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Interactive comment on “The heterogeneous chemical kinetics of N_2O_5 on $CaCO_3$ and other atmospheric mineral dust surrogates” *by* F. Karagulian et al.

Anonymous Referee #1

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General Comments

This experimental study of the interaction of N2O5 with bulk mineral surfaces has derived large uptake coefficients using the Knudsen reactor approach and dry samples. If these uptake coefficients are correct, this reaction can make a significant contribution to the NOy budget of some parts of the troposphere. HNO3 was observed as reaction product, and a mechanism proposed to account for the experimental observation of CO2 and H2O and their dependence on experimental conditions. The bottom line is that N2O5 uptake is faster than previously believed. However, as in all studies of heterogeneous processes using non-homogeneous bulk samples, a major challenge is to derive the surface area responsible for the observed uptake kinetics. Generally the choice is between the geometric surface area, the total (e.g. BET) surface area or using an empirically derived approximation of the rate of diffusion of the gas into interstitial space. As shown below, the arguments presented by the authors in favour of the geometric surface are difficult to follow and are not particularly convincing. The co-presentation of initial and steady-state uptake coefficients through much of the manuscript, before apparently rejecting the steady-state value in calculating atmospheric lifetimes is cumbersome. A explanation at the beginning of the manuscript why the steady state values are not of interest would clarify the issue, and make the paper more readable.

Significant revision is recommended.

Major Comments:

P10371, l0-15 This sentence implies that the uptake of HNO3, N2O5 and NO3 to dust is known to represent an important sink of NOy. Fact is that these are modelling results, based on poorly characterised uptake kinetics and dust loadings. It would be useful at this point to mention the model assumptions used in deriving the reported effect on nitrate. Similarly, on line 25, the model results of Dentener et al did not show that interaction of trace gases “will” effect the ptotooxidant cycle, they merely indicate the potential for dust to do this, based on estimated uptake coefficients. Try not to confuse model results with reality !

P10372, L19 The statement that there are no reports on laboratory experiments that deal with N2O5 interaction with mineral dust aerosol surrogates is not consistent with the next line that identifies a recent study of N2O5 + Saharan dust (is a bulk Saharan dust sample not a surrogate for airborne mineral aerosol ?)

P10372, L25 What is an “authentic” mineral dust sample ?

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P10373, L23. There is no mention of the mass, density or variation in depth of the bulk samples used.

P10374, L23. In the text preceding this line, the authors describe the MS fragment patterns and the influence of HNO3 on m/z = 46. and the fact that they monitored masses at m/z = 30, 46 and 63. They then contradict this by stating that N2O5 was quantified by its fragment at m/z = 46. Presumably this refers to the corrected signal at this mass?

P10375, L7 The observation that HNO3 uptake does not result in release of a species that contributes to the MS signal at m/z = 46 would appear to be incompatible with the present results in which HNO3 is formed at the surface and is released into the gas-phase. Are there differences in the experiments of Hanisch and Crowley, 2001b and the present dataset (e.g. concentration of HNO3 used, time of exposure) that might explain this ?

P10376, L24 The uptake of N2O5 (Figure 1) is said to “lead to steady state” at longer times. Figure 1 shows however that the N2O5 signal before and after the exposure is not the same and the authors explain this (P10377, L2) as due to a change in N2O5 flow rate over time. If this is the case, surely the data must be corrected for this drift. Once this has been done, is a “steady state” uptake still observable, or does it tend to zero at longer times ? Similarly, as the ion signal at e.g. m/z = 46 is a convolution of HNO3 and N2O5 , there appears to be little point in showing only uncorrected data.

P10378, L13-17 What is the relevance of this sentence to the present study ?

P10378,L20-25 The authors appear to suggest that N2O5 reacts with Ca(OH)(HCO3), which is formed by the equilibrium of CO2 and H2O in the presence of CaCO3 and that the formation of CO2 in reaction (7) “generates additional Ca(OH)(HCO3) according to reactions (4) and (5)”. How is this chemistry initiated in the absence of CO2 (i.e. as in the present experiments)? Would prior surface conditioning with CO2 (or long term evacuation) influence the uptake kinetics ?

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P10379, L26 What is the BET area of the $CaCO_3$ sample ? 5.06 m2/g as on this page, or 3.7 m2/g as on page 10377 ?

P10380, L1-15 The calculations of the surface concentration of N_2O_5 (based on the BET area, and assuming a 0.9 nm diameter for N_2O_5) are pointless. After all, the authors have just shown that N_2O_5 uptake is reactive (i.e. it doesn't just sit on the surface and occupy a site but forms products which desorb).

Also, the authors assumed here that, at steady state, the whole sample is accessible to N_2O_5. This implies that uptake coefficients calculated for steady state must also use the entire surface area, and not just the geometric area as the authors later conclude.

P10381, L25 Not only the residence time but (more importantly) the concentration of the trace gas is raised by reducing the size of the escape orifice.

P10383, L 25 - P10384, L21 This section deals with the problem addressed at the beginning of this comment. How do you convert an observed loss rate coefficient to an uptake coefficient for a solid sample with interstitial volume. I have not understood the arguments of the authors in this section describing why they prefer the geometric surface area, despite the observation of a mass dependence in the geometric uptake coefficient. The main arguments against the pore diffusion correction or use of the BET area at low masses are that the resultant uptake are orders of magnitude lower than the geometric one. This is however often the case for geometric uptake coefficients that are not large.

Some questions:

Why does Figure 5 suggest a grain size diameter that is larger than (on average) 3.5 microns ?

Why does Figure 4 show that a mass of 0.33 g correspond to one nominal layer of 57 microns ?. Where does this value of 57 microns come from ? The usual interpretation of the onset of non-mass dependent uptake is that a greater depth of the sample cannot be sampled within the time scale of the measurement, whereas at lower masses (linear mass regime), the whole sample is accessible.

Why does the good agreement between the pulsed valve and the continuos flow experiment show that only the uppermost surface of the sample is responsible for reactivity. Can the authors prove that no diffusion into the sample can take place within 300 ms ?

Why do the authors believe that field data can support their argument in favour of using a geometric surface area to calculate the uptake coefficient. Do the authors really believe that field experiments have adequately characterised this reaction to enable such conclusions to be made? If so, these laboratory experiments were not necessary.

P10385, L26 In Figs 6 and 7, the samples could not be saturated during the exposure. A brief glance at the data (especially figure 6) shows however a decrease of uptake with time. The long uptake surely simply reflects that more than the geometric surface area is available for uptake, implying once again that it is inappropriate to use a geometric surface area when calculating the so called steady state uptake coefficient.

P10386, L15 The amounts of water available on the surface are calculated for the entire sample mass (see page 10377). Given that the authors assume that the uptake coefficient can be calculated from the geometric surface area only, it would be interesting to read how many H2O are available for reaction at the geometric surface.

P10388, L1 The authors are obviously aware of the recent study of Seisel et al 2005 as they have cited it. Why do they now claim that there have been no experimental reaction probabilities for N2O5 on mineral dust to date ?

P10390, L 9 Why does a lifetime for N2O5 derived from field measurements in “Contra Costa Country” support the present data ? Did this field study measure the loading of mineral aerosol ?

Minor corrections / typographical errors

P10370, L7 The qualifier “At high and low” is not necessary.

P10370, L18 Reaction (1) does not release NO2 and NO3, rather it sequesters them temporarily in a reservoir.

P10372, L1 There are no references given for the field results that establish the interaction of trace gases with mineral aerosol. Observations of e.g. nitrate and sulphate formation (see Dentener) and the DeReus study should be cited here.

P10372, L12 Is HNO3 a precursor of O3 or a reservoir of NO2 (which really is an O3 precursor) ?

P10372, L16 mass = concentration or mixing ratio ?

P10373, Experimental setup: Mixture of present- and past tense used in describing the apparatus.

P10379, L22 Presumably reactions 6 and 8 compete (not 7 and 8)

P10382, L25 MS should be ms

Figure 1. Present a corrected data set where the masses can be associated with one species. Would be better to label the curves with the m/z value directly.

Figure 5. What was the mass of CaCO3? Are the dark areas the sample holder ?

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