**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "The interaction of N_2O_5 with mineral dust: aerosol flow tube and Knudsen reactor studies" *by* C. Wagner et al.

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Comment on "The Interaction of N2O5 with Mineral Dust: Aerosol Flow Tube and Knudsen Reactor Studies" by C. Wagner, F. Hanisch, N. Holmes, H. de Coninck, G. Schuster and J. N. Crowley

This is a nearly flawless study on a heterogeneous reaction of NOy that may yet reveal its importance for the atmosphere before long. The redeeming feature of this work is the critical comparison between Knudsen flow reactor and atmospheric pressure aerosol reactor results that strongly suggest that the uptake coefficient "gamma" is much closer to the upper limit value given by the geometric surface rather than by the BET surface area despite the uncertainties in the interpretation of aerosol kinetics that are adequately addressed in this work. This difference usually amounts to three orders

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of magnitude in gamma (factors of 500 to 1000 depending on the amount of material used), and the information conveyed in the present work may be of importance to atmospheric modelers.

In what follows I will list minor points of discussion that the authors may consider before submission of the final work. However, I would like to point out that these points will almost certainly not change the conclusions presented.

- Although the authors show that the reactivity of NO2 and NO3 does not influence the kinetic results on N2O5 in the present study, it may be of interest to point out that the 7s lifetime for NO3 given on pg. 13298 (bottom) likely refers to the homogeneous (decomposition) lifetime of NO3 (kdec = 0.14 s-1, reference R. Wayne et al., pg. 162 and 188). For the sake of information the rate constant for heterogeneous decomposition kdec of NO3 on Pyrex glass as a function of temperature is displayed in the enclosed Figure (available on demand at michel.rossi@epfl.ch) as a function of temperature and corresponds to kdec = 6.4 s-1 pretty much over the whole T-range corresponding to gamma = 0.08 ś 0.02 (PhD thesis no. 2158 (2000), EPFL, B. Flückiger, unpublished). The reaction product of this reaction is NO as detected by REMPI in addition to adsorbed NO3 and is formed according to NO3 ==> NO + O2 (DeltaH0r = +4 kcal/mol) in yields approaching 1.0 at T = 550K (Figure 6.14 in above-mentioned PhD thesis). The same rate constant for a FEP Teflon reactor wall has been measured as kdec = 0.6 ś 0.2 s-1, smaller by roughly a factor of ten (Table 2 in Karagulian and Rossi, Phys. Chem. Chem. Phys. 2005, 7, 3150-3162), but somewhat dependent on wall coverage (lower values with increasing surface coverage). In comparison to these values the authors find kw = 4x10-2 for N2O5 on FEP Teflon mentioned on pg. 13305 (aerosol reactor) which is roughly another factor of ten lower and is coherent with the general trend in the ratio of gamma(NO3)/gamma(N2O5) of ten for many investigated substrates. (Figure should fit in here)

Here are some questions/comments:

- 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 kdec = 0.04 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).

- At these low flows of N2O5 what was the signal-to-noise ratio of the HNO3 signal at m/e 63? I am not quite sure how the authors evaluated the degree of HNO3 contamination in their N2O5 sample (pg. 13302, 13312) expecting a very weak MS signal for HNO3.

- On page 13314 the authors claim a first-order rate law for N2O5 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 kd is truly first-order it must be independent of kesc or the escape hole diameter which is seldom the case, and N2O5 is no exception. Did the authors perform uptake experiments in reactors of different kesc that perhaps have not been presented?

- I am as 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°C. 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°C 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% rh. However, the measured BET surfaces were significantly different, 17.8 vs. 3.7 m2 g-1 for the former and latter, respectively.

- 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.

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

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