

***Interactive comment on* “Gas phase formation of extremely oxidized pinene reaction products in chamber and ambient air” by M. Ehn et al.**

Anonymous Referee #2

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General Comments The manuscript describes ambient air and chamber studies using APi-TOF-MS (Atmospheric Pressure interface- Time of Flight Mass Spectrometry) measuring naturally charged air ions. Mass spectral pattern of α - and β -pinene chamber studies and night time ambient measurements at Hyytiälä are remarkably similar, both showing high molecular weight naturally charged air ions. High resolution enables to determine the elemental composition of those ions which seem to cluster with NO_3 – and fluorinated acids in the chamber studies. Results from both, chamber and ambient air measurements, show remarkably high oxidized compounds with high O/C ratio and high H/C ratio, e.g. the compound $\text{C}_{10}\text{H}_{14}\text{O}_{13}$. Indeed the results reported are highly interesting, although no conclusive explanation of the possible structures of the compounds are given. The authors speculate on geminal diols and hydroperoxides to explain the experimental findings, however, several open questions remain. Our ma-

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major concern is that there exists no potential reaction pathway to incorporate so many oxygen atoms into the carbon skeleton, without breaking the molecules apart (even if gem-diol and hydroperoxides are considered). However, for the observations reported even very small amounts of products (i.e. very minor formation yields of side products) would be enough to explain the experimental findings. Thus, the reported results might stimulate further detailed products analysis also on highly oxidized products. Consequently, the paper fits perfectly to the scope of the journal and it will contribute to understand the role of organic molecules in new particle formation. The paper is well written and might magnify the interest of the community towards organic speciation. We highly recommend publishing the manuscript in ACP, however, have some minor comments on the manuscript.

Comments: Page 4595: “Particularly water, which is believed to be clustered with most of the ions at ambient conditions, is typically so weakly bound that it evaporates from the ions before reaching the TOF region”. Is that pure speculation or based on observations ? What if water molecules stabilize the cluster itself (creating an organic-water-NO₃-cluster) or in other words: without non-covalently bonded water the cluster (or more specific the negatively charged cluster) would not be stable ? The argument that the major peaks are separated by 16 Th (O) and not 18 Th (H₂O) (page 4606) are not absolutely convincing since such a separation would not be expected when the underlying compounds would have different oxidation states, however, would all contain water (as a cluster stabilization precondition so to say). Obviously such an assumption is speculation too, however, would slightly reduce the pressure to define chemical reaction mechanisms and thermodynamically stable structures for intact C₁₀-backbone oxidation products with the composition suggested.

Page 4597: Allowing the exponent n in Eq. (1) to vary, greatly improved the fit over the desired range. What does that mean instrumentally ?

P. 4599, L. 24: During which season were the measurements performed? Page 4603, L. 7: The HOMs have lower proton affinities ? You mean lower gas phase acidities !?

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P.4605, L. 10: replace the capital 's' in HOMS. P. 4606 L. 18: It would be advantageous to include citations of papers which indeed observed hydroperoxides in biogenic SOA (e.g. Chen et al., 2011, ES&T, 45 (11), 4763-4770; Reinnig et al., 2009, Rapid Comm. Mass Spectrom., 23 (11), 1735-1741))

P.4609, eq. (6): $2.78 \cdot 10^6 \text{ cm}^{-3}$

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 4589, 2012.

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