Atmospheric Chemistry and Physics Discussions

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Comment

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 #4

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Review of manuscript "Understanding the formation of biogenic secondary organic aerosol from alpha-pinene in smog chamber studies: Role of organic peroxy radicals" by Bonn et al.

This paper presents a hypothesis on how new particles may be formed from organic precursors in the absence of sulphuric acid. The authors propose a secondary ozonide, which is the product of a stabilized Criegee intermediate and a carbonyl compound, to be the nucleating agent, and peroxy radicals to be responsible for the initial growth. At a later stage "regular" condensation is assumed to take place. As a result, small particles exist of a mixture of stable and unstable compounds. The latter may remain

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undetected, explaining the often observed gap in detection for the smallest particles.

The process of what happens to a mixed stable/unstable particle in the instrumentation is not clearly explained in my opinion. The hypotheses put forward would not necessarily result in the observed behavior.

The hypothesis on the chemistry of nuclei formation and their early growth is not sufficiently grounded by evidence, and a critical discussion is lacking. If evidence is not available due to the nature of the small nuclei and reactive species, the need for a critical discussion is even higher.

Though the paper contains interesting results and hypotheses, it is very difficult to follow because of the poor use of the English language. There are many grammatical errors, but moreover, the sentence structure and explanations are often unclear, leaving the reader to guess what the authors are trying to say. This happens to such an extent that I deem the paper unsuitable for publication in its present form. Moreover, the points mentioned above (and discussed in more detail below) are important to address. I strongly urge the authors to seek external assistance, preferably from a native speaker of English, in thoroughly editing the manuscript. Editing should focus both on grammatical mistakes and on improving the clarity and logic of the arguments made. As it is, the paper misses its goal of informing potential readers about interesting results.

A few examples of the poor use of language are given below. Note that this list is not meant to be exhaustive, but rather illustrative.

P3903, line 7: "This leads to a dilemma": The dilemma is not explained. The authors probably mean that it is difficult to understand the formation processes. P 3903, line13: "the present ratio of peroxy radicals" Ratio to what? Omit the word "present". P3903, lines 15-20: "Consequently, there seems ... on." This sentence is unclear. As a result, it is unclear what "this alternative way" in the next sentence refers to. I guess the authors mean one of the two ways described in the previous sentence? "Different as"

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should be changed to "different than/from". P 3904, line 10: "Since this approach is not considerable ..." Do you mean "common"? p 3905, line 16: "This is caused byĚ" What does "this" refer to? The absence of nucleation? p 3905, line22: "Their reaction rate constants"? Of the complex C20 molecule or of sCI? It is not clear to me where you are talking about which compound in this section, and what their respective roles are. P3908, line 21: "vaporization entropy": change to enthalpy.

Other comments:

P 3905, line 13-16: It is mentioned how you don't assume homogeneous nucleation to occur, but I miss information on how you do assume it to occur. That information is only presented at page 3909-3910. However, in my understanding, homogeneous nucleation refers to only one phase being involved in the nucleation process. The activation scheme only involves one phase, so should still be regarded as homogeneous, at least by the description above. Rather, the authors seem to assume nucleation to be heteromolecular (involving multiple species) as opposed to homomolecular (involving only one species). I don't see the relevance of invoking the effect of the contact angle (p 3909, line 26) in this respect either, since this concept only applies to multiple phases. The discussion about the nucleation process should be changed or clarified.

P 3906, Eq 6: I assume that the last term in the denominator refers to reaction of the biogenic terpene with other compounds than water or carbonyls (i.e. [i] stands for additional alcohols or acids). Since in line 13-15 it was already mentioned that for lab studies these species can be omitted, I suggest to skip eq 6.

P 3910, lines 9-11: This requires some more explanation. I.e. are non-volatile compounds produced more slowly than the time that is available before nucleation starts? (I assume that "observations" refers to the time before nucleation starts, but that is not clear.) Is that statement specific to pinic acid or does it apply to all non-volatile compounds that may partition to the aerosol phase?

P3910, line 12: "The only other possibility ..." I find this too strong of a statement.

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A discussion of possibilities is at its place here, rather than claiming certainty about the process of nucleation and early growth. There could be trace amounts of H2SO4 and NH3, especially if SO2 has been used in the same chamber before. The fact that "none of the performed test simulations with sulphuric acid induced nucleation could explain the nucleation observed" (p 3907, line 16-18) does not disprove H2SO4 from having participated in nucleation. There is too much uncertainty in the dependence of the nucleation rate on H2SO4 (or other species) concentration to regard such a test as proof that H2SO4 did not induce nucleation. Moreover, the combination of carboxylic acids and H2SO4 produces more particles than either of these species alone (Zhang et al., Science 2004). Berndt et al (Science 2005) found evidence for particle formation for H2SO4 concentrations above 7*10ˆ6 cm-3. How can the authors be sure that this concentration was not exceeded? Other possibilities may include the presence of (unknown?) compounds with much lower vapor pressure. Or a combination of compounds that lowers the nucleation barrier.

P 3912, lines 18-22 and Figure 1. The Figure caption sais that different densities were used, but mentions only one value (1200 kg m-3), whereas in the text 1000 kg m-3 is mentioned. This should be corrected. The upper and lower plot in Figure 1 could be combined into one figure with two y-axes, since the two quantities displayed are proportional to each other (k_gas_RO2 is independent of particle size).

P3913, lines1-3: Current (commercially available) aerosol instrumentation cannot detect particles smaller than 3 nm. From 3 nm onwards, the reaction rate stays relatively constant. How then do all smog chamber studies commonly observe the growth of clusters to speed up once they are activated?

P3915, lines 5-7: Is the measured loss rate of SF6 applied generically to several/all gas-phase species? This would be problematic, since different (classes of) species have different loss rates. Alpha-pinene may not be lost to the wall at all, while condensable species may have a strongly enhanced loss rate.

P3916, lines 5-10: The temperature increase causes the RH to decrease, but shouldn't influence the mixing ratio of water vapor. Please mention the RH. P3916, lines11-13: delete SMPS info, this is described on the previous page.

P3916, lines 27-p3917, line 1: The nucleated particles seem to jump over a gap of the smallest size range, where they are not detected. I do not believe that a low time resolution by itself can explain the observations, though undoubtedly it is a contributing factor. The maximum number would not gradually increase if low time resolution were the only reason, but rather increase stepwise. Moreover, this feature of a gap is commonplace in size distribution measurement, whereas if low time resolution were the reason, this gap wouldn't be as persistent as it is for many different measurements. Probably, many small particles were lost by diffusion and/or evaporated away before reaching the detector. The low charging efficiency for these small particles also impedes their detection.

P3919, lines 13-15. The particle is assumed not to be detected if its stable fraction is smaller than the lower section size. But why in such a case (where the stable fraction is still much larger then the unstable fraction) wouldn't the particle be detected in one size bin smaller, rather than not detected at all? Both reasons given for the unstable part of the particle being destroyed would lead to different artifacts: Destruction in the charger would lead to undersizing of the particle, whereas destruction in the CPC would have no effect, unless it renders the remaining part of the particle too small to be activated by the butanol vapor, in which case it would not be detected at all.

P3921, lines 9-10. Increasing the initial alpha-pinene concentration in the model to mimic delayed mixing. This only makes sense to me if your model explicitly deals with mixing and locally different concentration fields in the chamber, which it probably doesn't. Otherwise you merely simulate the processes with an overestimated precursor concentration.

Figure 5a and b: Synchronize the legends in and caption text for both figures (regarding

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the factor 2 and 6).

Page 3921-3922: I miss a clear discussion of the difference in number concentration between measurements and model. Points i-iii don't make the connection to this number concentration clear enough.

P3923, lines15-17: If I understand this correctly, you could improve the match between model and measurements by decreasing the lifetime of the Criegee intermediates in the model. More information (based e.g. on a sensitivity analysis) on what factors determine the match between model and measurements would be useful. Is the model constrained at all, or could you get an equally good match with very different sets of parameters? Since so many parameters are very uncertain that could very well be the case. This issue should be more critically discussed. The robustness of your conclusions depends very strongly on this. As a reader I find it very difficult to assess the probability that your conclusions are correct, or merely a possibility amongst many other possibilities (which are not discussed to the extent needed). The evidence is not clearly laid out, and a critical discussion is missing.

Figures 6 and 7: Please make these figures internally consistent in terms of arrows, legend, axis titles.

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

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