

## ***Interactive comment on “New cloud chamber experiments on the heterogeneous ice nucleation ability of oxalic acid in the immersion mode” by R. Wagner et al.***

**R. Wagner et al.**

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We thank Referee #2 for the careful manuscript reading and critical comments to improve the quality of the paper. Below we will address the individual comments.

COMMENTS: General Comment: Although this is a good paper I have one major concern. To my view this paper would much better fit into a journal of physical chemistry than into ACP. If I had been asked to do the initial technical review I had recommended to transfer the paper to another journal. However, I only got the paper when it was already in ACPD, so I will not insist on transferring the paper to another journal. Major comment: Anyway, it would be beneficial for the paper when the authors include

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some statements on the atmospheric relevance of their research, in particular for cirrus clouds. The authors write that dicarboxylic acids make up 1-10% of the particulate organic carbon in various areas, but how does this compare to other substances that affect ice formation? Is oxalic acid (OA) an important player in cirrus formation or is it just a "footnote"? On Page 29457 (1st par) there is a long discussion why only a small number concentration of ice is produced in the AIDA chamber from the OA aerosol. As the AIDA is believed to mimic atmospheric processes, doesn't this imply that OA is an unimportant species for cirrus formation? Also on Page 29481/2 I find a discussion that suggests to me that OA is not really relevant for the atmosphere: "no early heterogeneous ice formation took place", "difficulty to detect a small heterogeneous mode..." give such indications. Given this, it was a bit surprising to find in the Summary (page 29488, l. 6-7) a statement "oxalic acid might play a considerable role in the Earth's climate system". At least the word "might" indicates that it is doubtful how considerable this role actually is.

ANSWER: We still think that the manuscript is appropriate for ACP, given the large quantity of recent studies addressing the hygroscopic behaviour, CCN properties, and ice nucleation behaviour of dicarboxylic acids that was partly published in the same journal. But we agree to revise and extend our summary section, as outlined in detail in our answer to referee #3. We will skip the statement "oxalic acid might play a considerable role in the Earth's climate system" and introduce a paragraph on the immersion freezing potential of other aerosol types like mineral dust and soot where, indeed, a somewhat larger shift of the heterogeneous ice nucleation onset from the homogeneous freezing point was observed compared to oxalic acid dihydrate. The discussions on page 29457 and 29481/2 specifically address a potential mechanism that could trigger the precipitation of oxalic acid dihydrate, namely heterogeneous crystallisation induced by the surface of nucleated ice crystals. As stated in the summary, we have indeed shown that the efficiency of this crystallization pathway was very low under our experimental conditions. But we have proposed different pathways by which immersed oxalic acid dihydrate crystals could form more efficiently.

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COMMENT: The paper is hard to read because the sections and subsections (and even single paragraphs) are very long. Please split them as appropriate.

ANSWER: Yes, we have included new subsections and new introductory comments before each main section, as outlined in detail in our answer to referee #3.

COMMENT: Otherwise I have only a number of minor and technical comments: P. 29452, l. 24-26: "This finding corroborates" - I cannot see this, please explain.

ANSWER: Yes, it is only an assumption that the particles probed by Baustian et al. (2010) had more surface defects than those investigated by Parsons et al. (2004), so to explain the observed differences in the ice nucleation behaviour. In the revised manuscript we will just state:

"Parsons et al. (2004) had already speculated that the investigated dicarboxylic acids could be more important in ice cloud formation if the particles had more surface defects than those generated in their study."

COMMENT: P. 29453, l. 15: I think, an emulsion is not the same thing as a solution. What is then an "emulsified binary solution"?

ANSWER: We will change the expression "emulsified binary solutions of oxalic, succinic, and adipic acid in water" to "emulsified aqueous solutions of oxalic, succinic, and adipic acid". This term has also been used by Zobrist et al. (2006), see first line of section 2.1 therein. A mixture of lanolin and mineral oil was added to the aqueous solutions of the dicarboxylic acids, and these samples were then emulsified.

COMMENT: P. 29453, l. 17: is "eutectic melting point of ice" a correct expression? Shouldn't it rather read "eutectic melting point of the mixture"? To my knowledge "eutectic" is a property of a mixture rather than of the single components.

ANSWER: Yes, absolutely right. We will change the statement accordingly.

COMMENTS: P. 29455, l. 5: According to the Köhler theory it should rather read "When

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exceeding 100% RH". P. 29455, l.13-17: The sentence is difficult to understand as it is rather long. Splitting it into two sentences would help.

ANSWER: Will both be corrected.

COMMENT: P. 29455, l. 23: Isn't it possible that in case A freezing happens before water saturation is reached?

ANSWER: Yes, we have here already anticipated our actual findings, as shown e.g. in the right panel of Fig. 5 (highlighted by the green circle) that the embedded oxalic acid dihydrate crystals were only ice-active when the solution droplets had become very dilute, i.e., when approaching 100% RH with respect to supercooled water. Ice nuclei of a higher activity in the immersion mode, of course, could induce freezing before water saturation is reached. We will change our manuscript text as follows:

"Also in experiment A, the aerosol particles could be ice-active in the immersion mode and induce freezing before water saturation is reached at point A2 of the trajectory. In case of lower heterogeneous ice nucleability, the aerosol particles will again be activated to a droplet cloud at point A2. Our previous experiments have shown that potentially immersed oxalic acid dihydrate crystals might then not get instantly and completely dissolved on the typical timescale of an expansion cooling experiment (Wagner et al., 2010). The embedded crystals therefore still can act as condensation mode ice nuclei in this experiment and could provoke the glaciation of the droplet cloud before the homogeneous freezing temperature of pure water droplets has been reached at point A3."

COMMENT: P. 29456, first par: I believe this par is about Zobrist's experiments, but it is not so clear. Please make clear which statements refer to Zobrist's experiments and which to AIDA.

ANSWER: At this position of the manuscript, we have introduced the new subsection 2.2 "Comparison with emulsion freezing experiments and envisaged strategies for the

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AIDA experiments” and an introductory statement that should clarify the purpose of our discussion. We have also added some expressions that the first paragraph indeed refers to Zobrist’s emulsion experiments.

COMMENT: P. 29456, I. 24-26: Why is the number concentration of ice crystals limited?

ANSWER: As can be seen e.g. in the left panel of Fig. 5, it only takes about 60 s before the relative humidity drops below 100% after the onset of ice nucleation (denoted by the second vertical green line). The increasing sub-saturation with respect to water causes the remaining, unfrozen cloud droplets (of smaller diameter and lower nucleation rate) to evaporate before they have a chance to freeze. The diameters of the cloud droplets roughly cover one order of magnitude on the size scale (1 - 10 microns), corresponding to a variation in the nucleation rate (if volume-dominated) by three orders of magnitude. During the residence time of the droplet cloud, the gas temperature only decreases (due to continued pumping) by about 0.6 – 0.7 K. As can be seen e.g. in Fig. 8 of Benz et al. (2005), this temperature decrease is far too low to induce a change in the nucleation rate by three orders of magnitude. Hence, as stated above, the smaller droplets of the cloud droplet size distribution have no chance to freeze before they start to evaporate.

Benz, S., Megahed, K., Möhler, O., Saathoff, H., Wagner, R., and Schurath, U., T-dependent rate measurements of homogeneous ice nucleation in cloud droplets using a large atmospheric simulation chamber, *J. Photochem. Photobiol. A*, 176, 208-217, 2005.

We will include a reference to the Benz et al. (2005) work in the revised manuscript text:

“Upon glaciation of the droplet cloud at about 237 K, however, ice crystals that have started to nucleate first in the chamber volume will grow at the expense of still unfrozen cloud droplets via the Bergeron-Findeisen process. The diameters of the cloud droplets

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roughly cover one order of magnitude on the size scale (typically 1 – 10 microns), corresponding to a variation in the homogeneous ice nucleation rate, if volume-dominated, by three orders of magnitude. During an expansion cooling cycle, the relative humidity starts to drop below 100% and causes the remaining cloud droplets to evaporate before they all have a chance to freeze (Benz et al., 2005). Even for the highest employable pumping speed or cooling rate, the absolute number concentration of nucleated ice crystals is thereby limited to a value of about  $100 \text{ cm}^{-3}$ , irrespective of the seed aerosol number concentration that is typically between  $10^3$  and  $10^4 \text{ cm}^{-3}$ .”

COMMENT: P. 29457, l. 27: please include "of the inorganic component" after "efflorescence".

ANSWER: Will be included.

COMMENTS: P. 29457, l. 28-29: I am puzzled by the word "pure" because it seems that you mean the solution (pure OA should not depend on RH; correct me if I'm wrong). P. 29458, l. 12: again the word "pure" disturbs me. I think this is NaCl crystals immersed in water.

ANSWER: In the first case, binary oxalic acid/water solution droplets are meant; and in the second case bare effloresced sodium chloride particles are referred to. Will be clarified in the revised manuscript text.

COMMENT: P. 29459, l. 17: what is Milli-Q quality water?

ANSWER: We will include a closer description of our purification method in the revised manuscript text. "Milli-Q quality" will be replaced by "purified":

"The water used for AIDA experiments is first treated by reverse osmosis (RO10, Werner) and then further purified using a filter cascade (NANOpure Infinity, Barnstead)."

COMMENTS: P. 29460, l. 16: wrong hyphenation of dia-gnostics. P. 29461, l. 1: probably you mean that the particle water is evaporated before the measurement is

done. The sentence is not clear.

ANSWER: The hyphenation will be corrected and the second sentence will be clarified. We indeed mean that the particle water is evaporated before the measurement is done.

COMMENT: P. 29462, l. 27: I am surprised that you need only an injection period of 5 s. This is certainly not the time it needs to reach a homogeneous concentration of  $10^{14}$  cm<sup>-3</sup> in the AIDA.

ANSWER: It took of course a few minutes before homogeneous conditions with respect to the aerosol particle number concentration were achieved throughout the chamber volume and before the aerosol was characterised by e.g CPC, SMPS, APS, and FTIR measurements. In the revised manuscript text, we will state:

“An injection period of 5 seconds typically yielded aerosol number concentrations in the order of  $10^4$  particles cm<sup>-3</sup> after homogeneous conditions were achieved throughout the chamber volume.”

COMMENT: P. 29466, l. 4-7: I cannot understand this sentence. In fig 5 (left) the traces for S<sub>ice</sub> do not coincide. So what is the sense of this statement?

ANSWER: This sentence refers to the two complementary methods for measuring S<sub>ice</sub>, the TDL absorption spectrometer and the frost point hygrometer (MBW). As stated in text, both traces for S<sub>ice</sub> indeed coincide, provided that no clouds of super-cooled water droplets/and or ice crystals (i.e., particle water) are present (i.e., before the first vertical green line shown in the figure and after t = 800 s when all ice crystals have evaporated).

COMMENT: P. 29467, l. 8: "only records the tail..." - not clear.

ANSWER: As stated on page 29461, line 5, the lower detection limit of the OPC2 is about 2.3 microns (spherical diameter). It therefore does not measure the entire size distribution of the effloresced NaCl crystals (see left panel of Fig. 3) but only the largest particles. We will change the manuscript text as follows:

"Note that the OPC2 only records the largest particles of the entire NaCl aerosol size distribution (see left panel of Fig. 3) whereas micron-sized cloud droplets and ice crystals are quantitatively counted."

COMMENT: P. 29467, l. 16: Again "reaching" should perhaps be replaced by "exceeding"

ANSWER: Will be changed.

COMMENT: P. 29467, l. 17: more precisely it should read "the largest seed aerosol particles".

ANSWER: When comparing the CPC3010 measurement of the NaCl aerosol number concentration before the start of pumping with the OPC1 and OPC2 count rates during the residence time of the droplet cloud (between the two vertical green lines shown in Fig. 5), we come to the conclusion that within measurement uncertainty indeed all seed aerosol particles are activated, as also stated e.g. on page 29456, l. 19-20.

COMMENTS: P. 29468, l. 3: Delete the reference to figure 6 here. P. 29468, l. 15: "explained in the caption of fig. 7" is clearer, and delete the word "explicitly".

ANSWER: Will both be changed.

COMMENT: P. 29469, l.12-21: Very difficult to understand. Isn't the assumption that OA dehydrate does not form the easiest (i.e. most parsimonious) explanation?

ANSWER: When comparing the results from Exp. 1 and 2a (Fig. 5), it is obvious that immersed solid ice nuclei must have been present after the deliquescence of NaCl in Exp. 2a in order to explain early heterogeneous ice formation before the homogeneous freezing temperature was reached (stated in l. 14 – 16 on page 29469). As discussed in the paragraph, we cannot prove that the embedded crystals were indeed oxalic acid dihydrate. So we have also speculated that a different oxalic acid species like the anhydrate might have been formed.

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COMMENT: P. 29470, l. 4: What is "the best part", how is that defined?

ANSWER: This depends on the eutonic composition of the mixtures, as stated in the sentence before. The statement should be better (and will be changed accordingly):

"The remaining part of the slightly water soluble organic compound forms a solid inclusion within the droplet."

COMMENT: P. 29471, l. 23: Is there really a Bergeron-Findeisen process? What is the actual  $p_w$  in the chamber and what is the saturation  $p_w$  of the solution droplets? A strong Raoult effect could prevent the Bergeron-Findeisen process.

ANSWER: Yes, we will change our manuscript text as follows:

"Due to the large number of nucleated ice crystals, the relative humidity quickly drops below 100%, i.e., the supersaturation with respect to ice is depleted. The increasing sub-saturation with respect to supercooled water causes the remaining cloud droplets to evaporate and to transform into interstitial NaCl/OA/H<sub>2</sub>O aerosol particles again."

COMMENTS: P. 29475, l. 8: "bears" instead of "bares". P. 29482, l. 7: delete "explicitly".

ANSWER: Will be changed.

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 29449, 2010.

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