

[Interactive
Comment](#)

Interactive comment on “Dependence of particle nucleation and growth on high molecular weight gas phase products during ozonolysis of α -pinene” by J. Zhao et al.

Anonymous Referee #2

Received and published: 2 June 2013

In the manuscript the authors report on measurements of gas phase products of α -pinene ozonolysis and nanoparticle (>10 nm) formation under dry and low NO_x conditions. Their results showed a high correlation ($r > 0.5$, r is the correlation coefficient) of category I product concentration with the concentration of nanoparticles of size 10–20 nm. Similarly, a high correlation was also observed for category II product concentration with the concentration of nanoparticles of size larger than 20 nm. No correlation ($r \approx 0$) was observed for category III product with nanoparticles of all sizes. The categories I, II and III, had the mass ranges of 430–560 amu, 140–380 amu, and 140–380 amu, respectively. On the basis of their observations, the authors postulated that cat-

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

[Discussion Paper](#)



egory I products contribute to early growth (or nucleation), while category II products contribute to later stage growth. While the manuscript is reasonably well written, there are several aspects that the authors would need to address before this work can be considered for publication in ACP. (1) On page 9334 line 15, the authors mentioned the growth rate enhancement factor Γ . Is Γ also concentration dependent? For example, a higher concentration of organics results in the larger value of Γ . Similarly, a lower sulfuric acid concentration results in larger Γ value. As a result, a comparison of the Γ value under different experiments of different concentrations may be less meaningful. (2) On page 9335 line 7, the authors claimed that the category I products are highly oxidized and high molecular weight compounds (or high molecular weight multifunctional, HOM). Since $\text{NO}_3\text{-(HNO}_3\text{)}$ is used as reagent ion in the detection, carboxylic acids could not be detected, because the proton affinity of carboxylate is larger than that of nitrate. Which category of compounds does HOM belongs to, polyol? Can the authors provide any speculation? (3) Still on page 9335 line 14, the authors mentioned that the category I products likely have even lower saturation vapor pressures than those (10-11 atm=0.01 ppb for category I, 10-9 atm=1 ppb for category II) estimated in Winkeler et al. (2012). The authors would need to provide some value as Winkeler et al. (4) On page 9336, the authors mentioned carboxylic acids are likely one of the products twice on lines 16 and 27. It is worthy pointing out that carboxylic acids alone may not be able to explain the early growth of nanoparticles smaller than 10 nm. This may not be a definite statement because most of the saturation vapors of carboxylic acids in the literature are highly uncertain. Based on the VBS formulation,

$$f_i = 1 / (1 + (C_i^* / C_{OA})(1.1)C_{OA}) = \sum_i (i = \text{allbins}) f_i C_i (1.2)$$

Where f_i is the fraction of i th bin in aerosol phase; C_i is the total concentration in i th bin; C_i^* is the saturation vapor (volatility) of i th bin; C_{OA} is the total concentration of aerosol phase. With C_i and C_i^* given, the equation (1.1) and (1.2) can be solved iteratively for f_i . If carboxylic acids are the only low volatility products and other products are higher in volatility, based on the equations (1.1) and (1.2) there will be no early

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



growth since C (carboxylic acids) in the manuscript is on order of 0.01 ppb level, much lower than the C^* (carboxylic acids) reported in the literature (0.1–1 ppb). Therefore, there must be other even lower volatility products ($C^* < 0.01$ ppb) to cause co-partition of carboxylic acids (by increasing COA will cause co-partition). These compounds are probably category I compounds. All of the above reasoning is based on the current literature value for C^* of carboxylic acids. Of course, if the literature is invalid, the above reasoning needs to be modified. Also, particle-phase reactions, such as acid-catalyzed or hydration reactions, may lead to non-volatility products, as previously demonstrated on bulk-phase surfaces and nanoparticles (i.e., Zhao et al., *Geophys. Res. Lett.* 32, L09802, doi:10.1029/2004GL022200, 2005; Zhao et al., *Environ. Sci. Technol.* 40, 7682, 2006; Wang et al., *Nature Geosci.* 3, 238, 2010). Such an aspect needs to be adequately discussed in their paper.

[Interactive comment on Atmos. Chem. Phys. Discuss.](#), 13, 9319, 2013.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)