

Interactive comment on “The interaction of N₂O₅ with mineral dust: aerosol flow tube and Knudsen reactor studies” by C. Wagner et al.

C. Wagner et al.

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We thank Michel Rossi for his comments on our manuscript. The comments made and our reply are listed below.

Comment: Have any reference experiments been performed on the interaction of N₂O₅ with the empty sample compartment of the Knudsen reactor? If yes, is the measured rate coefficient commensurate with the above-mentioned $k_{dec} = 0.04 \text{ s}^{-1}$ obtained in the aerosol flow reactor after taking into account differences of the surface-to-volume (S/V) ratio? I believe it to be important to understand both experiments in sufficient detail so as to result in constant, that is transferable, rate constants (at a given common S/V ratio).

Reply: Yes, as we state on page 13301, no uptake of N₂O₅ is observed to the empty

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sample compartment (Al_2O_3 crystal sample support). In contrast to the walls of the AFT, the Knudsen reactor sample compartment is Teflon coated, dry and not coated with a layer of dust. Comparison is thus meaningless.

Comment: I am not quite sure how the authors evaluated the degree of HNO_3 contamination in their N_2O_5 sample (pg. 13302, 13312) expecting a very weak MS signal for HNO_3 .

Reply: The HNO_3 signal was of course weak compared to that of N_2O_5 , but could be accurately measured by integrating at $m/z = 63$ for much longer. This took time, so the HNO_3 impurity level was determined prior to the uptake experiment, but at the same N_2O_5 flow rate. The $\text{N}_2\text{O}_5 / \text{HNO}_3$ ratio was assumed to be the same during the uptake experiment. This will be clarified in the revised manuscript.

Comment: On page 13314 the authors claim a first-order rate law for N_2O_5 interacting with SDCV based on a variation of the concentration by a factor of four. In my view, this test is not sufficient owing to limited sensitivity over a narrow variation of the concentration. Deviations from a first-order rate law are just not visible over the stated concentration change. If k_d is truly first-order it must be independent of k_{esc} or the escape hole diameter which is seldom the case, and N_2O_5 is no exception. Did the authors perform uptake experiments in reactors of different k_{esc} that perhaps have not been presented?

Reply: A factor 4 variation in concentration was sufficient to show that, within experimental error, there was no dependence of the uptake coefficient on this parameter. Recall that, by working at very low concentrations, saturation effects which may cause such a dependence are not expected to occur. Extension of this factor 4 by going to lower concentrations would have been difficult owing to detection limitations. Seeing that data at low concentrations should give better values of the initial uptake coefficient, extension to higher concentrations would not seem to be a particularly useful exercise. k_{esc} was not varied.

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Comment: I am astonished as the authors are regarding the discrepancy between the present results and our own for all three mineral dust substrates presented (Karagulian et al., Atmos. Chem. Phys. 2006, 6, 1373-1388). I concur with the authors that the difference must lie in the sample preparation method in that we did not heat the sample to 460 celcius. Could partial sintering be the cause for the smaller reactivity? This is perhaps similar to the case where an unexplained discrepancy between the amount of adsorbed H₂O was found when CaCO₃ was heated to 120 celcius during a certain time compared to no heating at all. Gustafsson et al. (Atmos. Chem. Phys. 5, 3415-3421, 2005) report 0.8 monolayer of adsorbed H₂O on CaCO₃ whereas Santschi et al. (J. Phys. Chem. A 2005, 110, 6789-6802) report 3.5 formal monolayers of adsorbed H₂O on CaCO₃, both taken at 33

Reply: The difference between the results of Karagulian et al and this work is indeed surprising. As stated in the text, the samples were from the same SDCV batch and thus identical apart from modifications induced by handling and preparation differences in the two laboratories. Again, this highlights the potential pitfalls when working with bulk samples of solid substrates. Note also that the (different) SDCV sample of Seisel et al, which was not heated resulted in uptake coefficients which were still about a factor of 4 larger than Karagulian et al found.

Comment: - In contrast, I have no problem accepting the trend of gamma with relative humidity (increasing gamma with decreasing rh). In unpublished experiments on SO₂ and NO₂ uptake on mineral dust substrates we found that gamma decreased with the amount of adsorbed H₂O. However, we were not able to unambiguously establish the relationship between rh and the amount of adsorbed H₂O.

Reply: It is difficult to compare the uptake of N₂O₅ to a surface with that of NO₂. One is efficient and reactive (N₂O₅) and the other (NO₂) is not. There have been some experiments that show a negative dependence of the uptake of organics with mineral dust with humidity but, unlike N₂O₅, this is a reversible process (Goss, K.-U., Env. Sci. Tech. 26, 2287-2294, 1992.)

Comment: Typos: pg. 13304, line 12 (space missing) pg. 13322, line 12 ("atmosphärischen") pg. 13333 (Figure 3, legend): "acquisition" pg. 13338 (Figure 8, legend), "assuming"

Reply: These typographical errors will be taken care of in the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 13291, 2007.

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