

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.

J. Zhao et al.

zhaoj@umn.edu

Received and published: 21 June 2013

The authors would like to thank the reviewer for valuable comments. The reviewer's comments are addressed point by point below.

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 value under different experiments of different concentrations may be less meaningful.

C4008

We agree. The cited reference and the following relevant sentence on p 9334 was deleted, “A recent chamber experiment of α -pinene photo-oxidation (Riccobono et al., 2012) showed that organic vapors contribute significantly even for particles close to 1.5nm (a growth rate enhancement factor Γ of about 3) even at the sulfuric acid concentrations of mid-106 cm⁻³.”

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 NO₃-(HNO₃) 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?

We do not agree with the reviewer that carboxylic acids could not be detected with NO₃-(HNO₃) as the reagent ion. The proton affinities of some carboxylates (e.g., oxalic acid: 322.6 kcal mol⁻¹; malonic acid: 318.2 kcal mol⁻¹) are smaller than that of the nitrate (323.5 kcal mol⁻¹) (Ehn et al., 2010). In fact, we carried out experiments that have shown that the Cluster CIMS can detect oxalic acid and malonic acid when the nitrate dimer ion is used as the reagent ion. It is possible that detection sensitivities would increase if a reagent ion (e.g., acetate dimer ion) with a higher proton affinity than nitrate dimer was used. Because the Cluster CIMS only has a mass resolution of unit amu, we cannot definitely determine the structures of category I products. A similar chamber study of ozonolysis of α -pinene (Ehn et al., 2012) has postulated that those high molecular species are highly oxidized multifunctional compounds and they may contain carboxylic functional groups. The proton affinities of the category I anions are not known, but they are likely lower than that of nitrate dimer ion because they were indeed measured with the nitrate dimer ion.

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

C4009

authors would need to provide some value as Winkeler et al.

We cannot provide accurate vapor pressures for both category I and II products based on the current data. However, we estimate a saturation vapor pressure of about 10-14 to 10-12 atm for category I products assuming a saturation concentration of about 105-107 cm⁻³. We modified the sentence as "The highly oxidized Category I products likely have even lower saturation vapor pressures (~ 10-14 - 10-12 atm) than those estimated in Winkler et al. (2012) due to their higher molecular weights and higher oxygen contents."

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. "... ..". 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.

As mentioned above (#3), we believe that the category I products are likely highly oxidized multifunctional compounds that may contain carboxylic functional groups rather than mono carboxylic acids themselves. Hence they might have lower saturation vapor pressures than mono carboxylic acids. We cannot accurately measure the saturation vapor pressures of those compounds. It is possible that their vapor pressures are in the 10-14-10-12 atm range (see #3 above). We also do not exclude the possibilities of the contributions from other pathways such as heterogeneous particle phase reactions.

C4010

Two sentences were added on p.9336 after "The identification of by Winkler et al. (2012).", "Those compounds may contribute to particle growth by particulate phase reactions such as acid-catalyzed reactions or polymerization (e.g., Wang et al., 2010; Zhao et al., 2006; Zhao et al., 2005; Hall and Johnston, 2012a; Hall and Johnston, 2011). Alternatively, reactions between carboxylic acid and basic gases on or within freshly nucleated particles may also contribute to nanoparticle growth (Barsanti et al., 2009; Smith et al., 2010; Yli-Yuuti et al., 2013)."

References:

Barsanti, K. C., McMurry, P. H., and Smith, J. N.: The potential contribution of organic salts to new particle growth. *Atmos. Chem. Phys.*, 9, 2949-2957, 2009.

Ehn, M., Junninen, H., Petäjä, T., Kurten, T., Kerminen, V.-M., Schobesberger, S., Manninen, H. E., Ortega, I. K., Vehkamäki, H., Kulmala, M., and Worsnop, D. R.: Composition and temporal behavior of ambient ions in the boreal forest. *Atmos. Chem. Phys.*, 10, 8513–8530, 2010.

Ehn, M., Kleist, E., Junninen, H., Petäjä, T., Lonn, G., Schobesberger, S., Dal Maso, M., Trimborn, A., Kulmala, M., Worsnop, D. R., Wahner, A., Wildt, J., and Mentel, Th. F.: Gas phase formation of extremely oxidized pinene reaction products in chamber and ambient air, *Atmos. Chem. Phys.*, 12, 5113–5127, 2012.

Hall, W. A. and Johnston, M. V.: Oligomer content of alpha-pinene secondary organic aerosol, *Aerosol Sci. Technol.*, 45, 37-45, 2011.

Hall, W. A. and Johnston, M. V.: Oligomer formation pathways in secondary organic aerosol from MS and MS/MS measurements with high mass accuracy and resolving power, *J. Am. Soc. Mass Spectrom.*, 23, 1097-1108, 2012a.

Smith, J. N., Barsanti, K. C., Friedli, H. R., Ehn, M., Kulmala, M., Collins, D. R., Scheckman, J. H., Williams, B. J., and McMurry, P. H.: Observations of aminium salts in atmospheric nanoparticles and possible climatic implications. *Proc. Natl. Acad. Sci.*, 107,

C4011

6634-6639, 2010.

Wang, L., Khalizov, A.F., Zheng, J., Xu, W., Ma, Y., Lal, V., and Zhang, R.Y.: Atmospheric nanoparticles formed from heterogeneous reactions of organics. *Nat. Geosci.* 3, 238-242, doi: 10.1038/NGEO778, 2010.

Winkler, P. M., Ortega, J., Karl, T., Cappellin, L., Friedli, H. R., Barsanti, K., McMurry, P. H., and Smith, J. N.: Identification of the biogenic compounds responsible for size-dependent nanoparticle growth, *Geophys. Res. Lett.*, 39, L20815, doi:10.1029/2012GL053253, 2012.

Yli-Juuti, T., Barsanti, K., Hildebrandt Ruiz, L., Kieloaho, A.-J., Makkonen, U., Petäjä, T., Ruuskanen, T., Kulmala, M., and Riipinen, I.: Model for acid-base chemistry in nanoparticle growth (MABNAG). *Atmos. Chem. Phys. Discuss.*, 13, 7175-7222, 2013.

Zhao, J., Levitt, N. P., Zhang, R., and Chen, J.: Heterogeneous reactions of methylglyoxal in acidic media: implication for secondary organic aerosol formation. *Environ. Sci. Technol.*, 40, 7682-7687, 2006.

Zhao, J., Levitt, N. P., and Zhang, R.: Heterogeneous chemistry of octanal and 2, 4-hexadienal with sulfuric acid. *Geophys. Res. Lett.*, 32, Art. No. L09802, 2005.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 13, 9319, 2013.