

Interactive comment on “Influence of aerosol acidity on the chemical composition of Secondary Organic Aerosol from β -caryophyllene” by M. N. Chan et al.

M. N. Chan et al.

mnchan@caltech.edu

Received and published: 10 February 2011

Response to Reviewer # 2

We would like to thank the comments and suggestions raised by the reviewer.

This manuscript describes experiments aimed at understanding the mechanistic details of the formation of secondary organic aerosol (SOA) from beta-caryophyllene in the presence of acidic seed particles. The authors employ an environmental chamber reactor and use ultra performance liquid chromatography/electrospray ionization time of flight mass spectrometry (UPLC/ESI-TOF) to detect and identify many of the individual chemical constituents of the SOA. Several new compounds are identified, including
C13402

the first organosulfates and nitrates observed in SOA derived from a sesquiterpene. Based on these results, three compounds found in ambient SOA are identified; it is suggested that these compounds can serve as tracers of beta-caryophyllene reactivity. Therefore, the work is quite appropriate for ACP, and is a significant contribution to the SOA literature.

The work has been carefully planned and executed, and the analysis is logical. While the mechanistic arguments are by necessity quite speculative, I found the explanations to be clear and appropriately tentative. However, there are some issues related to the clarity of the prose of the manuscript as well as some missing details that the authors should consider before preparing a final version of the manuscript.

A general question: I understand that the main goal in the work was to try to study beta-caryophyllene-derived SOA that would be as similar as possible to the ambient SOA measurements. However, especially since the three ambient SOA components are identified as two second generation and one third generation ozonolysis product, I wonder why separate ozonolysis experiments weren't carried out (i.e., no photochemically generated OH and an OH scavenger added to shut off any OH-initiated chemistry from secondary sources). Since many of the other identified products are speculated to arise from OH chemistry, it would have helped with the development of proposed mechanisms if the separate ozonolysis experiments had been carried out. Is there some reason that the authors didn't carry these out?

Response:

We agree with the reviewer that separate ozone and OH experiments can help us to better understand the formation mechanisms and the composition of beta-caryophyllene SOA. Beta-caryophyllene and its gas-phase products can react with both ozone and OH. Although beta-caryophyllene reacts mainly with ozone under typical atmospheric conditions, the first-generation ozonolysis products, which have an unreacted double bond can rapidly react with both ozone and OH. We observe that

the first- and second-generation ozonolysis products can react with OH to form higher-generation products, which have lower volatility and partition into the particle phase. These reactions likely occur in the atmosphere and cannot be investigated under separate ozone and OH experiments. The results of this work provides insight about the aging of beta-caryophyllene gas-phase products in the atmosphere in the presence of ozone and OH.

Ozonolysis of beta-caryophyllene has been extensively studied previously. Formation mechanisms of first- and second-generation ozonolysis products have been proposed. However, the acidity effect on the SOA yields and the composition has not been studied for the ozonolysis of beta-caryophyllene and is worthwhile for future investigation.

Specific issues:

p 29251, line 9, typo: "increase of" should be "increased"

Response:

The sentence has been changed.

p 29253, line 24, comment: It would be helpful if the authors reported the effective H⁺ concentration for the seed particles.

Response:

We have not measured the effective H⁺ concentration for the seed particles and do not report the values in the revised manuscript.

p 29254, line 6, comment: It would be helpful if the authors also reported an effective H⁺ concentration for an average SOA particle.

Response:

The in-situ aerosol acidity is very difficult to measure and is not known. We do not report the effective H⁺ concentration for an average SOA particle.

C13404

p 29257, line 26, comment: A reference should be given for the proposed RO₂ + HO₂ → carboxylic acid reaction.

Response:

Winterhalter et al. (2009) have proposed the peroxyacetyl-type radical can react with HO₂ to form a carboxylic acid in the beta-caryophyllene experiments. This reference is added in the revised manuscript.

p 29259, line 16, comment: Do the authors have any idea what the HO₂ levels are in their experiment? It seems surprising to me that an RO₂ + HO₂ reaction would dominant in the presence of 60 ppb NO.

Response:

We have not measured the HO₂ level in our experiments. In the presence of NO, the HO₂ level is expected to be low and may be at the ppt level. In the schemes, we suggest that some acids detected in the particle phase can be formed via RO₂+HO₂ reactions in the gas phase. However, it cannot be ruled out that the acids can form via other reaction pathways in the gas and particle phases. We have clarified this point in the revised manuscript.

"The acyl peroxy radicals can also react with NO and subsequently undergo decomposition or can react with NO₂ in the presence of NO_x to form peroxyacyl nitrates. The reaction of acyl peroxy radicals with HO₂ to form carboxylic acid may explain the formation of acids detected in the particle phase. For example, acyl peroxy radicals formed from the aldehydic hydrogen abstraction of β-caryophyllon aldehyde can react with HO₂ to form β-caryophyllonic acid (Scheme 2). However, it cannot be ruled out that the acids can form via other reaction pathways in the gas and particle phases."

p 29260, line 17, typo: "oxoium" should be "oxonium"

Response:

C13405

The sentence has been changed.

p 29263, line 16, comment: Do the authors mean that the gas/partitioning coefficients must be artificially increased to accurately model experimental data?

Response:

Although the mechanisms by which acidity affects the concentrations of individual compounds are not well understood, some observations can be made. It is found that not all particle-phase concentrations of gas-phase products increase with increasing aerosol acidity. Although gas/particle equilibrium shifts further toward the particle phase due to enhanced particle-phase reactions, the condensed gas-phase products can, as a result, react in the particle phase to form other products (e.g., hydrated compounds and sulfate esters) at an accelerated rate under acidic conditions. Because such reactions serve to convert the specific partitioning species to another compound, the enhanced gas/particle equilibrium does not necessarily lead to an increase in the particle-phase concentration of gas-phase products. Although an increase in gas/particle partitioning coefficients of gas-phase products may help to capture the acid-enhanced SOA formation in a model, increased acidity does not always lead to an increase in the particle-phase concentration of gas-phase products. We have revised the paragraph.

“Although the mechanisms by which acidity affects the concentrations of individual compounds are not well understood, some observations can be made. It is found that not all particle-phase concentrations of gas-phase products increase with increasing aerosol acidity. Although gas/particle equilibrium shifts further toward the particle phase due to enhanced particle-phase reactions, the condensed gas-phase products can, as a result, react in the particle phase to form other products (e.g., hydrated compounds and sulfate esters) at an accelerated rate under acidic conditions. Because such reactions serve to convert the specific partitioning species to another compound, the enhanced gas/particle equilibrium does not necessarily lead to an increase in the particle-phase concentration of gas-phase products. Although an increase in

C13406

gas/particle partitioning coefficients of gas-phase products may help to capture the acid-enhanced SOA formation in a model (Kroll and Seinfeld, 2005), increased acidity does not always lead to an increase in the particle-phase concentration of gas-phase products.”

p 29264, line 21, comment: It is stated that the Li et al identified all three ambient SOA components as second generation ozonolysis products. As my general comment above indicates, from Schemes 2 and 3, I interpret the formation of betadihydroxynocaryophyllon aldehyde as a third generation ozonolysis product. Am I incorrect, or is the present interpretation at odds with Li et al.? I also don't see how Scheme 4 has anything to do with rationalizing the three ambient SOA compounds, or why any OH chemistry is required to rationalize them.

Response:

As shown in Figure 4 in Li et al. (2010), beta-dihydroxynocaryophyllon aldehyde is formed from the further oxidation of beta-hydroxycaryophyllon aldehyde, which is a first ozonolysis oxidation product. In Scheme 3, we have shown that the oxidation of beta-hydroxycaryophyllon aldehyde forms beta-dihydroxynocaryophyllon aldehyde (270(+)). Beta-dihydroxynocaryophyllon aldehyde is a second-generation product. In Scheme 2, the further oxidation of beta-caryophyllon aldehyde forms beta-hydroxynocaryophyllon aldehyde (254a(+)) and does not give beta-dihydroxynocaryophyllon aldehyde (270(+)). Our reaction scheme is consistent with that proposed by Li et al. (2010).

Although the further reactions of beta-oxocaryophyllene aldehyde in the gas and particle phases do not lead to the compounds detected in the atmospheric aerosol, Scheme 4 shows the reaction pathways of the compounds detected in our samples originated from the reactions of beta-oxocaryophyllon aldehyde. The OH chemistry is proposed to explain the formation of acids and nitrogen-containing compounds.

General comment about tables and schemes: When printed on a regular piece of paper the chemical structures are were too small to read. Even when viewed as an electronic

C13407

document and enlarged to fill the screen of my 25" monitor, it wasn't easy to make out the chemical structures in the schemes.

Response:

We have revised the tables and schemes to improve their quality.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 29249, 2010.

C13408