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Atmospheric Chemistry and Physics Discussions

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

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acp-2009-558 Detection and identification of radical species formed from α-pinene/ozone reaction using DMPO spin trap J. Pavlovic and P. K. Hopke

Response to Anonymous Referee #1 and #2

First of all, we would like to thank two reviewers for their time and useful technical comments. We will address the comments in sequential order as listed by Anonymous Referee #1. Response to major comments: a) Radical species should be identified rather than using an R for that purpose. If necessary, MS3 experiments should be performed in order to identify these species. We understand importance of identifying

structures of radical species formed from α-pinene/ozone reaction. Currently we are in process of analyzing the possible chemical structures of observable spin trap adducts and structures of captured radical species. In the present manuscript, we wanted to introduce the possibility of using spin traps, combined with tandem mass spectrometry, in atmospheric studies. Thus, we have presented preliminary radical identification results and MS2 fragmentations that confirm presence of DMPO adducts and distinguish between carbon- and oxygen- centered radical species. For some studies, that information might be useful. Further action: The reviewers found that the word "identification" in the title is associated with detailed structural identification of species and thus is not appropriate in the current manuscript. Have changed the title to: " Technical Note: Initial use of DMPO spin traps to detect radical species formed from the α-pinene/ozone reaction" Also, it should be noted this paper was provided as a "technical note" and not a full research article.

b) The fragmentation pathway of m/z 130 has already been described, either using FAB (JASMS 2001, 12, 1214) or ESI (Rapid Commun Mass Spectrom 2003, 16, 1934) as ionization methods and thus it is not necessary to describe it in detail again In our manuscript (Page 23702, line 12), we compared spectrum of DMPO-OH adduct (m/z 130) observed in our study with the work of Yang and coworkers (Rapid Commun Mass Spectrom 2007, 21, 107). Dominques et al. (2001) and Jurva et al. (2003) also gave detailed fragmentation patterns for m/z 130 (even in more detail) and we agree that those papers should be referenced in the present manuscript as well. Moreover, those papers (especially Dominques et al. (2001)) revealed the presence of some other ions that they observed in full MS (m/z 243 and m/z 259) and those ions were observed in our study as well. That helped to support our detection of OH particle-bound radicals. We still think that Figure 3 (MS2 fragmentation of DMPO-OH adducts) is useful and should be part of the manuscript. First, this is the first atmospheric chemistry application (to our knowledge) that use spin traps and tandem mass spectrometry in order to detect radical species and we wanted to show the similarity in DMPO-OH adducts formed under biological and atmospheric chamber conditions and similarity in their fragmentation patterns. Second, considering the very short life-time of OH radicals in the atmosphere it is useful to present that OH radical can be captured and detected using described methodology. Higher molecular weight radicals have longer life-times and the same method should work for them as well. Some readers (Referee #3 for example) will even need more evidence and more details that m/z 130 is DMPO-hydroxyl radical adduct and not some pinene oxidation product. Thus, in the revised manuscript, we included material about ions with m/z 243 and m/z 259 and their fragmentation patterns, because those ions are also evidence for the formation of spin adducts of hydroxyl radical with two molecules of DMPO. Third, it is always easier for readers, who did not have opportunity to read previous published papers, if fragmentation is described here without presenting the current method as something never done before. Further action: Reference other papers in manuscript. Page 23702, line 11: “The same fragmentation patterns and fragment ions presented in the Figure 3 were described in detail by Dominques et al. (2001), Jurva et al. (2003) and Yang et al. (2007). Those studies assigned the ion with m/z 130 to a DMPO adduct with hydroxyl radical (HOâĂć) and therefore, it is reasonable to believe that HO radicals were formed during α-pinene/ozone reaction and were captured by the DMPO spin trap.”

c) The absence of the DMPO-peroxyl adduct is not clearly justifiable since: it has been observed in several other studies using DMPO; and the peroxyl radical is formed as identified in the oxygen-centered species. The peroxyl (HO2) radical has very short life time and it is rapidly consumed in reactions with other HO2 radical (R6) or with alkyl-peroxyl (RO2) radical to form alkoxyl (RO) radicals. It can react with O3 as well to form HO radical (R5). Other studies that were able to detect HO2 radicals used closed systems where DMPO was able to react immediately with internally formed HO2 radicals. During the 30 min collection step in the present study, HO2 was probably lost in above mentioned reactions. Peroxyl radical adduct (DMPO-OOH) was identified in the present study as fragment of oxygen-centered species (during MS2) and collection time at this point does not have influence on its formation.

d) In a mass spectrum it is not possible to observe the loss of charged particle. A mono-charged particle always fragments into another charged particle (which is observed in the mass spectra) and a neutral (which is not observed)! In this manuscript several losses of protonated ions have been attributed in the interpretation of the mass spectra. The authors agree about mistakes mentioned by reviewers on several places in the manuscript as well as in table 1 and Figures 5, 6, and 7. Further action: Corrected Table 1 and Figures. Corrected also: 1. Page 23696, Line 17 2. Page 23703, Line 19 3. Page 23704, Line 4 4. Page 23704, Line 8 5. Page 23705, Line 6

e) In page 23702, line 13 it is stated “The relative intensity of the peak with m/z 130 compared to the other peaks upports the role. . .” The intensity of the ions in the MS spectrum is related to the relative abundance in the aqueous phase but also with the proton affinity and the number of species that are present. Therefore, caution should be present when referring to the quantitative nature of electrospray without the use of proper controls. The authors agree about the comment. Further action: Sentence (Page 23702, Line 13) is changed to: “The formation of DMPO-OH adducts and the presence of the peak with m/z 130 supports the role of the ‘hydroperoxide channel’ as an important pathway in monoterpene ozonolysis.”

f) In figure 5, the selection of the precursor ion (at m/z 268) is defective. The selected ion was at m/z 269 And minor concern: e) In figure 6- The selection of the precursor ions (at m/z 314) is defective. The presence of an ion at m/z 315 turns difficult the interpretation of this mass spectrum. The analyzed (by MS2 fragmentation) ions were at m/z 268, 298 and m/z 314. As can be seen in the revised Figure 2, the most abundant ions are in the m/z 250-350 range. The problems in Figure 4, 5, and 6 arose because the MS2 conditions during the fragmentation step were adjusted to show the parent ion isolation width (m/z) of 3. In that way, ions that differ by 3 in m/z ratio were also fragmented and that caused confusion in spectral interpretation. Further action: New experiments were done, where the isolation width (m/z) was set to 1 and the results are now presented on new Figures 4, 5, and 6. The text that explains those figures was also changed to reflect the new fragmentation results.

Minor concern: a) Page 2370, line 2. The specie at m/z 268 is not observed in the mass spectra The authors decided to magnify m/z range from 100 to 350 in Figure 1. That figure now has 3 parts: A- m/z 100-250; B- m/z 250-350 and C- blank. According to comments from Referee #3, instead of using DMPO, water and quartz fiber filter (QFF) as blank, we collected α-pinene for 30 min on QFFs and then treated it on the same way as samples. Results of those blank samples are presented in Figure 2C. Further action: Revised Figure 2.

Minor concern: b) Page 2370, line 8. Although possible, it is improbable to observe a protonated radical fragment ion when using electrospray as ionization method and low energy collision energies. Some exceptions are observable when analyzing aromatic compounds. The authors were guided by studies done by Guo et al. 2003 (JASMS, 14, 862-871; scheme 1, m/z 113 and m/z 98), Yang et al. 2007 (RCM, 21, 107-111; scheme 2, m/z 88) and some other that also observed formation of protonated radical fragment ions during ESI-MSn analysis. Without final structural identification of the observed radical species, the authors did not want to exclude any possibility for that formation. Further action: That sentence was changed to one that is more appropriate to new Figure 5.

c) Table 1 does not provide any useful information Table does not exist in current manuscript version.

d) The species described in figure 4 (m/z 131, 132) are not observed in the mass spectra. Figures 1 and 4 are now merged into a single figure (Figure 1). This is also the reason why all figure numbers are different than in previous version.

Again, we would like to thank both reviewers for their time and comments, and to ask them to read new manuscript version and consider it again for future publication in ACP.

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

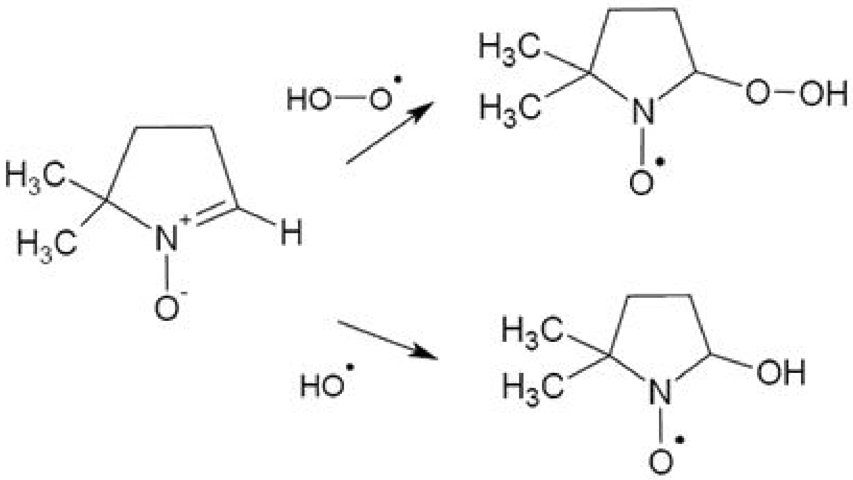

Fig. 1. Structures of DMPO and its hydroxyl and hydroperoxyl adducts

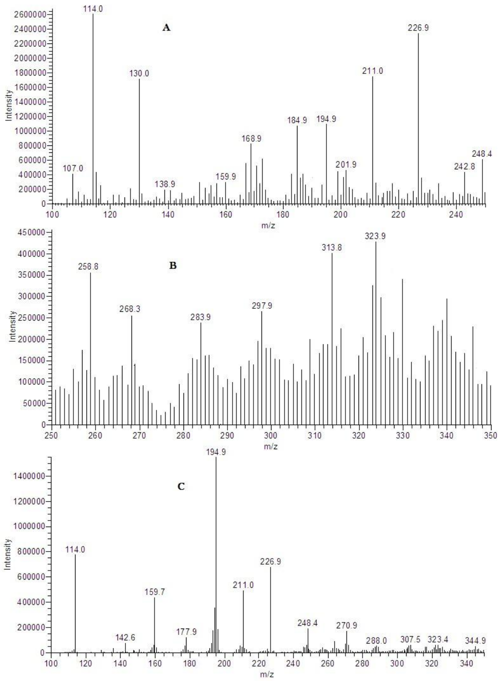

Fig. 2. Full MS of sample (a) m/z range 100-250; (b) m/z range 250-350 and (c) blank

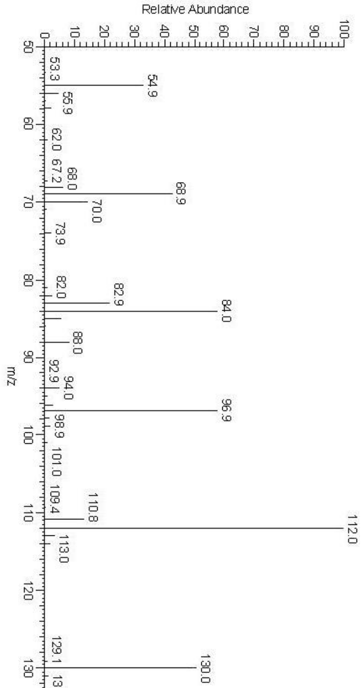

Fig. 3. MS2 spectrum of the adduct with m/z 130

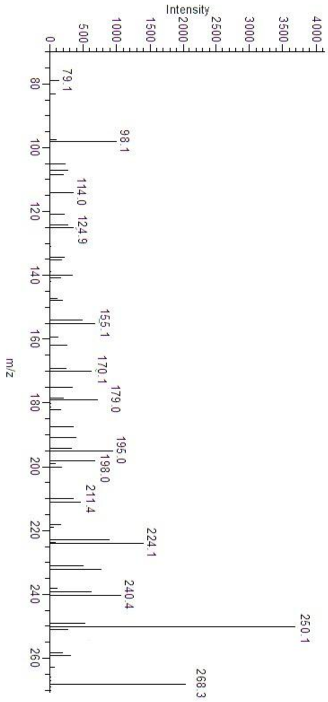

Fig. 4. . MS2 spectrum of the adduct with m/z 268

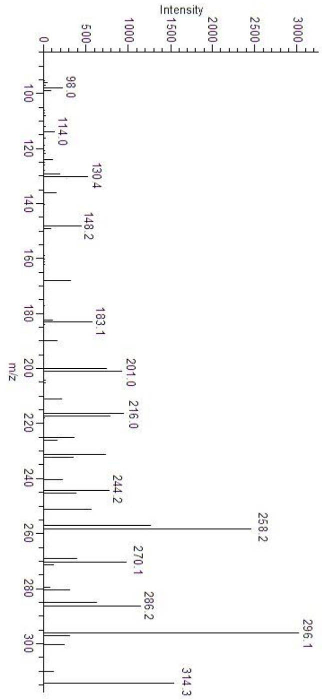

Fig. 5. MS2 spectrum of the adduct with m/z 314

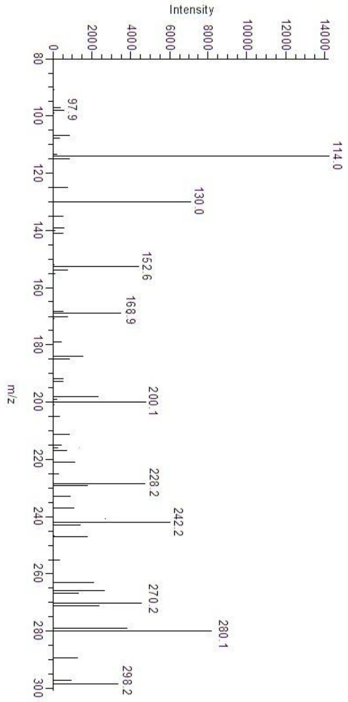

Fig. 6. MS2 spectrum of the adduct with m/z 298