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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Kinetics and mechanism of the uptake of N_2O_5 on mineral dust at 298 K" *by* S. Seisel et al.

Anonymous Referee #1

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Reply to the interactive comment by anonymous referee no. 2 on "Kinetics and mechanism of the uptake of N2O5 on mineral dust at 298 K" by S. Seisel, C. Börensen, R. Vogt and R. Zellner Submitted to Atmos. Chem. Phys. Discuss. 5, 5645-5667, 2005.

Several confusing statements made by anonymous referee no. 2 in his/her interactive comment on the above-cited paper prompted me to submit the following rebuttal regarding points no. 1 and 5:

Referee no. 2 misses the point made by the authors regarding the justification of the geometric surface area used for the evaluation of the uptake coefficient. The essence of the argument lies in the fact that the pulsed valve admission experiment yields results for the uptake coefficient virtually identical to continuous flow admission, albeit taken at “zero” time after the start of the uptake reaction (Figure 4). The assertion is that it is impossible for the gas to explore the BET surface area of the sample during a typical pulse decay episode taking place during a second or so. This was precisely the reason why the pulsed valve admission technique was invented, namely to keep saturation of the solid substrate to a minimum while at the same time working at concentrations used in steady-state experiments.

Let’s do an example using typical results/parameters obtained by the authors. For “gamma” (g) = 10-2, N2O5 at 300K and a N2O5 concentration of 1011 molecule cm-3 (3.1x10-6 Torr) the kinetic theory of gases obtains gZ11 = 6.1x1012 collisions cm-2s-1. Assuming a typical BET surface area of 40 m2/g for Saharan dust (Hanisch and Crowley, 2003) and a limiting low sample mass of 100 mg we “need” to saturate 4x104x1013 = 4x1017 sites if “saturation” starts already at a surface coverage of 1013 molecules cm-2 which is a very conservative lower limit. Usually, surface coverages of the active site population of 50% or more are required to obtain measurable saturations. This example shows that it would take 6.5x104 seconds (18 hours) to saturate the 100 mg substrate to 1% at these low pressures of N2O5 in a Knudsen flow reactor, an unrealistically long experiment. Even if we take the geometric surface (20 cm2) as the relevant surface area at short interaction times of less than a second, the characteristic pulse decay time in a Knudsen flow reactor, the gas pulse would have to “visit” 20x1013 = 2x1014 sites which would take 33 s at the 1% coverage limit and the gZ11 value calculated above. This goes to show that the pulsed valve admission experiment only “superficially” probes the solid substrate. This line of argument, by the way, is also valid for soot and other solid substrates where pulsed valve experiments have been performed in the past. Grassian and coworkers are completely ignoring this argument to this day and persist to report unrealistically low values (10-5 to 10-6) for a range of uptake experiments.

Although I agree with anonymous referee no. 2 that the uptake coefficients obtained

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on the basis of the geometric surface area of the sample have to be addressed as being upper limits (pg. S2068), I have to qualify that statement by emphasizing that the "gammas" so obtained are very close to the true uptake coefficient, perhaps within a factor of two. This is the estimated extent to which the gas "interrogates" deeper-lying layers of the powder sample during the short interaction times. In any case, from a gas-kinetic point of view, Z11 and the associated uptake coefficient are determined by the projection of the "real" surface to the geometric support surface despite potential asperities or the surface roughness of the sample (pg. S2069). Just because the surface is rough does not lead to an increase in Z11 or the rate of uptake gZ11! (Remember: g describes the kinetics of the irreversible removal of molecule M from the gas phase!) From the quantitative argument presented above I think that the authors DO show that mostly the uppermost layer is involved in the uptake of N2O5 on Saharan dust, and I take exception to the statement at the bottom of page S2068 made by anonymous referee no. 2 regardless of how many layers of Saharan dust have been exposed to the gas.

A last point concerns the comments on the mass dependence of "gamma" made by anonymous referee no. 2 on pg. S2069. It is trivial to see that the rate constant for heterogeneous uptake khet = g ($<$c$>$/4)(S/V) linearly scales with S, the relevant (active) surface of the sample. This increase takes place from S=0, that is at zero mass m, to some value of m that corresponds to complete surface coverage of the sample support by the first coherent sample layer. This point is attained for 1 "formal grain layer" in Figure 4 corresponding to a mass of probably between 100 to 300 mg of Saharan dust (in this respect I agree with anonymous referee no. 2 that it would be helpful if the authors gave additional data on the used grain diameter, etc.). In that sense it would be desirable to perform uptake experiments in the 0 to 300 mg range in order to observe the transition from the "linear mass dependence" (Grassian and coworkers) to the mass-independent regime. For low sample masses a mass-dependence of khet is always expected, and in fact observed. One may even deduce the effective grain size of the sample from this turnover point provided that the experiment correctly addresses

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the initial value of khet or g0.

As a concluding remark I would like to stress that field observations support g values on the order of 10-2 for N2O5 interacting with (urban) aerosol (Wood et al., ACP 5, 483, 2005). Despite the fact that most field studies were taking place in polluted urban environments and not in the desert in the presence of mineral dust it is very likely that uptake coefficients on the order of 10-5 or 10-6 that have been obtained from laboratory experiments using the BET surface are out of whack by several orders of magnitude.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 5645, 2005.