

***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.**

B. Bonn et al.

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Response to comments of reviewer #4

General comments

We need to thank reviewer #4 for his comments and his effort in understanding the present study. Some comments are pretty much usefully for improving the clarity of the present manuscript, others are confusing because of either references to earlier studies and clearly defined chemical expressions. We will try to tackle each detail separately below.

1. The reviewer questions that our hypothesis on the unstable or fragile and stable fractionation is not explaining the observed behaviour and badly given. As stated already to reviewer #3 the English and the clarity of our argumentation can be improved and will be in the revised version. The English grammar and sentence structure are certainly the main points of criticism and they will directly affect any understanding of the present study. Thus, we hope to modify these points within our revised manuscript as good as possible. A clear help would be the suggestions of reviewer #1 with a schematic of the processes and a table of the so-called hypotheses and their references.
2. The 'unstable' or 'fragile' and 'stable' aerosol fractionation is doubted and the reasoning criticized. This refers exactly to the comment 5 made to reviewer #3. Here we stated that: *'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 α -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*

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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.' Hopefully this will become clearer in the revised version with improved English.

3. For individual examples he or she names a few text passages such as 'This leads to a dilemma' (p.3903, l.7). We can change the word 'dilemma' to 'severe problem', because we stated right before that sentence that most of the proposed ways of particle mass production by e.g. Janget *al.* (2002), which are needed to explain the observed increase in particle mass, are disproven by Barsanti and Pankow (2004, 2005, 2006). The problem arises clearly from the fact that a model needs to take into account at least all important processes for reproducing the observations. However, if such a process is disproven to be relevant but a similar one is required to match simulations and observations, this evidently results in a dilemma for the scientist aiming to simulate the processes going on in the investigated experiment.

p.3903, l.13: The expression 'the present ratio of peroxy radicals' is not understood. The reviewer asks to what. This is clearly defined in chemistry. There are two different peroxy radicals in such kind of experiment, the hydroperoxy radicals (HO_2 , inorganic) and the organic peroxy radicals (RO_2). We had been convinced that those interested in the topic would be aware of this. We will insert it more clearly for a better understanding. The word 'present' is very important in this

context, because the ratio changes dramatically during the experiment as shown in Fig. 6 (lower plot).

p.3903, l. 15-20: We are not clear about the intention of the reviewer here. It was outlined just above that the previous assumed mechanisms to explain particle growth by catalyzed reactions is unreasonable, but that the concentration of HO₂ and RO₂ is established to play a major role. The word 'Consequently' simply refers to 'as a result of this' and means that a new not yet published mechanism is needed for explanation and that we will develop this within this manuscript. If this supports understanding, we can change that.

p.3904, l.10: Unclear. It was named that the former box model of Korhonen *et al.* (2004) included only sulphuric acid derived nucleation description. We have named in the comments to reviewer #3 that sulphuric acid is not supposed to play a key role in here, because nucleation takes place in a similar extend also in experiments with an OH scavenger (sucking away any formed OH), in which sulphuric acid cannot be formed. Certainly sulphuric acid can contribute to a minor extend, but the major nucleation mechanism is different from the one described by sulphuric acid schemes.

p.3905, l.16: 'This' refers to our assumption that no homogeneous nucleation of a single compound takes place. Will be emphasized more clearly.

p.3905, l.22: 'Their reaction rates' means the reaction rates of the compounds reacting with the stabilized Criegee intermediate [[Großmann\(1999\)](#)].

p.3908, l.21: Yes. Thanks, this will be changed.

Other comments

4. (p.3905, l.13-16) Regarding e.g. the process of initial cluster formation from stabilised Criegee intermediates and carbonyl compounds this refers to the work of Kamenset *al.* (1999) and others [[Bonn et al.\(2002\)](#), [Bonn and Moortgat\(2002\)](#),

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Bonn and Moortgat(2003)]. And unfortunately in this case arguments on the nucleation process separate to scientific groups currently: (i) the fraction searching for a single compound such as pinic acid that homogeneously nucleate and (ii) the fraction, which treats the nucleation process kinetically by reactions of different compounds to form a cluster. The latter hypothesis does not require a critical size as does the first. Because of experimental evidence that homogeneous nucleation of a single compounds is unapplicable for secondary organic aerosol formation and because of indications for the kinetically described nucleation process we consider the latter approach. We already tried to state these two possibilities, but with respect to the used English this might not have been sufficiently clear. One critical aspect is always, when do we speak of a nucleus, a cluster or a particle. If we assume a particle only in the case of possible detection (diameter beyond about 2 nm) the contact angle becomes important for larger molecule clusters behaving like a organic droplet. If we use the secondary ozonide molecules as single nucleation core molecules, there is a need to activate these by other molecules to form clusters and from clusters to particles. Because of that the contact angle needs to be considered.

5. (p.3906, I.6) Yes, this can be done. We wanted to start from the exact formulation to end at the reduced one. But it is not essentially needed. A skipping of Eq. 6 on the other hand might confuse laboratory experiments aware of this and trying to compare the importance of different species.
6. (p.3910, I.9-11) This refers especially to pinic acid, but is applicable to most of the other aerosol constituents too. The production of a compound is not a process of milliseconds here but of several seconds to minutes at least. To exceed saturation level is even more time consuming, depending on the volatility and the yield of a specific compound. Except pinic acid (ca. 10 min) most compounds require hours to reach saturation, if they reach this level ever during the experiment. However, the more low- or non-volatile an organic compound gets, the

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more functionalities such as -OH or -C(O)OH bonds it requires to have. This needs a reaction for each functionality, mainly initiated by OH. Therefore each of the non-volatile compounds require time to be formed. The only one produced nearly immediately by the reaction of the monoterpene and ozone is pinonic acid, resulting from the attached ozone molecule that splits up. But this first reaction is the only possibility for ozone to interfere. A more detailed statement will be done.

7. (p.3910, I.9-11) The statement is indeed rather strong. Although the presented mechanism is able to reproduce the results within the uncertainty limits, a clear proof such as gained by direct chemical analysis of ca. 1 nm in diameter particles is currently missing and will not be available in the near future. Sulphuric acid is among the most speculative topics of new particle formation at the moment and because of the gap of knowledge no link between observations of particles and sulphuric acid can be ruled out at the moment. However, we might ask vice versa if e.g. in the study of e.g. Berndt *et al.* (2005) just as an example minor traces of organics have influenced the results, because of the disagreement by orders of magnitude from earlier studies. This is not meant to blame the authors for this, but to show the complicated task to perform any experiment without both possibly involved. The detailed interference and the presence of sulphuric acid can only be ruled out in experiments, which prevent OH to form notably and thus suppress sulphuric acid formation. Because of these points mentioned, we will weaken 'The only remaining possibility...' to 'The most likely possibility...' and hope the reviewer to agree with this.
8. (p.3912, I.18-22 and Figure 1) Correct and good point. This will be done in the revised form.
9. (p.3913, I.1-3) Clusters are actually not observed. The growth of larger particles is downscaled to smaller sizes, assuming identical processes to be responsible for the size range below 3 nm. This is certainly a critical topic for any of the

studies made. In atmospheric studies sometimes air ion instruments, relying on a sufficient charging of clusters taking place, are used, which start from 0.35 nm using high flow rates to reduce diffusion losses to their minimum.

10. (p.3915, l.5-7) We agree partially. Yes, the loss rate of SF₆ is used for all gaseous species because the EUPHORE smog chamber is Teflon bag, which is slightly semi-permeable for the species and which adsorbs compounds on its surface. The wall effects are minimized by the geometry of the half-spherical bag and the minimum surface to volume ratio. Since there are no other techniques to estimate the wall losses, a very unreactive volatile compound (SF₆) is commonly used to determine an average loss rate. This is applied to all gas-phase compounds. Usually the reactor walls are cleaned after the experiments by washing and the reactor is flushed with clean air to minimize effects of previous experiments on the subsequent ones. It is clear that low/non volatile compounds will stick to the wall more likely than volatile ones. Usually the experiments are conducted during daytime when the chamber walls are either heated by solar radiation itself or as in our case by the warmed air between the Teflon bag and the roof cover exposed to sun light causing an elevated wall temperature reducing this artefact. Samples are taken from the lower center of the bag in order to minimize wall effects. At this point participation to any pre-existing aerosol particle is more likely than diffusion to the next wall. Please note also that the other products (vast majority) is semi-volatile or entirely volatile, which can be treated by the presented SF₆-approach.
11. (p.3916, l. 5-10) Yes. Mixing ratio is certainly constant and will be named (150 ppmv). The words 'at 14.7°C' will be deleted. This was stated for the initial conditions used for calculation.
12. (p.3916, l.11-13) Will be deleted.
13. (p.3916, l.27-p.3917, l.1) We agree to the arguments given by the referee except the diffusion losses as the major cause of non-detection. Diffusion losses are

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certainly among the candidates contributing to the total loss of particles and will contribute here too. Also the lower charging efficiency is a worth noting. But in this case the lower charging efficiency is taken care of after the measurement (corrected) in case any particle is detected. For particle size measurements a twin DMPS set-up was used, i.e. smaller particles from 3 nm on were analyzed with Vienna type DMAs, a short one with and an ultra-fine particle counter (TSI 3025, lower detection limit is 3 nm) and a medium one attached to a TSI 3010 (10 nm to 500 nm in diameter). This set-up is capable to detect the smallest particles even at about 7 nm and does so for non-volatile particles by contrast to the gap in observations for the investigated experiment. This is one of the reasons, why we focussed on the explanation using fragile and stable compounds.

14. (p.3919, l.13-15) The question of detection or non-detection is more complicated. This goes back to point 2. It does not mean that a particle will be entirely skipped automatically if a fraction consists of 'fragile' species. But the removal of this fraction or a part of causes the particle to reach a different equilibrium situation. A removal of mass causes for each partitioned species to find a new equilibrium according to the new organic aerosol mass. This process seems to be most obvious for the smallest particles below about 10 nm in diameter. For longer timescales oligomerization might transfer these fragile compounds into 'stable' ones. About the oligomerization and the destruction process within the DMPS system we can currently only speculate. More studies are required, which is named already in the manuscript but will be emphasized more strongly.
15. (p.3921, l.9-10) Partially true and good remark. This model does not resolve mixing and in a later stage the precursor concentration is somewhat overestimated. The increase of the α -pinene mixing ratio from 9 to 11 ppbv is used to capture the onset of nucleation, which sets in rapidly after injection, when the monoterpene isn't mixed well in the chamber. Usually the mixing fans are used for several minutes to provide sufficient mixing. Using the diluted mixing ratio right away

clearly leads to a delayed and less intense nucleation. This is stated and will be described in more detail.

16. (Figure 5a and b) Yes. The correct value is two.
17. (p. 3921-3922) This was aimed with the listing of points (i), (ii) and (iii), but will be given more extensively to support understanding and possible discussion about it.
18. (p.3923, l.15-17) Indeed, the lifetime of the stabilized Criegee was reduced to provide a better match between model and observations. We will insert a new section dealing especially with the critical assumptions and sensitivity analysis. It is very unfortunate that some of the important results of phd studies haven't been published except as a monograph to the local university [[Großmann\(1999\)](#), [Bonn\(2002\)](#)], which are used and are considered as hypotheses by reviewers.
19. (Figures 6 and 7) They are consistent. If any arrow is misplaced by a single digit we'll take care of, but the injection times are similar and matching the ones stated in the experimental protocol. We can and will certainly replace 'injection' in Fig. 7 (upper plot) with 'addition', but they are complementary. The monoterpene is injected by a heated inlet and by doing so added to the chamber.

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