

Review article : Temperature and acidity dependence of secondary organic aerosol formation from α -pinene ozonolysis with a compact chamber system

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Temperature and acidity dependence of secondary organic aerosol formation from α -pinene ozonolysis with a compact chamber system

Yange Deng, Satoshi Inomata, Kei Sato, Sathiyamurthi Ramasamy, Yu Morino, Shinichi Enami, and Hiroshi Tanimoto

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General remarks:

In this paper, Temperature and acidity dependence of secondary organic aerosol formation from α -pinene ozonolysis with a compact chamber system have been investigated. This is a nice piece of work where the temperature and acidity dependence of SOA yields and chemical components were investigated. In addition, the formation of organosulfates (OS) was observed under acidic seed conditions. The data presented are of significant importance; however some modifications would be good to improve the article. The article should be published after major modifications.

Some characteristics of the new chamber are missing. We have developed a new chamber, it would be good to have more specifications. The temperature effect on the SOA formation has been relatively little studied, mainly due to the low number of temperature controlled chamber. Give more precision on the temperature controlled chamber.

There is no uncertainties, it would be good to add it in the text, in the figure and in the table. For example, no uncertainties has given for the temperature, the yield, the concentration It would be good also to correct the SOA yield obtained by all wall losses (particle and also oxidized organic vapors) to improve the article.

It would be good to add also some comments and reference (list of some references given at the end of this pdf file) about the relative humidity (RH) because it's not the same in each experiment and the humidity can also influence the SOA yields and chemical compounds. The effect of RH on aerosol formation has yet to be optimized. Some experiments performed in flow reactor have shown that the aerosol yield was dependent on RH and other studies performed in simulation chamber have reported no effect. For example, the study of Saathoff [2009] on the ozonolysis of α -pinene have shown that water had little influence on aerosol yields at room temperature, however, a significant positive effect of water is observed for lower temperatures. Relative humidity is dependent on temperature.

For more explanation, see specific comments.

Specific comments:

Introduction

Line 41-59: The role of acidity is really good explain. However, the role of the other parameters as the temperature is very succinct, just one sentence. It would be good to explain more the influence of the other parameters on the SOA yields and chemical composition.

Line 63-81: The dependence of humidity is not explained for the specific case of α -pinene ozonolysis. It would be good to add also some sentences and references (list of some references given at the end of this pdf file) about the relative humidity (RH) because it's not the same in each experiment and the humidity can also influence the SOA yields and chemical compounds. The effect of RH on aerosol formation has yet to be optimized. Some experiments for α -pinene ozonolysis performed in flow reactor have shown that the aerosol yield was dependent on RH and other studies performed in simulation chamber have reported no effect. For example, the study of Saathoff [2009] on the ozonolysis of α -pinene have shown that water had little influence on aerosol yields at room temperature, however, a significant positive effect of water is observed for lower temperatures. Relative humidity is dependent on temperature.

Experimental

Line 109-140: A new chamber is developed. It would be good to have more specifications of this chamber and the analytical tools. Which instrument allow to control and to measure the temperature and the humidity in the chamber? What is the range possible in the chamber? What is the uncertainties and the precision of each measurement? The temperature is homogeneous in all chamber?

Line 125: Add more precision on the PTRMS analysis: flow of sampling, time resolution, m/z range, E/N

Line 136: Add the uncertainties for each temperature

Line 137: Modify the sentence "For experiments with the same temperature setting, the RH settings were also similar (Tables S1 and S2). » There is more of 10% of difference for RH for a same temperature, it's not really similar. Add the range of humidity in the text for each temperature. Furthermore, the humidity is really variable between 26 and 55% for the three temperature.

Line 141-146: I would like to know if you have perform some blank filter and some blank of chamber. If yes, it would be good to add a sentence as « These control runs led to no detectable SOA production, hence confirming that no "memory effects" of the chamber were contaminating our results ».

Line 150: It would be good to have the parameters for the LC-MS (at least in Supporting Information). For example, what is the configuration of the ESI source in this analysis in negative mode.

Line 162: 362 products have been identified. I would like to know if some standard has been analyzed in LCMS to confirm the compounds in this study. If it's not the case, it would be good to say that the identification method was based on retention times and on mass spectra interpretation. Note that in absence of authentic standard, the identification should be regarded as tentative. A recent article Kenseth et al, EST 2000, shows that the use of unrepresentative surrogates can lead to substantial systematic errors in quantitative LC/ESI-MS analyses of SOA.

Line 164-176: What type of seed (neutral, acidic?) is used to determine the aerosol wall loss in the chamber? In which conditions (RH, T) this experiment of aerosol wall loss has been performed? In SI, it's written that this experiment has been performed under an RH range of 17–23 %, but this range is different during the experiment (26-55%). Can this difference cause different wall losses?

There are not only aerosol wall loss but there is also the wall-loss of oxidized organic vapors. I think it would be good to add some sentence on this wall loss even if no experiment would be performed. It's already mentioned in this article in line 250 but it's too late. To improve the article, I would correct the yield by all the wall losses.

Line 165: When a new Teflon bag is used? After a blank experiment?

Line 168-176: It would be good to model (i.e. Lai and Nazaroff) of the wall loss performed with seed. This well-known process depends on chamber geometry, static charge build-up on the walls, air flow and particle size.

Since aerosol deposition was measured for $(\text{NH}_4)_2\text{SO}_4$ seed with $d = 1.77 \text{ g/cm}^3$, due to the gravitational effect the wall loss rates for SOA (with different density) would be different. For more explanation, see the article of Lai and Nazaroff 2000.

Data analysis

Line 179-201: It would be good to correct also the SOA yield by the wall loss of oxidized organic vapors. Maybe give a range of yield with the particle wall loss correction for the smallest value and the vapor wall loss correction for the largest value.

Line 193: « α_i is assumed to be temperature-independent ». Do you have a reference to assume that α_i is assumed to be temperature-independent? If yes, it would be good to add it.

Result and discussion

Line 230 figure 1: It would be good to homogenize the axe of the figure, for example use the same nomenclature in the figure and also in the text. For example, in this figure it would be good to modify SOA ($\mu\text{g/m}^3$) by m_{SOA} ($\mu\text{g/m}^3$). In figure 1, it would be good to add a banana plot for the aerosol. I think it would be a good idea to correct the data by also the wall loss of oxidized organic vapors.

Line 235 figure 2: It would be good to compare the yield corrected by all wall loss and not only by the particle wall loss. A comparison is performed with Pathak et al. 2007, it's good to do

this comparison but it's difficult to understand why a comparison is performed with two curves (less of 10% RH and another with a range between 50 and 73%) because in our data the experiment are performed at 26% RH. I would like to know if no literature data exists for this range of humidity (26%). If yes, it would be good to compare the data with this reference. If not, it would be good to say that this data are new and it's difficult to compare with literature because no data have been performed at 298K and 26% RH in presence of seed.

Line 267: Thanks to add the uncertainties on the ΔH_{vap} obtained in this study

Table 1: Add the humidity in the table and give the same number of significant number

Table 2: It would be good to compare the data on a graphs, the comparison would be more visual.

Why the comparison with CMAQv4.7 model in the table? It would be good also to perform it.

Line 321-324: « Among the 362 compounds identified through LC-ToF-MS analysis in this study (Table S3), 331 compounds were ascribed to VBS bin ranges of -8-3. The other 31 compounds were ascribed to higher VBS bin ranges of 4-6, which is unrealistic for the compounds in the aerosol phase. Additionally, those latter compounds only accounted for an average of 12 % of the total mass of identified compounds. Thus, only the former 331 compounds are targeted in the following discussions. »

I think that the conclusion is very rapid. The VBS is not good consequently you remove 31 compounds. It would be good to add more comments on this compounds even if you decide to follow the discussion with 331 compounds.

31 compounds were ascribed to higher VBS bin ranges of 4-6, which is unrealistic for the compounds in the aerosol phase; it's not the first time this observation is performed.

This observation strongly supports the resistance to diffusion imposed by the viscosity of the aerosol to the products formed inside the aerosol itself. As previously mentioned in the literature (Shiraiwa et al 2013) this observation indicates that volatility can be strongly minimized by viscosity and that relying only on gas-phase equilibria to represent partitioning can be misleading.

Line 332: How is obtained the total amount? By SMPS? It would be good to add a sentence to explain that.

Line 350, Figure 4: There is no axes for the yield in the graph B; it would be good to add it.

Line 448-449: Replace « M/z 223 was the most abundant OS identified at 298 k, followed by m/z 279, 281, 269, 283, 265, 253, 267, 251, 249, and 247. » by « m/z 223 was the most abundant OS identified at 298 K, followed by m/z 279, 281, 269, 283, 265, 253, 267, 251, 249, and 247. »

Line 500, Table 3: it's difficult to follow the table 3, it would be good to simplify to know what is really proposed by this study. Pleased find an example of table.

m/z [M-H]-	Formula [M-H]-	VBS bin	Tentative structure proposed in this study	Literature

SUPPORTING information

Table S1 Remove the C near O3 in table S1. I would add if it's possible a column with $\Delta\alpha$ -pinene IN THE TABLE S1. It would be good to add the uncertainties in the table. For the yield, it would be good to correct it by all the wall losses. Replace also SOA by m_{SOA}

Table S2 I would add if it's possible a column with $\Delta\alpha$ -pinene in the table S2. It would be good to add the uncertainties in the table. For the yield, it would be good to correct it by all the wall losses. Replace also SOA by m_{SOA}

Figure S2: It would be good to model these experiment of wall loss and add the model in this figure

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