Review of ‘Phase partitioning and volatility of secondary organic aerosol components formed from α-pinene ozonolysis and OH oxidation: the importance of accretion products and other low volatility compounds’

This study utilized the Filter Inlet for Gases and AEROsols (FIGAERO), coupled with the high resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS), to explore the chemical composition and volatility of SOA generated from the α-pinene ozonolysis and OH oxidation in a glass chamber. This novel particle sampling and analysis technique showed its strong power in the molecular characterization of particle-phase organic components: in addition to the previously identified products i.e., small carboxylic acids mostly, a spectrum of high molecular weight products, with assigned molecular formulas, is identified as well via a thermal desorption program. Overall, this study is a great complement to previous publications that employ LC/MS as a common analytical technique, and together, sheds light on the question of the SOA composition. Regardless of the fact that chemical structures of identified species are still unknown, the current observations are of significant value. A concern, however, is that the authors’ primary conclusions regarding the mass fraction of acyl-containing compounds in the particle phase and the agreement between measured and modeled gas-particle equilibrium partitioning depends, at least to a certain degree, on a variety of factors in the experimental conditions, data processing protocols, and model parameterization. Uncertainties arising from these processes can potentially mask the current conclusions. To verify the reliability and generalizability of these results, systematic sensitivity tests in both experiments and simulations could be carried out, which might be beyond the scope of the present study. Nevertheless, I would suggest the authors soften the conclusions by considering and discussing the factors that might bias their conclusions.

Major comments:

1. One of the conclusions is that the particulate organic compounds detected by FIGAERO HR-ToF-CIMS can explain 20-50% of organic aerosol mass measured by

AMS. This conclusion is drawn by 1) applying an instrument sensitivity of formic acid uniformly to the entire spectrum to obtain the mass concentration of each ion in the particle phase, and 2) measuring the overall organic mass by AMS. Uncertainties need to be given to constrain the calculated fraction, 20-50%, of identified products in α-pinene-derived SOA. Specifically, what is the collection efficiency of the ammonium sulfate seed particles parameterized in AMS? Is it the default value 0.5 that is used for filed environments? As the authors note in the experimental methods section, effloresced AS particles were used in the chamber experiments at RH varying from 35% to 65%. Could dry particles exhibit different bounce behavior than hydrated particles when impacting the heater? Can recent studies that focus on AMS collection efficiencies in chamber and filed measurements help constrain the CE value used here (Matthew et al., AST, 2008; Middlebrook et al., AST, 2012)? Another way is to derive the total organic mass concentration from the SPMS measured total particle volume, together with the AMS measured org/sulfate ratio. Would that give a confirmatory result?

2. The authors suggest that equilibrium gas-particle partitioning is applicable to chamber conditions by showing in Figure 4 decent agreement in the particle-phase fractions of pinic acid, pinonic acid, and norpinic acid between measurements and predictions. There are too many uncertainties in both modeling and measurements to draw this conclusion very firmly. From the modeling perspective, the prediction of vapor pressure from different estimation methods varies by orders of magnitude (see comparison in Compernolle et al., ACP, 2011). This introduces large uncertainties in the predicted particle-phase fraction of compounds (F_p). Next, what measurement is used here to yield C_OA? Do the AMS measurements agree with those from SMPS? These issues need to be clarified. For the experimental measurements, my impression is that the compound particle-phase fraction (F_p) is calculated directly from the gas/particle-phase measurements. How do particle and vapor wall losses influence the calculated F_p? The turbulence mixing status is influential in determining the wall loss rate for both particles and vapors. As in Ehn et al. Nature, (2014), the wall loss rate of ELVOC is predicted as ~ 0.011 s^{-1} in an actively mixed reactor, for which that the lifetime of ELOVC with respect to wall loss is only 1.5 min, much less than the residence time of 50 min in the glass chamber.

Minor comments:

1. Page 4472, Line 10-15: As shown in the calibration experiments, benzoyl peroxide was detected as the benzoate anion, and less efficiently, benzoic acid. A recent study also found the transformation of isoprene-derived peroxides (ISOPOOH) to carbonyls (MACR and MVK) in GC and PTR-MS (Rivera-Rios et al., GRL, 2014). If the decomposition of O-O bounds occurs during the thermal desorption process, how would the authors estimate the fraction of peroxide functionality that is originally in the particles? Another related question, for each ion detected in the particle phase, is there a corresponding ion with the same molecular assignment detected in the gas phase?

2. Page 4473, Section 3.1: The initial concentrations of a-pinene and O_3, and the amount of a-pinene reacting with O_3 and OH radical at the end of the experiment need to be given. Also, could the authors estimate the overall OH exposure in the chamber? If the reaction timescale is the same as the residence time, 50 min, the existence of a substantial amount of high molecular weight organic products suggests an intense reaction pathway either in the gas phase or the particle phase.

3. Page 4482, Line 6-7: Recent evidence has shown that a-pinene-SOA might be semi-solid. Might be helpful to cite here (e.g., Renbaum-Wolff et al., PNAS, 2013).