

## ***Interactive comment on “Cloud droplet activation of mixed organic-sulfate particles produced by the photooxidation of isoprene” by S. M. King et al.***

**S. M. King et al.**

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The authors thank the reviewer for the helpful comments, which are pasted in the following text and preceded by the symbol \*\*. The author responses to each comment are preceded by the symbol ».

\*\*General: The manuscript deals with the investigation of the activation behaviour of mixed organic-sulfate particle originating from the photooxidation of isoprene. The activation behaviour of such particle is an important issue in quantifying the effects of atmospheric aerosol particles on both, cloud formation and the aerosol indirect effect. Therefore the paper deals with a topic highly relevant to the field of atmospheric research and is consequently suitable for publication in ACP. The manuscript is well-structured and nicely written. Earlier work is adequately recognized and credited and to

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my knowledge no portions of the manuscript have been previously published. In summary, the manuscript represents a significant contribution to the field of atmospheric science and should be published after minor revisions.

Specific: page 217, line 17ff: I suggest to give a little more detail concerning the chamber here.

»The first sentences of the paragraph are modified as follows:

“The Harvard Environmental Chamber (HEC) consists of a 4.7-m<sup>3</sup> Teflon bag outfitted with lines for chemical flows in and out of the bag as well as for sampling and analysis by instrumentation (Shilling et al., 2008; King et al. 2009). The bag is within a temperature-controlled housing. In the present study, the HEC was used to form mixed organic-sulfate particles by the condensation of the products of isoprene photooxidation onto inorganic seed particles (Fig. 1).”

As stated, longer accounts of the chamber are recently (years 2008 and 2009) in the literature, so duplication does not seem warranted in the present publication. However, we included all details necessary for understanding the pertinent elements of the current set of experiments.

\*\*page 217, line 23: I suggest to also indicate the variability of temperature and rh here.

»The uncertainties for temperature and RH are now included in the revised manuscript.

\*\*page 218, line 11: It should explained/mentioned which type of particle generator was used here.

»The atomizer model (TSI Model 3076) is now included in the revised manuscript.

\*\*page 218, line 15ff: Why is dryer located downstream of the DMA ? At first sight that seems kind of counter intuitive ! A short explanation and discussion of the implications is needed. There is no dryer in Fig. 1 !

»We thank the reviewer for bringing this to our attention. The wording was unintention-

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ally misleading, and the dryer was actually located upstream of the DMA. The sentence has been modified as follows: "The seed particles were passed through a diffusion dryer (<5% RH) and size-selected by a differential mobility analyzer (DMA1, TSI Model 3071) before they were injected into the chamber."

\*\*page 218, line 22: "The H<sub>2</sub>O<sub>2</sub> radical precursor used in these experiments followed the method of . . ." A precursor is not a method! Rewording is needed here.

»The sentence has been reworded as follows: "Injection of the H<sub>2</sub>O<sub>2</sub> radical precursor used in these experiments followed the method of Kroll et al. (2006), who described SOA production by OH-initiated VOC oxidation."

\*\*page 219, line 12: "for an OH-C<sub>5</sub>H<sub>8</sub> bimolecular rate constant of  $1.02 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>" I suggest to give a reference here.

»The reference (Lei et al., 2000) is added to the manuscript.

\*\*page 220, line 22: ". . ., the larger sheath-to-aerosol flow ratio in SMPS2 compared to that in the DMA2 obviated the need in our application, and the TSI algorithm was used for inversion of the SMPS2 data." This is only correct if distribution widths differ by a factor of ten which is not the case here ! However, if only mean sizes and or integral properties are determined, it should be OK ! Nevertheless, some discussion is needed.

»Since further discussion of this topic is not essential to our manuscript and has been covered extensively in other publications, we removed this sentence.

\*\*page 222, line 6: "The lines through the data points show the predicted CCN activation curves of the particle population based on the model described in King et al. (2009)." In Fig. 3, it should be indicated which line corresponds to what diameter.

»The suggested addition is added to the figure caption.

\*\*page 222, line 7ff: "In the model, particles within the population have different critical supersaturations because of heterogeneities in particle diameter and organic volume

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fraction. One underlying source of heterogeneity is the distribution of diameters for the sulfate seed particles; this distribution is affected both by the resolution of DMA1 and by the presence of multiply charged particles. For similar reasons, there is heterogeneity in the particles that pass through DMA2. These heterogeneities explain the inflection point apparent in the predicted activation curves (as well as in the data) shown in Fig. 3." I have a hard time to understand what the authors are trying to explain here. More explanation and some rewording could be helpful.

»This section seeks to explain the slope and inflection point in the activation curves. More specifically, if DMA1 selected perfectly one size of seed particles and DMA2 selected perfectly one size of SOA particles, the particle population would be homogeneous (of one size and organic fraction) and the activation "curve" would be a step function, with all the particles activating at the same supersaturation. However, given the transfer functions and passage of multiply charged particles that are associated with the DMAs, the particle population is not homogeneous. We modified the section as follows to clarify the presentation:

"One underlying source of heterogeneity is the distribution of diameters for the sulfate seed particles, which arises from both the resolution of DMA1 and the presence of multiply charged particles. For similar reasons, there is heterogeneity in the particles that exit DMA2."

\*\*page 222, line 21: "A sensitivity analysis showed that the predicted activation curves were reproducible for up to a 25% change in the optimized value of  $V_{m,ORG}$ , corresponding to  $\pm 0.03$  for  $\kappa_{ORG}$ ." I personally find this sentence pretty confusing. There should be at least a measure for reproducibility here. Maybe something like: A 25% change in  $V_m$  results in only a ??% change in critical supersaturation . . .

»A reference to the Supplementary Material in King et al. (2007) has been added to this sentence. In this reference, Table S3 lists the results of a sensitivity analysis performed in a similar case (ozonolysis of  $\alpha$ -pinene). The sentence proposed by the

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reviewer is a sound suggestion but not included here because: (1) this study does not report critical supersaturations except in the case study applied to AMAZE-08, where we define an apparent critical supersaturation, and (2) the effect of a 25% change in  $V_m,ORG$  leads to different % changes depending on particle size and organic fraction.

\*\*page 223, line 6ff: "Therefore, within uncertainty, the CCN activity of secondary organic material produced by the photooxidation of isoprene and that resulting from other investigated precursor gases are equivalent." I personally find the word "equivalent" a little awkward here. May stating that kappas are similar and therefore CCN activities are comparable would be more appropriate here.

»The sentence in question is modified as follows:

"Given the similarity within uncertainty of these  $\kappa_{ORG}$ , the CCN activity of secondary organic material produced by the photooxidation of isoprene and that resulting from other investigated precursor gases can be considered equivalent."

\*\*page 223, line 11ff: "King et al. (2009) showed that, in the case of the dark ozonolysis of  $\alpha$ -pinene, the CCN activity abruptly increased as the percent contribution of signal intensity at m/z 44 to the total organic signal intensity passed a threshold at 11%, which was concomitant with a decrease in organic particle mass concentration to less than 1  $\mu\text{gm}^{-3}$ ." Maybe I'm missing something here, but why does an increase in m/z 44 come together with a decrease in organic particle mass concentration? At least a short explanation would be useful.

»The observed increase in m/z 44 with decreases in organic particle mass concentration is discussed in detail in the reference provided (King et al., 2009). The clause beginning with "which was..." is not essential to the discussion in this paragraph and is removed to eliminate the confusion.

\*\*page 225, line 5: Is there any reason why Fig. S2 is not shown in the main text? It's discussed here anyhow, so why not show it?

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»We cannot methodically interpret the data by constrained model fits, i.e., in a way that results in parameters such as those in Table 2. The absence of model fits is apparent in Fig. S2 (i.e., no lines through the data points). We can (and did) fit the data with poorly constrained parameters, but the high range in "good fit" parameters made the exercise of little value to readers and fellow scientists. For these reasons, we judged that this aspect of the study was not refined enough for inclusion as a figure in the main text. Nevertheless, the results are interesting and possibly important, so we wanted to make the interested reader aware of their existence, which might possibly motivate additional detailed studies that could collect a more extensive data set geared toward the effects of the combined influences of temperature and NO<sub>x</sub> concentrations.

\*\*page 225, line 29ff: I suggest to remove the whole paragraph and just state that adjustment of  $V_m$ ,  $i$ ,  $\sigma$  resulted in unreasonable values.

»We certainly appreciate the reviewer's opinion. Our thinking, however, is nevertheless different, and we argue for inclusion of the paragraph because the discussion therein provides our reasoning behind the conclusion that adjusting the indicated variables results in unreasonable values.

\*\*page 226, line 11ff: Maybe I'm missing something here. I get the impression that you are trying to explain the changes in activation by oligomerization. Couldn't it simply be explained by loss of soluble mass due to evaporation? A little more discussion would be nice here.

»As the reviewer correctly understood, we suggest in this section that the changes in activation may be due to oligomerization. It is likely that there is loss of soluble mass due to evaporation, but our argument here is that the changes cannot be solely explained by this loss. We have included the following modification to clarify this point:

"Alternatively, the observations can be explained by a decrease of the soluble fraction upon heating. Such a decrease could arise in part from the evaporation of soluble species and in part from the formation of n-mers, with  $n \ll 100$  as discussed above."

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\*\*page 228, line 6: "Furthermore, the chamber studies cited earlier also suggest that secondary organic components produced from the oxidation of anthropogenic precursor gases also have  $\kappa_{\text{ORG}}=0.1$ ." It should be mentioned that this holds for activation only, hygroscopic growth might be different.

»The suggested modification is incorporated in the sentence as follows:

"Furthermore, the chamber studies cited earlier also suggest that secondary organic components produced from the oxidation of anthropogenic precursor gases also have  $\kappa_{\text{ORG}} = 0.1$  in regard to CCN activity."

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 213, 2010.