

Interactive comment on “New particle formation during α - and β -pinene oxidation by O_3 , OH and NO_3 , and the influence of water vapour: particle size distribution studies” by B. Bonn and G. K.Moortgat

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We would like to thank the anonymous referee 2 for his specific comments and suggestions for technical corrections. These will be considered in the final version of our paper. Concerning each individual point of his comments some things need to be said, to clarify the statements, results and the conclusions of our paper. Therefore, the comments of the referee will be tackled below in the same order as done in his statement:

1. The expression “further oxidised” used on page 471, in the context of particle formation in NO_3 -reactions, was used for primary reaction products like carbonyls (e.g. nopinone in the case of β -pinene) that will be (further) oxidised in a second reaction by NO_3 . The products of these secondary reactions then affect the particle formation

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remarkably as found in the measurements.

2. The expression “pre-existing aerosol” in the context of the partitioning process of semi-volatile products is meant as suspected by the referee: First, aerosol particles has to be formed homogeneously by the formation of clusters of non-volatile species. Secondly, the semi-volatile products will partition on these. Of course, no seed aerosol was present during all described experiments as stated in the text.

3. Our statement on page 472 should express the usual procedure for the preparation of the reactor. There were no other gases, which were filled in the reactor in any of the experiments.

4. p. 473: The water vapour concentrations used in this study represent very dry environments at the present temperature. The first experiment at a dew point of -80°C (3 ppmv) is conducted at a relative humidity of nearly 0%. The second, performed at a dew point of 4°C (8400 ppmv) was conducted at nearly 30% of relative humidity. But in this context it has to be mentioned that the focus of this study was set on the water vapour concentration or absolute humidity, because these aspects describe the amount of water vapour present to take part in the reaction scheme.

5. Our measurements were performed with a long differential mobility analyser (LDMA) with a size range depending on the adjustments of 7-1000 nm in diameter. Of cause a nano-DMA with a lower limit of 3 nm in diameter would have been better to collect all particles in the ultrafine size regime and therein the smallest ones. On the other hand, this instrument has a very low upper limit of 150 nm, that removes all the larger particles. But a lost of the larger particles will affect the aerosol volume measurements remarkably, and therefore the LDMA was chosen for the detection of the broadest size spectra. A simultaneous measurement of both instruments would be best way, if enough reactor volume is available, which was not in this case.

6. p. 474: The referee questions the effect of cyclohexane addition during the ozonolysis in such high concentrations. Therefore we can state that cyclohexane does not

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form new particles neither itself nor together with ozone (blank runs). Moreover, it has a saturation vapour pressure of nearly 120 mbar at room temperature and reacts only with the OH radicals formed during the ozonolysis. However, we found a reducing effect on the nucleation during experiments with cyclohexane addition (Bonn et al. 2002). This is caused by the formation of cyclohexanol and cyclohexanone with each 50% of the OH yield. These substances will affect certainly the competitive reaction scheme of the stabilised Criegee intermediate (CI) and will reduce the reaction of the stabilised CI with e.g. nopinone. By contrast, if there is no OH scavenger present, the reaction of OH with the monoterpene will lead to a higher carbonyl yield such as for nopinone in the case of β -pinene. Consequently, there is no additional contribution of cyclohexane to the aerosol formation.

7. p. 475: The point that ozone might be formed in our reactor because of the presence of high NO_x-concentrations as well as high peroxy radicals levels is irrelevant, because of the high OH concentration levels. These converted the initially added monoterpene immediately, so that no reaction of ozone with the monoterpene can be expected to occur. Nevertheless, the photolysis of NO₂ is possible with the used Xenon arc lamp (200 nm < λ < 400 nm) and will occur. But it has to be remarked that the NO level is highest, not the NO₂. Consequently ozone will be formed in the reactor only slowly and too late to interfere the reaction of OH with the monoterpene.

8. p. 476: N₂O₅ was produced prior to the experiment by adding a small amount of ozone to an NO₂-containing air stream. The NO₂ reacted with ozone, forming NO₃ that itself reacted with NO₂ producing N₂O₅. This was frozen out at a temperature of 70°C on the surface of a glass vessel. Later on, the N₂O₅ was added in the planned concentration by a gas mixing unit to the reaction chamber used for the experiments.

9. p. 479: Wall losses in the reaction chamber are only taken into account for the aerosol volume. Therefore an experiment with a high amount of a sesquiterpene (α -humulene) was reacted with ozone and the particle size distribution was observed for one hour. Due to the fast reaction of the sesquiterpene, the aerosol formation was

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finished after some minutes. A volume loss rate of $21.2\% \text{ h}^{-1}$ were obtained for the following volume concentration decay and will be mentioned additionally on page 479.

10. The OH level used in this study was quite high, much higher than in the atmosphere in order to prevent interfering reactions of other oxidant such as ozone with the monoterpene. A measurement of the OH concentration was not possible in this reactor.

11. p.484: We observed a formation of ca. 400 ppbv HNO_3 during the humid experiments in the gas phase and none during the dry experiments. Additionally, the particle size distributions during both conditions were found identically. Therefore, it seems that there is no measurable artefact on the aerosol volume formed.

12. The presented experiments are different to the ones of e.g. Hoffmann et al. (1997), Griffin et al. (1999) and Odum et al. (1996) because these authors (see article) used a smog chamber, that is not evacuable as the used glass vessel in this study and no sunlight was used in our study in contrast to the smog chamber experiments. Moreover, we planned the experiments in that way that only a single oxidant (O_3 , OH or NO_3) was able to react with the monoterpene. All these authors did not use scavengers like cyclohexane. No reactions of multiple oxidants as found under usual smog chamber conditions were possible in our study. Therefore an estimation of the contribution of the single reactions can be made without all the assumptions of a model like yields and saturation vapour pressures. Additionally, the studies already published in the literature were all performed at water vapour concentrations above 2000 ppmv, which is by far higher than used in this study. Only with the assumption that water vapour does not affect the aerosol yield the literature values can be transferred to the real atmosphere! The use of seed in the smog chamber studies have prevented the analysis of the homogeneous particle formation and the intercomparison of the different oxidation types.

13. p. 485: The referees comment concerning the effect of water vapour on the

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nucleation during monoterpene ozonolyses and the concentration of the carbonyls is quite good. Because of the high concentration of the reactants of all published and our experiments, the concentrations of the carbonyls are quite high inside the reactor. Their concentration level in the atmosphere is somewhat lower. But, if the carbonyl compounds form aerosol particles by reacting with the stabilised CI (secondary ozonide formation), the saturation vapour pressure of these products is required to estimate the contribution of these kind of products to atmospheric nucleation.

14. Concerning the his point of "doubtful data" Oused in this article (p. 486), our argumentation has to be clarified. In a first series of experiments, not used for this paper, we observed a memory effect of the reactor walls in the next experiment. Therein, we mentioned the higher number concentration in experiments with 50 ppbv of the monoterpene than in the one with 500 ppbv. This artefact was suppressed by addition of extra N_2O_5 prior to the experiment, as done by Hallquist et al. (1999). But we demonstrated the effect of this artefact by the two experiments conducted in the flow reactor. We tried to consider all possible artefacts.

15. p. 487: For the ozonolysis experiment in the flow reactor we did not use cyclohexane.

16. Of cause the NO_x level inside our reactor was higher than the one inside the smog chamber of Griffin et al. (1999). But because of the high photolysis rate of methyl nitrite in this study and the resulting intensive OH production, the ozone is not able to interfere the studied reaction of the monoterpene with the OH radical. Its rate constant is by far too low. The high NO level will only affect the product yields as describe by Peeters et al. (2001). In this context, it has to be mentioned that the "low humidity level" of Griffin et al. (1999) during the photosmog experiments with β -pinene is in the range of water vapour concentrations between 2900 and 4300 ppmv, during the ozonolysis experiments between 2600 and 2800 ppmv and during the NO_3 -experiments between 2000 and 3100 ppmv, which is roughly 1000 times higher than in our "low humidity level reactions". With respect to this, they only studied "humid" conditions. 17. The Figures

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3a, 4 and 7 were included with all measured particle size distributions to express the uncertainty of these small aerosol number measurements.

We have include the referees comments in the final paper in order to improve the meaning.

References:

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Peeters, J., Vereecken, L., Fantechi, G., The detailed mechanism of the OH-initiated atmospheric oxidation of α -pinene: a theoretical study. *Phys. Chem. Chem. Phys.*, 3, 5489-5504, 2001.

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