

Interactive comment on “Phase partitioning and volatility of secondary organic aerosol components formed from alpha;-pinene ozonolysis and OH oxidation: the importance of accretion products and other low volatility compounds” by F. D. Lopez-Hilfiker et al.

Anonymous Referee #2

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General Comments:

This paper describes a set of experiments that investigated the gas-particle partitioning and volatility of SOA formed from the reactions of alpha-pinene with O₃ and OH radicals. The experiments were conducted in glass and Teflon reaction vessels and the gas and particle composition and SOA volatility were analyzed using a Filter Inlet for Gases and Aerosol coupled to a high resolution chemical ionization mass spec-

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rometer (FIGAERO HR-ToF-CIMS) and also an Aerosol Mass Spectrometer (AMS). Acetate ions were used for ionization, which is fairly specific for carboxylic acids and similar compounds. The results indicate that a large fraction of the SOA is composed of carboxylic acids and similar compounds, and that the SOA contains both monomers and oligomers, with the latter decomposing at high temperatures to form the detected monomers. When effects of oligomers on observed gas-particle partitioning are accounted for in a gas-particle partitioning model the agreement between the measurements and model are significantly improved. The results provide important new insights into SOA composition, particle phase reactions, SOA volatility, and gas-particle partitioning. The paper should certainly be published in ACP, although I have a few comments and suggestions the authors should first consider.

Specific Comments:

1. Page 4470, lines 19–24: Do the authors have any idea about wall losses of gaseous organic compounds in the stainless steel line or Teflon line?”
2. Page 4472, lines 15–20: I’m a little confused by this discussion about detection of compounds containing acyl groups. Are the authors saying that all compounds with an acyl group: carboxylic acids, peroxyacids, diacylperoxides, esters, aldehydes, ketones, acylperoxynitrates, etc., have detection sensitivities approximately similar to formic acid? This could be stated more clearly by saying more specifically which compounds they are talking about. Many readers may not know that acyl group-containing compounds is a very large class of compounds.
3. General comment beginning with Section 3.2: I encourage the authors to read the paper by Docherty et al., ES&T,39, 4049–4059 (2005). They conducted a very similar study on SOA formed from monoterpene ozonolysis using temperature-programmed thermal desorption with electron ionization (TPTD-EI) and reached many of the same conclusions as this study regarding monomers and oligomers in SOA and the volatility distribution, and also showed that much of the SOA was organic peroxides.

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4. General comment beginning with Section 3.2: The discussion regarding oligomer decomposition to form monomers could probably be explained using a plausible mechanism based on what is known about the chemistry of these compounds. To my knowledge, the only reversible bimolecular reactions that are likely to form carboxylic acids involve the decomposition of esters to a carboxylic acid + alcohol + water. Although carboxylic acids that contain an aldehyde group can cyclize to form a hydroxyfuranone, which can then ring-open to form the carboxylic acid-aldehyde, the corresponding bimolecular reactions are unlikely due to entropy effects. Considering, however, that ester decomposition involves acid catalyzed hydration, and that no strong acid is present in the system and water is probably lost from the particles during sampling and in the early stages of heating, it seems unlikely that the carboxylic acids observed at high desorption temperatures have come from ester decomposition. A more likely scenario is that the SOA contains peroxy-pinic acid, peroxy-norpinic acid, peroxy-pinalic acid, and peroxy-norpinalic acid, and that these peroxide compounds react in the particles with pinonaldehyde (a major reaction product) to form the corresponding low volatility acylperoxyhemiacetals, which thermally decompose upon heating to pinic acid, norpinic acid, pinalic acid, norpinalic acid, and pinonic acid. See general mechanism in Ziemann and Atkinson (2012) in reference list and Docherty et al. (2005) referenced above, which draws from the alpha-pinene ozonolysis mechanism in Jenkin, ACP, 4, 1741-1757 (2004). The authors may also want to look at the paper by Strollo and Ziemann, Atmos. Env., 77, 534–543 (2013), which uses TPTD-EI to demonstrate the effects of reversible and irreversible oligomerization reactions on SOA formation and volatility for a different system.

Technical Comments:

1. Page 4465, line 16: Probably should be “high molecular weight organics” or “large organic molecules”.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 4463, 2015.

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