

## ***Interactive comment on “Oxalic acid as a heterogeneous ice nucleus in the upper troposphere and its indirect aerosol effect” by B. Zobrist et al.***

### **Anonymous Referee #3**

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This paper combines experimental results about the heterogeneous ice nucleation of oxalic acid particles with model studies investing the atmospheric implications of the laboratory results. A differential scanning calorimeter was used to demonstrate that solid crystals were formed when homogeneous ice nucleation occurred in supercooled solution particles of oxalic acid. This is an interesting pathway for the formation of heterogeneous ice nuclei. Other dicarboxylic acids also froze homogeneously as expected, but did not crystallise. In a second cooling cycle, the crystalline oxalic acid particles acted as heterogeneous ice nuclei and induced freezing at warmer temperatures. A microphysical box model was applied to investigate the effect of the heterogeneous ice nucleation on the ice number densities in cirrus clouds. The possible effect of the

changed cirrus properties on climate was investigated with a global climate model.

In general, the applied experimental and modelling methods are sound and the results are appropriately presented and discussed. However, I am in particular concerned about the apparent disagreement of the pure oxalic acid results shown in Figure 2 with the homogeneous freezing line after Koop et al. (Nature 406, 611, 2000) as well as the definition and formulation of the nucleation rate and the conclusions drawn from that for atmospheric implications (see below). Nevertheless, the paper is of interest for the atmospheric sciences community and can be accepted for publication in Atmos. Chem. Phys. after the authors have addressed the points mentioned below and have accordingly revised the manuscript.

### **Comments and questions:**

(1) The term 'atmospheric conditions' used e.g. in Section 3.1 suggests that the lab results can directly be applied to atmospheric models. This needs further definition of what means atmospheric conditions her. In my view, only limited information is available for the concentration concentration and mixing state of oxalic acid in the atmospheric aerosol. Therefore, with 'atmospheric conditions' the authors may only refer to the temperature with regard to their laboratory studies. But only a narrow range of freezing temperatures is covered by the experiments with the pure oxalic/water system.

(2) In my view, the three points on page 3573 may define the laboratory, but not necessarily the tropospheric situation. For instance, what about deposition to other solid surfaces, e.g. minerals, and subsequent heterogeneous crystallisation. What about deposition nucleation directly to solid oxalic acid particles? On page 3574, the authors argue against the deposition mode because oxalic acid mixes internally with other co-emitted substances. On the other hand, they mention that oxalic acid can also be formed as a secondary product from organic precursors. I suspect this also involves gas-phase reactions. Can one really exclude from the sparse knowledge and data basis that oxalic acid may be deposited to other solid surfaces like minerals, crystallize

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heterogeneously, or act as an ice nucleus in different modes? The atmospheric fate of oxalic acid ending as immersion mode ice nucleus appears to me too simple and restrictive.

(3) Concerning Figure 1: Is the dashed curved scaled vs. the solid? In other words, did all droplets in the first cycle induce OAD formation? Can the fraction of OAD particles acting as heterogeneous IN in the second cycle be estimated from the data? At least the homogeneous nucleation rate is a steep function of the temperature. Shouldn't the DSC peaks therefore be more narrow? How compares the peak width of the pure water runs with the oxalic acid runs? In other words, can one conclude from the peak width for the dependence of the nucleation rate on temperature (as mentioned in the appendix) or is the peak width mainly determined by instrument parameters? The question if the heterogeneous ice nucleation rate follows the same  $\partial \ln J / \partial T$  or not is critical for the application of the shifted homogeneous freezing rate equation. This should be mentioned somewhere in the manuscript.

Can the definition of the 'freezing point' be indicated in Figure 1? The freezing point given for the homogeneous run (solid red line) is different from that in Table 1. Please check for consistency.

(4) In Figure 2, the heterogeneous ice freezing points appear to show better agreement with the Koop line than the homogeneous ice freezing points, at least for most of the data points at lower temperatures which are of major importance for the conclusions of the present paper. For the further data evaluation and model application the homogeneous freezing points are rigorously shifted to be in agreement with the homogeneous freezing formalism suggested by Koop et al. (2000). On Page 3582 the authors argue for this procedure with unknown or uncertain water activity data. However, as long as the homogeneous nucleation rates for oxalic acid are not measured as function of temperature and relative humidity (or water activity), the application of the formalism by Koop et al. (2000) may also be considered as uncertain for the system under investigation. This apparent inconsistency must be addressed by the authors and an

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estimate should be given for the the impact on the modelling results which arises from a possible systematic overestimation of freezing temperature due to the data shift.

(5) Just a comment about the idea of a Bergeron-Findeisen-like OAD growth mechanism: This effect applies only if pure OAD particles grow in a vapour environment controlled by the solution phase. However, the working assumption of immersion freezing applied in the present paper implies that the 'nano-crystals' are embedded or immersed in solution particles. The vapour difference between a solution particle containing an OAD crystal and a completely deliquesced oxalic acid particle may be very small, and hence also the growth rate of the solid phase particle. The growth equation A2 only considers diffusion growth. For the small particles of interest here, a transition regime formalisms between the kinetic and diffusion growth may be more appropriate.

(6) Concerning the conclusion for dependence of the heterogeneous nucleation rate as steep function of the temperature: Can this also be biased by the size distribution of the droplets in the emulsion? Can it be assured or was it controlled to be similar in all experiments? Or would the authors expect that the results are almost identical for the same sample mass but different droplet size and number?

(7) At the beginning of Section 4 it is stated that the experimental results may be parameterised with water-activity based nucleation theory for model application. However, nucleation theory was not yet applied up to this point. Strictly speaking it was just shown that heterogeneous freezing occurs at a somewhat higher mean temperature. The experimental results e.g. provided no information about the ice formation rate or respective nucleation rates. The applicability of nucleation theory was not demonstrated or derived from the data, it is just used as a working hypothesis (see comment above).

(8) The statement about the reduction of ice number due to heterogeneous IN on page 3586, line 11 ff. is not correct in my view, or at least not complete. I think, the effect also very much depends on e.g. the cooling rate. At very low cooling rates the ice number

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can be limited to very low heterogeneous IN concentrations. In this case, the IN number and therefore the ice number can be much smaller than in the case of homogeneous freezing. This makes the strongest effect on the ice number concentration, as far as I understand the approach by Kärcher and Lohmann (2003).

**Minor comments and typos:**

*p.3572, l.6:* '2 and 5' instead of '2-5' (which reads 2 minus 5).

*p.3577, l.22:* ... assuming a single spherical nucleus?.

*p.3579, l.7:* Remove the word highly.

*p.3582, l.21:* 2 % of what?

*p.3584, l.12:* Was the mass 89 identified as a characteristic peak in lab experiments with pure oxalic acid particles?

*p.3589, l.22:* Is the upper troposphere really 'heavily loaded' with oxalic acid?

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