The role of organics for atmospheric nucleation of H_2SO_4/H_2O particles

T. Berndt, O. Böge, F. Stratmann and J. Heintzenberg

Leibniz-Institut für Troposphärenforschung e.V., Permoserstraße 15, 04318 Leipzig, Germany

Keywords: particle formation, sulfuric acid, ultrafine particles

Atmospheric data from simultaneous measurements of newly formed particles and H_2SO_4 at ground level show consistently that about 10^7 cm^{-3} of H_2SO_4 are necessary in the atmosphere for particle formation (Kulmala *et al*., 2004). Laboratory data on binary sulfuric acid nucleation with water using sulfuric acid from a liquid reservoir, however, indicate particle formation for H_2SO_4 concentrations of 10^{10} cm^{-3} or more (Ball *et al*., 1999). Ternary nucleation, involving the additional ubiquitous species ammonia, has been suggested from theoretical considerations as an explanation for observed particle nucleation in the atmosphere (Coffman & Hegg, 1995). To date, no direct experimental evidence for or against this ternary nucleation has been presented.

Recently, the formation of new particles has been investigated in a laboratory study starting from H_2SO_4 produced in situ via the reaction of OH radicals with SO_2. Newly formed particles were observed for H_2SO_4 concentrations of about 10^7 cm^{-3} without ammonia addition in the carrier gas (Berndt *et al*., 2005). To date, no definite mechanistic explanation for the different H_2SO_4 concentrations needed for particle formation of about 10^7 cm^{-3} (in situ produced H_2SO_4) and 10^{10} cm^{-3} (H_2SO_4 from liquid reservoir) can be given. In the experiments with in situ-produced H_2SO_4, the following simple reaction scheme was considered:

$$OH + HC \rightarrow \text{products} \quad (1)$$

$$OH + SO_2 \rightarrow H_2SO_4 \quad (2)$$

$$H_2SO_4 \rightarrow \textit{wall} \quad (3)$$

The hydrocarbon (HC: cyclohexane, *n*-heptane, mesitylene, or furan) was added to the reaction mixture for OH radical titration allowing the calculation of the H_2SO_4 concentration.

Subject of this work is to find out whether or not hydrocarbons can influence the nucleation process. If there is any effect, the oxygenated reaction products from pathway 1 (carbonylic substances, etc.) are probably more suitable candidates than their precursor molecules. In a recently published study, a distinct contribution to the process of particle growth from oxidation products of mesitylene (carbonylic substances) was observed experimentally (Kalberer *et al*., 2004).

In our experiments, carbonylic substances were added to the reaction gas with concentrations close to atmospheric levels. Figure 1 as an example shows the number of newly formed particles with and without added acetaldehyde ($5.2 \cdot 10^{10}$ cm^{-3}). For OH radical titration cyclohexane ($4.5 \cdot 10^{12}$ cm^{-3}) was chosen and the SO_2 concentration was $7.4 \cdot 10^{10}$ cm^{-3}. After adding acetaldehyde, a small but significant decrease of the particle number is visible. This fact is obviously caused by additional consumption of OH radicals by acetaldehyde in competition to pathways 1 and 2 lowering the amount of H_2SO_4 formed. Consequentely, no significant influence of acetaldehyde or aceton on the number of produced particles was obseverd.

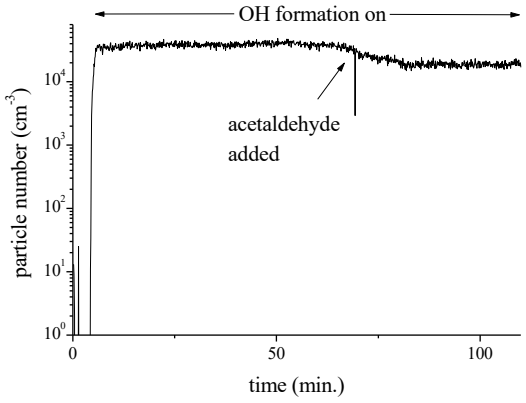

Figure 1. A typical experiment with acetaldehyde addition.

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