Atmos. Chem. Phys. Discuss., 10, C5487–C5497, 2010
www.atmos-chem-phys-discuss.net/10/C5487/2010/

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.

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Received and published: 19 July 2010

The authors would like to thank referee #1 for the careful manuscript reading. Please find below our answers to the individual comments.

Comment: 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.

Answer: Such comparison is certainly worthwhile, and we will add a brief reference to the Marcolli et al. paper at the end of section 3.1 (page 11538, line 6) in our revised manuscript:

“Recently, Marcolli et al. (2007) have modelled freezing experiments on the heterogeneous ice nucleation ability of immersed Arizona test dust (ATD) particles with an occurrence probability function of active sites. Their analysis indicates that an ATD particle must have a diameter of at least 0.1 microns to exhibit on average one active site. Based on the results from Exp. 3, the minimum threshold size for rapidly crystallised oxalic acid dihydrate particles is significantly smaller than that for ATD, further underlining their extraordinary high ice nucleability, as also evidenced by the low critical ice saturation ratio in comparison with heterogeneous ice nucleation by 50 nm – sized dust particles (Archuleta et al., 2005).”

New references:

Archuleta, C. M., DeMott, P. J., and Kreidenweis, S. M., Ice nucleation by surrogates for atmospheric mineral dust and mineral dust/sulfate particles at cirrus temperatures, Atmos. Chem. Phys., 5, 2617-2634, 2005.

Marcolli, C., Gedamke, S., Peter, T., and Zobrist, B., Efficiency of immersion mode ice nucleation on surrogates of mineral dust, Atmos. Chem. Phys., 7, 5081-5091, 2007.

Comment: 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, 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 ∼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).

Answer: It is indeed true that the gas temperature during the first expansion run from Exp. 4 almost reached the homogeneous freezing temperature of pure water droplets, i.e., the upper temperature limit of the temperature intervals for which homogeneous nucleation rates were deduced in the Benz et al. (2005) study. Nevertheless, we still

think that our interpretation of a modified crystalline surface structure better explains the observation of the second ice crystal mode for the following reasons: The referee suggested that there might be a step function in the ice-active fraction near the homogeneous freezing temperature. We indeed observed such sudden increase in f_ice during the experiment, but only at t = 270 s (fourth green line in the left panel of Fig. 8), i.e., 60 s after pumping had been stopped when the gas temperature had already increased to 239 K. The second ice crystal mode is also clearly apparent in the OPC scatter plot (third panel) as a denser point cloud. In order to explain this second ice crystal mode by homogeneous freezing, one would have to find a reason for the delayed detection of the nucleated ice crystals by the OPC, as also indicated by the referee. Such delay of ice particle detection, however, will only be an issue when studying ice nucleation at very low temperatures, i.e., when the ice particle detection is delayed by the growth time of pristine ice crystals to detectable sizes. Respective growth times were estimated by Möhler et al. (2006) to 4 s at 223 K, 8 s at 210 K, and 50 s at 196 K. In contrast, if already micron-sized supercooled water droplets would have frozen close to 238 K in the first run of Exp. 4, the micron-sized ice crystals should have been immediately detected by the OPC and not only after a delay of 60 s. The marked change in the depolarisation ratio after t = 210 s occurs because the spherical cloud droplets evaporate and leave behind the aspherical, crystalline sodium oxalate particles.

We have also indicated in the manuscript (page 11542, lines 7 – 11) that the second expansion run in Exp. 4 yielded a higher ice-active fraction compared to the first expansion run, i.e., more than those particles that nucleated ice in the first expansion run contributed to early deposition mode ice nucleation in the second freezing run. This is a clear indication that the ice nucleability of a larger number of aerosol particles must have been modified by the first expansion run. Note that the second nucleation event was not referred to as ‘condensation’ freezing but was explained by deposition ice nucleation on bare sodium oxalate crystals with a modified surface structure.

Furthermore, we have observed a similar modification of the ice nucleation ability also for the oxalic acid dihydrate particles in Exp. 6 (see Fig. 11 and the related discussion on page 11547, line 6 ff). Also here, a distinct second mode of ice crystals appears as soon as the afore-generated cloud droplets have evaporated and the bare oxalic acid dihydrate particles are again exposed to a supersaturated environment (second vertical green line in the right panel of Fig. 11). In this experiment, however, the second ice crystal mode starts to form already at a temperature of 239 K, i.e., this expansion run in fact represents an experiment as proposed by the referee to exclude the possibility of homogeneous ice nucleation. The reduced ice nucleability of the oxalic acid dihydrate particles from Exp. 7 (Figs. 13 – 15) might just be explained by a different particle morphology.

To address the referee's concern about the potential influence of homogeneous freezing, we propose to change our manuscript text as follows:

The statement: "Note that the AIDA gas temperature never dropped below the homogeneous freezing temperature of pure water droplets during the expansion." on page 11539, line 25, will be deleted.

The discussion of Fig. 8 on page 11540, line 9 ff, will be extended as follows:

"After the stop of pumping at t = 210 during run 1, it took about one minute for the cloud of supercooled water droplets to evaporate. At t = 270 s (fourth green line), the depolarisation ratio has regained its original value before the droplet cloud has formed, indicating that again crystalline sodium oxalate particles are present. I_back,par has decreased by an order of magnitude, reflecting the contribution of light scattering gone lost by the evaporation of the cloud droplets. The remaining signal in relation to the background level at time zero now contains only the scattering contribution from the nucleated ice crystals that are still present. Directly after the evaporation of the cloud droplets, f_ice suddenly increases up to a value of about 0.03. This second ice nucleation event can also be clearly seen in the OPC2 scatter plot by the appearance of

a new, denser point cloud after t = 270 s. Note that the gas temperature has almost reached the homogeneous freezing temperature of pure water droplets during the first expansion run, i.e., when pumping was stopped at t = 210 s, T was only a few tenth of a Kelvin higher than the upper threshold of the temperature intervals for which homogeneous ice nucleation rates were determined in the former AIDA study by Benz et al. (2005). One might therefore be tempted to explain the second ice nucleation event by homogeneous freezing. In such a case, however, one would have to give explanation for the delayed detection of the nucleated ice crystals since the second ice crystal mode only appeared in the OPC2 scatter plot 60 s after pumping had been stopped when the gas temperature had already increased to 239 K. Such delay of ice particle detection is a crucial issue when analysing ice nucleation experiments at very low temperatures because the growth time of pristine ice crystals to detectable sizes has to be taken into account (Möhler et al., 2006). Respective growth times were estimated by Möhler et al. (2006) to 4 s at 223 K, 8 s at 210 K, and 50 s at 196 K. In contrast, if already micron-sized supercooled water droplets would have frozen close to t = 210 s in the first expansion run of Exp. 4, the generated micron-sized ice crystals should have been immediately detected by the OPC2 and not only after a delay of 60 s. We therefore propose a different explanation for the second ice crystal mode. Note that after the evaporation of the cloud water at t = 270 s, the bare sodium oxalate particles are exposed to an environment that is still supersaturated with respect to the ice phase (S_ice about 1.27) and can thus again act as deposition mode ice nuclei."

New reference:

Möhler, O., Field, P. R., Connolly, P., Benz, S., Saathoff, H., Schnaiter, M., Wagner, R., Cotton, R., Krämer, M., Mangold, A., and Heymsfield, A. J., Efficiency of the deposition mode ice nucleation on mineral dust particles, Atmos. Chem. Phys., 6, 3007-3021, 2006.

On page 11541, line 20, "the continuous increase in f_ice after t = 90 s due to condensation freezing" will be changed to "the continuous increase in f_ice from t = 90 s to 270 s due to condensation freezing" in order to underline that the second nucleation event after t = 270 s is due to deposition nucleation and not due to condensation freezing.

On page 11547, line 15, we will add the statement: (discussion of Exp. 6, involvement of homogeneous freezing can be safely excluded).

"Note that homogeneous freezing cannot account for this second ice crystal mode because the gas temperature was still above 239 K at t =125 s."

Comment: 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 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?

Answer: There is indeed a disagreement in our analysis – we think that particularly the lower limit of 18 wt% of the estimated oxalic acid concentration is highly uncertain due to the following reasons which we will also outline in more detail in the revised manuscript. First of all, the retrieval of the particle diameter from the FTIR extinction spectrum only gives a rough estimate because the particle size is at the lower size limit for which a unique retrieval result for the particle size distribution can be inferred, i.e., a set of different values for the mode width and median diameter of the particle size distribution might satisfy the same optical data. Also, we employed the refractive

indices for pure supercooled water in the retrieval. More importantly, the oxalic acid concentration is estimated from the measured relative humidity (by TDL absorption) and Raoult's law (solid black trace in Fig. 1) whose validity for lower temperatures is also uncertain. As suggested by referee 2, we will add some information about the accuracy of the TDL measurements into the revised manuscript. The absolute accuracy of the TDL measurements is dominated by the line strength uncertainty of ± 3%. This comparatively small uncertainty transforms into a much larger uncertainty in the aerosol composition in particular for small oxalic acid concentrations due to the small negative slope of the solid black trace in Fig. 1 when approaching RH_liq = 100%. So for a relative humidity of 96% (maximum value of RH_liq immediately after aerosol addition, see Fig. 1), Raoult's law yields an oxalic acid concentration of 15 wt% (erroneously stated as 18 wt% in the original manuscript). When considering the uncertainty regime from 99 – 93% RH, oxalic acid concentrations ranging from 3 to 25 wt% would be obtained. So the oxalic acid solution droplets might indeed be much more dilute at the initial time period of Exp. 6, as indicated by the FTIR retrieval result and the size distribution measurement shown in Fig. 3d. An accurate determination of the aerosol composition at points a, b, c, and d would necessitate temperature- and composition-dependent infrared optical constants for oxalic acid which are currently not available. For a relative humidity of 89% (initial relative humidity that was restored again about 10000 s after aerosol addition), Raoult's law yields an oxalic acid concentration of 35 wt% (erroneously stated as 38 wt% in the original manuscript). When considering the uncertainty regime from 92 – 86% RH, oxalic acid concentrations ranging from 42 to 28 wt% would be obtained.

We will change our manuscript text as follows, starting from page 11543, line 10:

"Having observed a fast crystallisation of highly supersaturated oxalic acid solution droplets to oxalic acid dihydrate at T = 244 K, we decided to inject the aerosol particles into AIDA at a much higher temperature (T = 266 K) in order to probe whether less concentrated solution droplets would remain in a supercooled liquid state. The initial relative humidity with respect to supercooled water for the crystallisation and ice nucleation experiments started at T = 266 K was typically about 89%, yielding an approximate equilibrium solute concentration of only 35 wt% oxalic acid in comparison with about 67 wt% for an AIDA temperature of 244 K (see Fig. 1 and the discussion in Sect. 3.1). The top panel of Fig. 9 depicts the temporal evolution of the depolarisation ratio after spraying an aqueous solution of 4 wt% oxalic acid into the cooled cloud chamber with the dispersion nozzle at time zero for a time period of about 10 s (Exp. 6). The AIDA gas temperature is shown as a comparison. For a very long observation time of almost 3 h (t = 10000 s, first green line in Fig. 9), delta remains constant at a value of 0.02, indicating that the injected droplets indeed initially remained in a supersaturated liquid state. Note that a small background value for delta of typically 0.02 – 0.03 is observed even when only spherical droplets are present in the chamber. This is a result of Rayleigh scattering by air molecules, an imperfect alignment of the polarisers in the optical set-up, and a less than 100% horizontal or vertical polarisation of the laser light. At later times, however, the depolarisation ratio starts to increase although the chamber temperature was still kept constant at 266 K. This delayed onset of crystallisation is most probably the result of a changing solute concentration. As indicated in Sect. 2, the spraying technique was an efficient method to inject substantial aerosol mass loadings into AIDA within a few seconds. Because a dilute oxalic acid solution was sprayed in, excess water released from the evaporation of the solution droplets provoked a sudden rise in the relative humidity from 89 to 96 % after aerosol injection, as monitored by TDL absorption spectroscopy (red trace in the bottom panel of Fig. 9). It took about 10000 s to dissipate the excess of water vapour and to restore the initial relative humidity of 89 %. Due to the small negative slope of the ice-melting point curve at higher temperatures, the comparably slight increase of RH_liq from 89 to 96% leads to a substantial change in the equilibrium concentration of the oxalic acid solution droplets from about 35 to 15 wt% (Fig. 1). Note that these estimated acid concentrations are affected by a large uncertainty because the small negative slope of the ice-melting point curve also provokes that the comparatively small uncertainty

of about ± 3% in the TDL humidity measurements is transformed into a much larger uncertainty in the aerosol composition. Taking into account these uncertainties, the injected aqueous droplets initially attain an oxalic acid concentration in the range from 3 to 25 wt% and then slowly lose water and concentrate to 28 - 42 wt% within the first 10000 seconds of the crystallisation experiment. The shrinking of the solution droplets due to the loss of water is nicely mimicked by the decrease in the forward-to-backward scattering ratio from the laser light scattering measurements, shown as black trace in the lower panel of Fig. 9. Oxalic acid solution droplets with < (35 ± 7) wt% solute concentration can thus be maintained in AIDA for some hours in a supercooled liquid state without any detectable crystallisation, either homogeneously or heterogeneously on suited active sites in the chamber interior. This is in agreement with the result from Zobrist et al. (2006) that emulsified solutions of up to 20 wt% oxalic acid did not crystallise homogeneously upon cooling. Only for a sufficiently high solute concentration of about 28 – 42 wt%, the crystallisation of the solution droplets becomes detectable on the timescale of the AIDA experiment. To identify the chemical nature of the crystallised particulates, FTIR extinction spectra were again recorded at different time steps during the crystallisation experiment (see small vertical bars on the time scale in the top panel of Fig. 9 and the corresponding spectra in Fig. 10). Spectrum (a) features a broad extinction band in the O – H stretching regime, characteristic of aqueous oxalic acid solution droplets, as well as a pronounced light scattering contribution at non-absorbing wavenumbers > 3600 cm-1. Using the optical constants of pure water in this wavenumber regime in a Mie fitting procedure, the diameter of the oxalic acid droplets can be estimated to be about 1 micron. This is much larger than the droplet size simultaneously measured by the SMPS instrument (panel d, Fig. 3) because this device is not operated at the high relative humidity that is prevalent in the chamber interior and thus a significant shrinking of the particles size due to evaporation of water takes place. Note that the FTIR retrieval result is also somewhat ambiguous because the particle size is at the lower size limit for which a unique retrieval result for the particle size distribution can be inferred, i.e., a set of different values for the mode width and median diameter of the particle size distribution might satisfy the same optical data (Echle et al., 1998). Nonetheless, the retrieved particle size in combination with the size distribution measurement from Fig. 3d suggest that the injected oxalic acid solution droplets were initially very dilute, i.e., corresponding to the lower limit of the estimated range of acid concentrations from 3 to 25 wt%. An accurate determination of the aerosol composition would necessitate temperature- and composition-dependent infrared optical constants for oxalic acid."

New reference:

Echle, G., von Clarmann, T., and Oelhaf, H., Optical and microphysical parameters of the Mt. Pinatubo aerosol as determined from MIPAS-B mid-IR limb emission spectra, J. Geophys. Res. (Atmos.), 103, 19193-19211, 1998.

Comments: 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'.

Answer: Will be corrected in the revised manuscript.

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