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Atmospheric Chemistry and Physics Discussions

Interactive comment on "High variability of the heterogeneous ice nucleation potential of oxalic acid dihydrate and sodium oxalate" *by* R. Wagner et al.

Anonymous Referee #1

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Overview Comments

This manuscript presents ice nucleation results from oxalic acid dihydrate and sodium oxalate particles, based on measurements using the AIDA cloud and aerosol chamber. The authors carry out a series of experiments intended to shed light on seemingly conflicting results from previous measurements of ice nucleation on oxalic acid dihydrate particles. In the deposition mode, these new data suggest that the ice nucleation efficiency of the particles is directly tied to crystal structure of the oxalic acid dihydrate, which in turn is based on saturation conditions of the solutions from which the particles crystallize. The arguments (and supporting data) are convincing and I believe these

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Interactive Discussion

Discussion Paper

results go a long way toward explaining discrepancies between previous studies. The authors then go on to discuss condensation/immersion freezing from less active oxalic acid dihydrate and sodium oxalate particles. Although the discussion presented from this aspect of the work is reasonable, my primary concern is that the measurements occur very near homogeneous freezing conditions, and that these results are driven more by proximity to 238 K than by any heterogeneous nucleation process. Below I make specific references to this issue. Despite this concern, the manuscript is well-written and the new results and discussion are welcome additions to the literature, and I recommend publication after the comments are addressed.

Specific Comments

p. 11537, line 29 – 11538, line 6. Marcolli et al. (2006, ACP, 7, 5081-5091) use active sites to interpret their ice nucleation data on Arizona Test Dust (ATD). Based on their analysis, these authors suggest that some minimum size is required for ATD to act as an effective IN. The data presented in this study suggest that such a minimum cut-size for oxalic acid dihydrate would be significantly smaller than that for ATD, based on the results from Experiment 3. This is a somewhat unexpected, and it would be worthwhile to note to give the reader an idea of the efficiency of oxalic acid dihydrate versus ATD as an ice nucleus.

p. 11539, lines 25-27, and Figure 8. In these experiments, the temperature is reduced to approximately -35.2 °C, which the authors note is above the homogeneous freezing temperature of water droplets. Benz et al. (2005), who the authors reference for more information regarding the chamber, report that homogeneous freezing is measured in the chamber at -35.5 °C. Given that there must be some variability in the measurements, including potential thermal gradients in the chamber, can the authors really rule out that homogeneous nucleation might be occurring at the experimental conditions? Further, when the pumping is stopped, the authors note the marked change in the depolarisation ratio (p. 11540, lines 9-11) and the ice fraction continues to increase (Fig 8). I think it is likely that the experiment nudged into the homogeneous freezing regime,

ACPD

10, C3059–C3062, 2010

Interactive Comment

and the growing (homogeneously nucleated) ice crystals were responsible for much of the signal from t = 210 s onward.

p. 11540. lines 19-21. Following the previous comment, I think this increase in signal may simply be the homogeneously nucleated ice crystals growing; the delay in growth resulting because the pumping was stopped just as these particles would have nucleated. A test of the hypothesis put forth in this and the previous comment would be to run these experiments 2 K warmer, so that the authors could be certain that there is no interference from homogeneous freezing. They appear to have done something along these lines, which I address in the next comment.

p. 11549, line 25 – p. 11552, line 11, and Figures 13-15. For all expansions shown in Figure 13, the temperature never reaches 238 K, and the 'condensation' freezing which was discussed in the previous two comments was not observed.

Summary of previous 3 comments. I think the deposition mode nucleation results are convincing. However, for condensation freezing, I believe that there is a small fraction of particles which nucleate heterogeneously during the first expansion, and then this population is augmented when the chamber reaches $\sim$238 K due to homogeneous freezing. During subsequent expansions, ALL particles which nucleated ice (heterogeneously or homogeneously) retain some enhanced ice nucleation ability. For the 'condensation nucleation' results during the initial expansions, it would be interesting to see (although not necessarily in the manuscript itself) results plotted as fraction activated versus temperature. I feel certain that there will be a step function increase near homogeneous freezing (238 K).

p. 11544, lines 12-14, Figure 3d, Figure 10, and p. 11545, lines 2-4. There is something here that is not consistent. We are told that the concentration of the aerosol particles generated by this final method is in the range of 18-38 weight percent, before the particles are cooled to lower temperature. However, the representative size distribution in Figure 3d for oxalic acid solution particles has a peak near 100 nm (and

ACPD
10, C3059–C3062, 2010

Interactive Comment

contains water). Given that the oxalic acid droplets in the chamber are, ‘estimated to be about 1 micron’ (p. 11545, lines 3-4), this corresponds to droplets which are less than 1 weight percent oxalic acid. So based on the SMPS data for dry oxalic acid mass, and determining droplet size from the Mie scattering at wavenumbers >3600 cm-1, what weight percent are your particles at points a, b, c, and d in Figure 9? If these are drastically different from 18-38 weight percent (which I’m guessing will be the case), then what can the authors say with confidence about the composition of the particles which are converting to oxalic acid dihydrate?

Minor Corrections

p. 11528, lines 7-9. Remove, ‘, we considered it confusing for the reader to begin this section with an overall compilation of the results from all experiments. Instead’ Simply present your arguments as you see most appropriate.

p. 11528, line 20. Replace ‘In a first type of experiments’ with ‘In the first type of experiment’.

p. 11539, line 20. Replace ‘of’ with ‘off’.

p. 11540, line 10. Replace ‘forth’ with ‘fourth’.

p. 11548, line 18. Replace ‘rising’ with ‘raising’.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 11513, 2010.