

Interactive comment on “Influence of relative humidity and temperature on the production of pinonaldehyde and OH radicals from the ozonolysis of α -pinene” by R. Tillmann et al.

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We thank the referee for the helpful and constructive comments. We carefully considered all of them.

General comments

The manuscript describes the results and their detailed interpretation of alpha-pinene ozonolysis experiments in the AIDA chamber under different humidity and temperature conditions. The scientific focus lies on the interpretation of the formation of pinonaldehyde. Based on the differences of the PA yield at different humidities and the gas/particle partitioning of PA at the different temperatures, the authors conclude that

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the higher SOA yields at higher humidities (especially at low temperatures) is essentially caused by the higher chemical yield of PA at higher humidities and not (or just insignificant) the physical uptake of water. They also describe the formation of OH radicals under these reaction conditions and discuss potential explanations for the observed differences. The data interpretation is certainly based on high quality experimental work and the conclusions drawn are generally sound. In my opinion the results of the work are very useful for the scientific community, since despite the fact that the importance of natural SOA formation is more and more acknowledged, high quality experimental work that also is aiming on a better process understanding on the molecular level is scarce. The manuscript is generally well written and the topic certainly appropriate for the readers of ACP. Therefore, I recommend to publish the paper in ACP after considering the following comments.

Specific Comments

Comment: The authors discuss the results presented in Figure 7 and conclude that the relatively large K value (derived from Fig. 7) of 0.005 of PA might be explained by reactions with SCIs (a gas phase reaction). I cannot follow this line of argumentation, since the plot shows the measured PA gas phase concentrations (more precisely its inverse) vs. Mo – hence such an explanation could just be valid if the hypothetical reaction product (the C20-SOZ) also gives the same signal in the PTRMS (with the same intensities). If the SCI reaction just diminishes the PA concentration in the gas phase this would be independent from Mo (and it certainly makes no sense to assume that with increasing Mo the PA-SCI reaction gains importance). Therefore, I think this discussion has to be reexamined. Furthermore, the whole discussion is based on the experiments under humid conditions and under these conditions it can be expected that the SCIs predominantly react with water. Alternatively, a condensed phase reaction of PA could perhaps explain the observations, however, this might be unlikely. Indeed an aerosol mass dependent activity coefficient might be the most likely explanation, since clearly the organic aerosol composition in these experiments depends from the organic

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aerosol mass (i.e. uptake of more and more PA-like compounds with increasing Mo).

Reply: The product of the activity coefficient with the effective vapour pressure of PA derived from figure 7 is significantly lower than the values reported in the literature (Hallquist et al. 1997). This results in a relatively large K value of PA. Although the assumed values of MW_{om} and γ PA still impose an uncertainty on the low vapour pressure derived, the effective vapour pressure of PA determined is significantly reduced (by 3 orders of magnitude). We agree with the referee that indeed a very low activity coefficient cannot be excluded. As a further possibility we still believe that thermolabile adducts of PA are formed which preferentially reside in the particulate phase. These could be formed by reversible reaction of Pinonaldehyde with either gaseous or particulate phase compounds. Thermolability of these adduct was silently assumed in the old manuscript, and will now be expressed. We tentatively suggested a reaction of Pinonaldehyde with stabilized Criegee Radicals as this would 1) result in a much lower vapour pressure 2) the experimental conditions would facilitate their formation, as criegee radicals are formed in the presence of Pinonaldehyde from the previous experimental section 3) secondary ozonides are known to be thermally labile yielding the corresponding acids and carbonyl compounds (lit.: Story et al. 1968). We assume that the respective SOZ formed from PA with a Criegee Radical would thermally decompose in the heated sampling line of the PTRMS inlet (heated to 60°C) However, we agree with the referee that this type of reaction may not be so important in the presence of large amounts of water and will state that as a modifier in the new manuscript. Considering the preceding remarks we extended our discussion by the following paragraphs:

“In other chamber studies and field measurements PA was also often found in a significant fraction in the condensed phase demonstrating that PA can contribute to aerosol mass even at ambient temperatures (Plewka et al., 2006; Yu et al., 1999a). In our study γ PA has to be in the order of 10⁻³, to achieve such a low effective vapour pressure considering the previously measured p₀PA of 8.4 Pa. Such low activity coefficients would

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normally imply specific chemical interactions e.g. adduct formation. Stabilized criegee intermediates (SCI) have been suggested to form adducts with carbonyl compounds to yield secondary ozonides (SOZ) (Bonn et al., 2002). A reaction of e.g. a C10-SCI with PA would yield a C20-SOZ that will have a significant lower vapour pressure than pure PA. The observed effective vapour pressure of PA would thus be reduced. In fact, the sectional experimental procedure adopted in the present study will enhance the probability of C10-SCI to react with PA since initially produced PA will be present as reactive SCI are produced in the subsequent steps of α pinene additions. SOZ are known to be thermally labile yielding the corresponding acids and carbonyl compounds e.g. PA (Story et al., 1968). Furthermore, experiments dedicated to low temperatures would enhance the lifetime of the SOZ so that they can partition to the particulate phase. The measurements with a filter in line held at experimental temperature retains the particulate SOZ. Without the filter in line the respective SOZ formed from PA with a Criegee Radical would thermally decompose in the heated sampling line of the PTRMS inlet and PA would be detected. Assuming formation of SOZ could explain the observations from low temperature with and without the filter in the sampling line as well as the low effective vapour pressure determined at 303 K. However, quenching of SCI with water may reduce the importance of the proposed SOZ formation under humid conditions. Therefore other reversible adducts of PA in gas or particle phase cannot be excluded.“

Comment: Figure 6 can easily be misunderstood – I suggest to plot $[(\Delta) \alpha\text{-pinene}]$ vs. [PA] (and not just $[\alpha\text{-pinene}]$ vs. [PA]).

Reply: We calculated the molar yield of pinonaldehyde from the absolute of the slope ($\Delta\text{PA}/\Delta\alpha\text{-Pinene}$) as plotted in Fig. 6. This is advantageous since the initial α -pinene mixing ratio has an uncertainty which would then enter the calculated molar yield of pinonaldehyde. We therefore prefer to stick to the presentation of Fig. 6 of plotting Pinonaldehyde vs α -Pinene and refer to an extended explanation on page 3143 line 3ff.

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