Atmos. Chem. Phys. Discuss., 9, C9964–C9972, 2010
www.atmos-chem-phys-discuss.net/9/C9964/2010/

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

J. Pavlovic and P. K. Hopke

hopkepk@clarkson.edu

Received and published: 21 January 2010

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 #3

First of all, we would like to thank the reviewer for his time and useful technical comments. We will address the comments in sequential order as listed by Anonymous Referee #3. 1) Page 23696, introduction part. There are unnecessary information in the introduction. For example, equation R1 is the very commonly known inorganic gas-phase chemistry but not importantly utilized in this paper for product identification.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

The reviewer think that the authors should provide the better flow and include reactions that are necessary to explain product identification With this reaction (R1) the authors wanted to illustrate formation of OH radicals in the upper troposphere. It is removed from the manuscript.

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. Purpose of this study was not to capture and detect OH radicals (although they were detected using described methodology) but to detect other organic radicals formed from the same reaction and those radicals are expected to have longer life-time. The authors also did not want to imply that captured radical species were primarily formed radicals (reactions R2 and R3). Products of R2 and R3 reaction can further react and form new radical species that are also harmful and probably more likely to be found under realistic atmospheric conditions where we rarely have the opportunity to capture the initially formed products. The purpose of this study was to demonstrate the potential spin traps provide in studies of atmospheric reaction products.

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. “Experiments were carried out at 296±2 K and relative humidity 5-30%.” This sentence is included in revised manuscript.

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 concnetration of alpha-pinene rather tha placing into the aerosol. The reaction R3 is not the only source of OH radicals. Docherty et al. (2005, EST, 39, 4049-4059) found (after 60-90 min filter collection) that SOA, that originates from α-pinene/O3 or β-pinene/O3 reaction, is comprised from organic peroxides ($\sim$47% and 85%, respectively). Organic peroxides can be also important source of OH radicals as discussed in the manuscript (Page 23702). Chen and Hopke (2009, Indoor Air; 19, 335-345) suggest that we could estimate OH formation coming from the pinene ozonolysis reactions. The authors also talk with caution about where OH radicals were formed under described experimental conditions and in the conclusions, you can find sentence: “It is still unclear whether the OH radicals are formed during condensation processes directly from the reaction chamber or they are generated afterwards by reactions on filters during the collection interval”

5) Page 23700, experimental section. The authors have used the 23 mm quartz filter for the aerosol sampling. In general the quarts 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. In experimental procedure the authors used quartz fiber filters (QFF) previously baked 16 hours at 550°C. In the manuscript we provided evidence that OH radicals were not formed when the blank QFF was treated on the same way as sample (no peak at m/z 130) and no other peaks that we analyzed in our study and assigned to organic radicals. In the revised manuscript we also included: “To get insight into possible artifacts and to eliminate them, as a negative control (blank), a pre-baked quartz

fiber filter exposed to a flow of α-pinene (without ozone) for 30 min, was treated on the same way as sample and analyzed under the same instrumental conditions."

6) Page 23701, experimental section. The appropriate blank should be the quartz filter exposed to the bath air or alpha-pinene without ozone for the 30 minutes We did the experiments with QFFs exposed to flow of α-pinene for 30 min and included it in experimental procedure. The reviewer can see that there are also no peaks with m/z 130 (possible OH radical adducts) and no peaks at m/z 268, m/z 298 and m/z 314, that we analyzed as possible organic radical adducts.

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 reviwer believe that the concnetration 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. The authors did not capture only OH radicals, but also RO and RO2 radicals in the aerosol phase (look chapters 3.3. and 3.4 in the manuscript). At this point, we have not structurally identified them. We provided information how to distinguish between C- and O- centered radicals and what the probable molecular weights of captured radical species are likely to be. We are currently unable to provide information what fraction of total SOA belongs to radical species. There is no method available that can quantify total radical species. Our group has developed method for total ROS quantification (Venkatachari and Hopke, 2005, J. Atmospheric Chem 50, 49-58), but this method measure H2O2 and organic peroxides as well and is not applicable for measurement of only radical species. Furthermore, radical species quantification was not subject of present study. We would hope to move to quantitative estimates in the future.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

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. Corrected in the revised manuscript.

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.

We tested this by having examined the âĹİ-pinene blank as noted above.

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. In revised manuscript, new blanks were presented as suggested by reviewer and in new results we did not find that differences between blank and sample mass spectra.

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. The authors carefully checked literature data and studies done by Dominques et al. (2001, Journal of American Society for Mass Spectrometry, 12, 1214-1219), Jurva et al. (2003, Rapid Communications in Mass Spectrometry, 16, 1934-1940) and Yang et al. (2007, Rapid Communications in Mass Spectrometry, 21, 107-111). Those studies also found hydroxyl radical adducts at m/z 130 and presented identical MS2 fragmentation results of that parent ion. Each fragment ion found in those MS2 spectra is also found in the present study. Moreover, the most abundant ion with m/z 112 is also the most abundant ion in the present study with 100% relative abundance. “Moreover, full mass spectrum (Figure 2a and 2b) revealed the presence of ions with m/z 243 and m/z 259. After MS2 fragmentation, detected fragments for the parent ion with m/z 243 were: m/z 130 and

m/z 114, and for the parent ion with m/z 259 were: m/z 241, m/z 146, m/z 130 and m/z 114. Those ions and the same fragmentation results were found in the study done by Dominques and co-workers (2001). In that study the ion of m/z 243 was identified as the result of formation spin trap adducts of a hydroxyl radical with two molecules of DMPO [(2DMPO+O)+H]+, and the ion with m/z 259 as spin trap adduct of two hydroxyl radicals with two molecules of DMPO [(2DMPO+2O)+H]+". That is one additional confirmation for existence of OH radical adducts. In the cited literature the authors did not find any information about alpha-pinene SOA product with m/z 130. For some alpha-pinene SOA products after MS2 fragmentation we found fragments with m/z 57, 59, 71, 99 after ESI(-)/MS/MS (Warscheid and Hoffmann, 2001, Rapid Communications in Mass Spectrometry, 15, 2259-2272; Warnke et al., 2006, Anal. Bioanal Chem, 385, 34-45, etc.), but the authors were not able to find fragments with 97, 84, 69, and 55 for the ESI(+)/MS/MS.

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-QROF 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. The further explanation is included in revised manuscript: "Similar patterns in the ESI-QTOF mass spectrum were found by Tolocka et al. (2004) for SOA produced by reaction of α-pinene and ozone without a spin trap agent. Those experiments were performed in a batch reactor (Teflon bag) and oxidation products were analyzed after 1 hour reaction. Residence time in the present study for the described flow reactor is much shorter (3.85 min) and expected reaction products are more in the mass range of first generation α-pinene oxidation products (monomer species) than in the range of possible dimmer, trimer, and tetramer species observed by Tolocka et al (2004). Two years later paper by Tolocka et al. (2006) investigated products of the same reaction after 3 s and 22 s

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

reaction time using flow-tube reactor. The intensities measured in the PIAMS spectra of monomer species were about 100 times more intensive than intensities measured for possible dimmer species. The residence time in the present study is closer to that later paper and measured intensities in mass spectra of ions with m/z 250-350 are about 10 times less intensive than intensities for the ions with m/z 100-250. Higher intensities in that higher mass range (m/z 250-350) than observed by Tolocka et al. (2006) can be due to formation of DMPO adducts (spin trap + radical species with m/z similar to that of monomer species), longer residence time, and also some possible further reactions on filters during 30 min collection interval. In the present work, some peaks into clusters are tentatively identified as possible DMPO adducts with reactive radical species based on their fragmentation patterns after MS2 experiments.

13) Page 23701, Table 1. The reviewer cannot understand why mass peaks in Table 1 are DMPS adducts other than SOA products. The more evidence is needed, although the mass intepretation is tentatively done. In the revised version of the manuscript, the authors removed table 1 and analyzed and presented MS2 fragmentation only for ions with m/z 268, m/z 298 and m/z 314.

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. Brief discussion is provided: “The α-hydroxyhydroperoxides are found in the aerosol phase as first generation products in many studies (Winterhalter et al., 2003; Warscheid and Hoffmann, 2001). After its decomposition, formation of ROâĂć and HOâĂć radicals can take place also in the aerosol phase. Considering short life time of ROâĂć and HOâĂć radicals and long collection interval it can not be excluded that those radicals are formed during the collection or extraction process as well and not directly in the flow-reactor.”

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 partition 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.

The HO2 radicals would be less volatile than OH and they would certainly have a moderate Henry's law constant for partitioning into the polar organic droplets that are being formed in this system. We are not looking at adsorption onto solid particles, but absorption into liquid droplets.

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. The authors mentioned that spontaneous transformation as possibility described by Bacic et al. (2008). There were studies that were able to detect and measure DMPO/OOH adducts. On the Figure 6, m/z 146 represent fragment formed during MS2 fragmentation inside of ion trap.

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? The DMPO-O-O-R adducts can experience neutral loss of R molecule and in that case [DMPO-O-OH]+ will show up in MS2 spectra of that adduct.

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. That sentence is deleted.

19) The implication of this study to actual atmospheric aerosol is needed. As the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

authors wrote in the introduction part: “However, to date, there have been no studies performed to analyze and identify reactive radical species, other than HOâĂć and HOOâĂć radicals, formed either from monoterpene/ozone reactions or under ambient conditions.”

Again, we would like to thank the reviewer for his time and comments, and to ask him to read new manuscript version and consider it again for future publication in ACP.

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