

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

B. Zobrist et al.

Received and published: 13 July 2006

The authors would like to thank anonymous referee #1 for his/her constructive comments. We have addressed the referee's concerns point-by-point below.

Succinic and Adipic acid as immersion IN:

The solubility of these dicarboxylic acids is very low at temperatures of about 235 K, as supported by the deliquescence measurements of Parsons et al. (JGR 109, D06212, 2004) which are close to 100 % RH. In our experiments, the droplets of these acids are completely liquid in the first cooling cycle with concentrations of 7.3 wt% for succinic acid and 1.6 wt% for adipic acid, which is why they nucleate ice

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

homogeneously at temperatures below that of pure water. When the acids precipitate, the concentration of the remaining liquid corresponds to the equilibrium solubility at each temperature when the samples are cooled in the second cycle. Because of the low solubility at lower temperatures we expect the observed rise in the homogeneous ice nucleation temperature when compared to the first cooling run. In fact, if we use the measured freezing temperatures and assume they are due to homogeneous ice nucleation, we can use water-activity-based ice nucleation theory to deduce the water activity of the liquid part of the samples. The results are $a_w = 0.989$ for succinic acid and $a_w = 0.995$ for adipic acid. Both these numbers are in very good agreement with the deliquescence relative humidities determined by Parsons et al. Therefore, our data reveal that the measured freezing temperatures in the presence of succinic and adipic acid crystals are consistent with homogeneous ice nucleation. Hence, if these acids act as immersion IN at all, their effect is so tiny that it is indistinguishable from homogeneous ice nucleation.

Oxalic acid dihydrate as deposition IN:

We do consider the immersion mode as more likely than the deposition (see also reply to Referee3 Comment 2). We have added a paragraph at page 3574 line 11: "Criterion (iii) asks for IN in immersion mode, not in deposition mode. This is justified by considering that dicarboxylic acids are directly emitted into the atmosphere together with other aerosol components and mix internally via gas phase diffusion (Marcolli et al. 2004b). In addition, the smallest dicarboxylic acids are produced by slow conversion of organic precursors in aqueous liquid-phase oxidation reactions in the free troposphere, and, therefore also end up in aerosol particles that consist of a mixture of solutes (Ervens et al., 2004; Legrand et al., 2005). If an organic substance precipitates from a multi-component mixture, its crystals will be embedded in an aqueous solution consisting of inorganic and/or other soluble organic solutes and, therefore, can only act as an immersion IN.

To act in deposition mode, all solutes would have to co-crystallize, which is highly

unlikely when considering that many solutes do not crystallize readily such as H_2SO_4 or other non-precipitating organics. Aqueous solution aerosol particles consisting of only a single organic component from which a pure organic could crystallize are thermodynamically not favored in the atmosphere. Also the deposition nucleation of organic substances on solid particles are kinetically inhibited as this process requires high supersaturations, however, for water soluble organics high gas phase supersaturations are reduced due to their solubility in aqueous aerosol particles."

Oxalic acid precipitation:

At low temperature the saturation concentration of oxalic acid is decreasing rapidly (e.g., the saturation concentration of oxalic acid at 236 K is around 0.35 wt%), leading to aerosol particles that are supersaturated with respect to this substance for typical atmospheric concentration levels. For air masses with low oxalic acid fraction this saturation level will probably not be reached. However, once ice forms in such droplets at low temperatures the saturation ratio of oxalic acid (and most other organics) will increase by orders of magnitudes, which is why we believe precipitation is likely under atmospheric conditions, just as observed in our experiments. (The same is true for adipic and succinic acid, however, as pointed out above they do not show to be efficient immersion IN.) The first experiment listed in Table 1 cannot be used as an argument that oxalic acid will not form in the atmosphere. The fact that this solution does not show heterogeneous ice nucleation in the second cooling cycle is due to the fact that oxalic acid dihydrate melts at the conditioning temperature, because the concentration of oxalic acid is smaller than the eutectic concentration. This is, however, just an artifact of our laboratory trajectory and will not occur in this way in the atmosphere. That oxalic acid can act as immersion IN at even lower concentrations is evident from the second experiment in Table 2, where an oxalic acid concentration of 0.33 wt% is sufficient to provide oxalic acid dihydrate nuclei for heterogeneous ice nucleation.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Global modeling:

In the global radiative modeling the difference between cirrus clouds that are exclusively formed by homogeneous nucleation are compared to those where a competition between homogeneous and heterogeneous nucleation on OAD is possible. Therefore we will change the first sentence on page 3587 to "We calculated the shortwave and longwave radiative effect at the top-of-the atmosphere (TOA) using the ECHAM4 climate model (Appendix C) in order to investigate the global impact of the reduction of n_{ice} caused by heterogeneous freezing in the presence of OAD compared to cirrus clouds exclusively formed by homogeneous nucleation." Of course this is just the maximum possible effect of OAD, which is why we state that the observed TOA effect is only an upper limit. Future work should indeed compare the influence of different IN on the microphysical properties of cirrus and their effect on global radiative transfer. However, at present too little is known about the global concentrations and distribution of different IN.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 3571, 2006.

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper