of destruction during the charging process nothing is known yet. Any idea concerning this is welcome. But showing that our assumptions are fulfilling the requirements for aerosol formation might be a first step to identify these processes and to check these by modified set-ups. This will all be explained more clearly within the revised version.

6. The last point made has been commented already in 2. We have applied this mechanism for different experiments and the set-up was capable to simulate for both different structures ( $\alpha$ -pinene - endocyclic and  $\beta$ -pinene - exocyclic) the observed particle size distributions. Including all would have a huge extension of the present manuscript and didn't ease but complicate understanding. That is

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why we concentrated on a single experiment. Naturally, there are a lot of studies needed in the future and this manuscript presents the outline and description of this second (activation by organic peroxy radical) hypothesis mainly. Hopefully this will improve in the future and reviewer #3 agrees with this. the extended version.

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