

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 #1

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The manuscript “Detection and identification of radical species formed from α -pinene/ozone reaction using spin trap” by J. Pavlovic and P.K. Hopke describes the use of tandem mass spectrometry with a spin trap for detecting radical species from α -pinene. The identification of the radical species consists in describing if they are carbon centered or oxygen –centered (peroxyl). No actual identification of the radical species is performed. A portion of this manuscript is used in describing the fragmentation mechanism of DMPO hydroxyl (m/z 130) and discussing the absence of the peroxyl adducts (m/z 146). This manuscript has serious flaws concerning the interpretation of the mass spectra and the identification of the radical species. Therefore I recommend that this manuscript, at the present form, should not be published. How-

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ever, if the authors can provide a positive identification of the radical species, this could be considered for publication. Major concerns: 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. 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; 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. 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. e) In page 23702, line 13 it is stated “The relative intensity of the peak with m/z 130 compared to the other peaks supports 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. f) In figure 5, the selection of the precursor ion (at m/z 268) is defective. The selected ion was at m/z 269 Other minor concerns: a) Page 2370, line 2. The specie at m/z 268 is not observed in the mass spectra 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. c) Table 1 does not provide any useful information d) The species described in figure 4 (m/z 131, 132) are not observed in the mass spectra. 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.

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