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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Campholenic aldehyde ozonolysis: a possible mechanism for the formation of specific biogenic secondary organic aerosol constituents" *by* A. Kahnt et al.

Anonymous Referee #2

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Overall Comment and Recommendation

The present study examines how the ozonolysis of campholenic aldehdye might be a possible source of previously measured alpha-pinene-derived SOA constituents found in ambient aerosol samples collected from a number of forested field sites. Importantly, the authors synthesize campholenic aldehyde in high-purity (98% according to GC/MS only) to be used in their experiments described here. This aspect of their study is transformative since organic synthesis of potential critical intermediates to SOA formation is lacking in atmospheric chemistry and needs to be more seriously considered (in the opinion of this reviewer) in future studies. The challenge of course still remains

in convincing our organic synthesis colleagues to synthesize small organic molecules. The campholenic aldehyde + O3 experiments are systematically carried out in the 19-m3 LEAK chamber at 50% RH and 21 degrees C. 60 ppb of O3 was used in these experiments. This manuscript is extremely well written and the results are carefully described and related to prior work. Furthermore, the analytical techniques (i.e., LC/ESI-MSn) applied here are well described and utilized by this group. Besides having a few questions outlined below related to their experimental/analytical approach, this work is certainly publishable in Atmospheric Chemistry and Physics once they address these questions. Furthermore, my only major question I have is related to the formation of campholenic aldehyde. The main mechanism the authors seem to consider is the heterogeneous reaction of alpha-pinene oxide on acidic aerosols (Figure 2a). My only concern with this mechanism is would this be the main mechanism to occur in atmospheric aerosols, as many groups find that when they try to estimate aerosol acidity by E-AIM (Simon Clegg et al.) or charge balance approaches that atmospheric aerosol appear to be more or less neutralized? Furthermore, alpha-pinene oxide is considered a minor product based on recent work by Eddingsaas et al. (2012, ACP) and based on past work conducted by some of the authors present on this manuscript. Thus, I wonder does this aldehyde form from a more direct pathway that doesn't rely on several steps (including heterogeneous chemistry)? That is, could campholenic aldehyde form almost immediately in the gas phase by some unknown gas-phase mechanism (such as radical rearrangements)? For example, in isoprene oxidation chemistry, radical rearrangements, such as RO2 rearrangements (Peeters et al., 2009, PCCP; Crounse et al., 2011, PCCP), are proving critical to consider for the formation of previously unrecognized gas-phase oxidation products.

Specific Comments:

1.) Introduction, Lines 10-13:

Wouldn't these prior lab SOA yields from monoterpenes already have campholenic aldehyde chemistry included? That is it was already contributing to SOA mass but it wasn't yet recognized.

2.) Experimental section, Chamber Experiments:

Why is no wall-loss corrections applied to report SOA yields? This doesn't reflect the "true" values due to chamber wall losses of semivolatiles or lower volatility products as well as aerosol losses. I worry that if you report SOA yields here that modelers will use them. Maybe some clarification is warranted here, especially for the benefit of modelers?

3.) Ambient Filter Samples Section:

What does "rural background site" really mean? Can you be more specific? Does that mean a certain threshold of NOx, O3, or sulfate particles?

4.) Ambient Filter Samples Section:

Can the authors comment on how good filters are after 5-7 years of archiving them presumably in a freezer at -20 degrees C? Someone might ask: "Did long-term storage after these campaigns cause changes in the "true" composition of the aerosols?" Have the authors conducted tests to confirm how things change over storage time, especially with regards to the compounds of interest described in this study?

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 22487, 2013.