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Discussions

Interactive comment on "Elemental composition and clustering of α-pinene oxidation products for different oxidation conditions" *by* A. P. Praplan et al.

Anonymous Referee #1

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In this paper the initial particle nucleation from α-pinene ozonolysis and OH-photooxidaiton are compared using a number of mass spectrometric techniques that allow the authors to detect the positive and negative ions as well as the neutral molecules that make up the nucleated and growing aerosols. The work was done at the CLOUD chamber at CERN where the contents of the chamber were able to be well regulated and well known. High resolution mass spectrometers were used and exact masses were obtained allowing for information on exact chemical composition to be obtained. This allows for an interesting analysis on the elemental composition of the nucleated and growing aerosols from the two different systems as well as the ability to observe

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the oxidation state of the molecules within the aerosols and see how it varies over the course of the growth or aging of the aerosols.

This is an interesting analysis of the formation and growth of α-pinene derived SOA. The observation of highly oxidized products at short time after reaction initiated supports high degree of isomerization reactions and is of interest to the community for better understanding of aerosol formation and growth. There are, however, a number of concerns that need to be addressed prior to publication.

General comments

First of all, more detail is needed in the experimental section for a paper where the results will be dependent on the conditions. Below you will find specifics. Second, there are a number of places within the results and discussion where interpretation is based on small differences with no mention about uncertainty or reproducibility (most notably average oxidation state discussion and time series), this should be addressed. For instance, the section on average oxidation state, as the mass spectrometry techniques are not calibrated versus all products and sensitivity will vary depending on the functional group, number of functional groups on a molecule, and the size of a molecule how do you find an average oxidation state? More detailed discussion on each section is below.

Comments on each section

2. Experimental

Please talk about the source of NH3 and (C2H5)2NH, was it from trace contamination or were they explicitly added?

You only state that you use UV light to initiate photooxidation. Looking at the paper cited it indicates that the light provided could be from 300 nm and above or below 300 nm (down to 200 nm or possibly lower) please provide a more through description of the light irradiation, especially the “”UV-sabre”. This is important because UV light (especially intense UV light) can result in photodissociation of conjugated molecules, many organics with oxidized functional groups (carbonyls, hydroperoxides, peroxyacids. . .) as well as α-cleavage of alkenes. Please provide a better description of your light source. If intense UV light below 300 nm was used was potential photodissociaiton studied?

In the experimental you explicitly mention the ability to remove or add more ions to the chamber; did you do either of these? Would either produce different results to those reported?

With the discussion presented later in the paper, a section on what types of molecules (i.e. with what functional groups) are detected with each mass spectrometric technique is needed. In addition, can you comment on the sensitivity of each technique to different compounds (functionality, multifunctional, large molecular weight). This last part is especially important for the oxidation state and elemental composition discussions (sects. 3.2 and 3.3).

Results and discussion

3.1 Mass defect

In figure 2 and the discussion on page 30807 you discuss that there are organonitrates present in the OH oxidation experiment due to the presence of NOx, my question is why is there organonitrates present in the ozonolysis experiments when no NOx was added? In addition, where does the nitric acid come from?

3.2 Average carbon oxidation state

As the mass spectrometers are not calibrated and could potentially have different sensitivities to different types of molecules doe a small difference in the “average oxidation state” between positive and neutral detected compounds in figure 3 mean anything? It is hard to determine how you determined the average oxidation state; did you sum up all the signal at a given number of carbons from each of the mass spectrometric techniques? If so, how does this represent the average oxidation state if you do not know functionality of the compounds and thus the sensitivity in each mass spectrometric technique?

3.3 Elemental composition

Are the numbers in figure 1 reaction partners or numbered reactions? In your discussion on page 30810 (lines 20-28) you seem to use them for both.

4 Clusters time series

For the figures (6-8) were the results reproducible? Was this one run or the average of many runs?

You state on page 30813 lines 5-6 that the positive signal (fig. 6) from the most oxidized species decreases after it reaches its maximum while the other signals become stable (for ozonolysis). I am not sure I see what you mean. First of all in the first panel you should zero out the single at time zero if you are also going to normalize to maximum signal as you are only giving about 90% decimation of the green line (starting at $\sim$0.1) as the pink line (starting at 0). Second, as I am assuming that the fluctuation in signal after 23:30 is an indication of the noise. Given this noise level, all signals appear to show the same trend within error or noise.

Second, and potentially more important, comparing the two ozonolysis panels (addition of NH4+ or C2H8N+) why are the trends different, even with species with the same molecular formula? There is no discussion about this. Why does the species that it clusters with have a much greater effect on its time trace than the molecular formula? Are they being converted from the ethyl ammonium species to the ammonium species? Why is this trend not observed from OH oxidation? Please provide a discussion.

For your discussion on the time trace of the negative signal for ozonolysis (figure 8 top panel) you state that this figure indicates that species with two sulfuric acids are produced later that with one sulfuric acid (page 30813 lines 26-28). The noise level from the species with one sulfuric acid molecule makes this claim hard to evaluate. The trace with one sulfuric acid shows signal of up to 0.4 prior to oxidation (black vertical line) and does not surpass that again until the other signals (ones with two sulfuric acids) begin to rise as well. With the amount of noise it is tough to draw any conclusion on this time trace. Again it must be asked, where these results reproducible or is this from one experiment?

Technical corrections

Please letter (A, B, C..) each sub figure, this will make it much easier to follow.

Provide a distinction between product classifications and reactions (Figure 1 and discussion thereof). In the text or figure 1 please provide a reaction scheme for reactions 4 and 5.

Figures 4 and 5 are very hard to read, I had to put the pdf on 300% magnification in order to read the molecular formulas.

Figure 6 first panel, you should zero out the response at time zero (vertical line) so that the normalized response from each mass spectrometer can be compared.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 30799, 2014.

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