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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Homogeneous nucleation rates of nitric acid dihydrate (NAD) at simulated stratospheric conditions – Part II: Modelling" *by* O. Möhler et al.

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We acknowledge the comments and questions addressed by both referees of our paper. Here we reply to referee #1.

Answer to the specific comment: It is obvious that the NAD nucleation rate strongly depends on temperature and the saturation ratio S_{NAD} with respect to the solid phase. Both parameters are highly variable in the polar winter stratosphere. In a recent paper (Knopf, J. Phys. Chem. A, 110 (17), 5745 -5750, 2006), NAD and NAT pseudo-heterogeneous nucleation rates where estimated for a stratospheric pressure of 50 hPa and volume mixing ratios of 5 ppm, 10 ppb, and 0.5 ppb for H_2O, HNO_3, and H_2SO_4, respectively. At these conditions, the aqueous sulphuric acid particles take up signifi-

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cant amounts of nitric acid at temperatures below about 192 K. Assuming equilibrium composition of the ternary solution particles as a function of the ambient temperature, S_{NAD} reaches a maximum value of about 4.2 at a temperature of 191 K. For these conditions we obtain, with the parameterisation suggested in Eqs. 5 to 7 of our paper, an activation energy of 33.3 kcal/mol and a respective volume-based nucleation rate of 4×10^{-17} cm^{-3}s^{-1}. For a total aerosol volume of 1 μm^{3}cm^{-3} we obtain a NAD formation rate per unit time and air volume of about 1×10^{-25} cm^{-3}h^{-1}. This is by far too low to explain large particles observed in the polar stratosphere with number concentrations in the range 10^{-4} cm^{-3} to 10^{-3} cm^{-3} and interpreted as NAD or NAT (Fahey et al., Science 291, 1026, 2001, Brooks et al., J. Geophys. Res. 108, 4652, doi:10.1029/2002JD003278, 2003, Larsen et al., Atmos. Chem. Phys. 4, 2001-2013, 2004, Voigt et al., Atmos. Chem. Phys. 5, 1371-1380, 2005). The formation rates should, as a rough estimate, be larger than 10^{-6} cm^{-3}h^{-1} in order to yield the observed number concentrations within a few days.

However, the conditions taken for the estimate above are certainly not representative for the entire polar vortex. In particular at lower temperatures, pressures, and humidities, S_{NAD} can be markedly larger than 4. With the parameterisation suggested in the present paper, NAD formation rates of 10^{-6} cm^{-3}h^{-1} are reached for saturation ratios of about 8 and 9 at temperatures of 190 K and 185 K, respectively. From that we conclude that homogeneous NAD nucleation can only play a role in the formation of polar stratospheric clouds if S_{NAD} approaches or exceeds these values. The actual values of S_{NAD} throughout the polar vortex are not easy to assess because this depends on quite uncertain parameters like relative humidity with respect to water, water activities, or saturation pressures at very low temperatures. A thorough analysis is beyond the scope of the present paper.

The above discussion will be added to the conclusion section of the manuscript (page 2137, line 1). We would not like to speculate about a possible heterogeneous pathway to NAD or NAT formation on the basis of our laboratory results.

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Answer to minor comments:

page 2121, line 6-8: That is right. We will change it to ”grow to sizes larger than STS particles”.

page 2123, line 3: Yes.

page 2135, line 17: Nice comment, and correct. Will be changed.

page 2138, line 9: This is a good question. We have no good answer right now.

Table 1: Units will be added.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 2119, 2006.