

***Interactive comment on* “Technical Note:
Detection and identification of radical species
formed from α -pinene/ozone reaction using DMPO
spin trap” by J. Pavlovic and P. K. Hopke**

Anonymous Referee #3

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Summary:

Overall, the idea of the use of radical trap is great but application to atmospheric aerosol is problematic due to artifacts by the quartz filter, the lifetime of intermediate radical species, and the sampling method. If the proposed method is operational to dynamically changing atmospheric aerosol, the sampling method should be near in situ. This paper is not suitable for the journal publication without serious revision. Please find the comments below.

Major comments

1. Page 23696, introduction part. There are unnecessary information in the intro-
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duction. For example, equation R1 is the very commonly known inorganic gas-phase chemistry but not importantly utilized in this paper for product identification. The reviewer think that the authors should provide the better flow and include reactions that are necessary to explain product identification. 2. Page 23700, experimental section. A serious issue appears in the sampling time of this study. The authors described that the particulate matter samples were collected for 30 minutes on the 25 mm quartz filter. Considering the reactivity of OH radicals with other organic chemical species, 30 minutes of the sampling time of this study is very long. No matter what is the residence time in the flow reactor or how the sample was immediately extracted using water, the short reaction time in both the flow reactor and extraction cannot provide any advantage to hold reactive radical species such as OH radicals and other radical species. In addition, intermediate radical species are unstable and can be transformed to other products during 30 minute sampling time prior to the DMPO reaction. 3. Page 23700, experimental section. Humidity and temperature information are missing. Especially humidity is influential on OH radical production in the gas phase and SOA product distribution. 4. Page 23696, Introduction associated with the experimental section. The probability of accommodation of the gas phase OH radical to the particle phase is very low. At the given experimental condition with high ozone and alpha-pinene concentrations in the flow reactor, the major reaction is the ozonolysis of alpha-pinene. The discussion of OH radical production in equations R2 and R3 are not practically usable for the long sampling time because OH radical can be immediately consumed by the high concentration of alpha-pinene rather than placing into the aerosol. 5. Page 23700, experimental section. The authors have used the 23 mm quartz filter for the aerosol sampling. In general the quartz can produce OH radicals. This has been believed by health community for why the quartz fiber can be harmful for the pulmonary system. In general, the fresh quartz materials have more active for production of radical species. The authors should provide the evidence in that the quartz filter has no artifact on OH radical production or analytical characterization of radical trap products. 6. Page 23701, experimental section. The appropriate blank should be the quartz filter

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exposed to the bath air or alpha-pinene without ozone for the 30 minutes. 7. Overall product analysis. It is hard to understand why the authors can identify mainly inorganic radical species rather than RO radicals and RO₂ radicals. The OH radical life time would be much shorter than other RO and RO₂ radicals in the aerosol phase. This indicates that the probability to trap RO and RO₂ radicals should be higher. I believe that authors may use the excess amounts of DMPO reagent to trap all possible radicals. This issue should be clarified. In addition, the reviewer believe that the concentration of radical species in aerosol would be very little compared to non-radical SOA products after 30 minute sampling. Please provide what are the fraction of radical species of the total aerosol products. 8. Page 23701, Line20-21, In Fig. 2(a), m/z 211 had higher intensity than m/z 130 as a new peak. Thus m/z 130 is not the highest one except m/z114 and m/z 226. 9. Page 23701, experimental section. The quartz filter material has the strong adsorption properties especially for semivolatile organic compounds. The possible artifact by adsorption of the gas-phase organic compounds on the quartz filter should be discussed. 10. Page 23701, Line 21-23, some peaks in the blank mass spectrum does not show in the sample mass spectrum. This should be clarified. 11. Figure 3. The mass fragmentation of 97, 84, 69, and 55 are very common fragmentation patterns of alpha-pinene oxidation products. The evidence to prove that m/z 130 is a OH radical trap adduct is weak. This can be also SOA products. The additional derivatization of adduct (e.g., Jose et al, Oxidative Stress Biomarkers and Antioxidant Protocols, p 89, 2002) is needed to prove the structure. 12. Page 23702, Line 5-7. Provide the brief explanation for why peaks into cluster represent possible DMPO adducts with reactive radical species. Since the cited paper shows similar patterns in the ESI-QTOF MS without radical species trap agent, it is hard to believe that DMPO adducts react with other than radical species. Specifically, oxidation product from the flow reactor within a short residence time and the high ozonolysis contribution on oxidation of alpha-pinene can be very different from products in the batch reactor (e.g., Teflon chamber). This should be clarified. 13. Page 23701, Table 1. The reviewer cannot understand why mass peaks in Table 1 are DMPS adducts other than SOA

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products. The more evidence is needed, although the mass interpretation is tentatively done. 14. Page 23702, MS2 fragmentation results. Without discussion of the life time of the RO radical and OH radicals in the aerosol sample in equations R4 and R5, the DMPO radical trap method cannot support the structure shown in MS2 fragmentation data. 15. Page 23703. Equations R6 and R7 are for the reactions in the gas phase. The authors mainly characterize the aerosol phase products. In order to explain the HO₂ contribution to formation of OH radicals in aerosol, the authors should explain how HO₂ radical is partitioned to the aerosol phase. HO₂ radicals would be very volatile due to the low MW (33). What is the chance to be found in aerosol for 30 minute sampling time. 16. Page 23703, Line 8-9. If DMPO/OOH is unstable and spontaneously transforms to DMPO/OH, then no m/z 146 can be identified. However, Fig.6 shows the m/z 146 indicating that DMPO/OOH is detectable. Please provide the stability of this DMPO/OOH compound during the analytical workup procedure prior to GC/MS injection. 17. Page 23704, Line 23-25. Why can the m/z 146 [DMPO-O-OH]⁺ provide the evidence of the presence of ROO radicals? Is there reaction of DMPO adduct with an oxygen molecule? 18. Page 23706, Line 12-13. Why does the residence time at 3.85 minute support that OH radicals are formed during the collection? The discussion should consider the long sampling time within 30 minutes and the possible artifacts by quartz materials. The 3.85 minute residence time is operational only for last seconds sampling. The OH radical has very short life time and is very powerful to react other organic species especially for 30 minute sampling time, although further aerosol phase reaction can be present forming OH radicals. 19. The implication of this study to actual atmospheric aerosol is needed.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 23695, 2009.

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