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Interactive Comment

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.

F. Karagulian et al.

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Answer to anonymous Referee #1:

Our sincere thanks go to both referees for carefully reading the manuscript and making several cogent remarks that will lead to significant clarifications and to a marked improvement of the text.

Regarding the general comment at the beginning of the report we share our surprise with Referee 1 at the large measured 0 values for the interaction of N2O5 with mineral dust surrogates. The situation for N2O5/mineral dust substrates is significantly different compared to N2O5/salt where we have concluded that N2O5 is non-sticky in



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contrast to mineral dust, presumably because of the difference in the number and types of surface OH-groups that seem to be more prevalent on mineral dust compared to alkali salts. We will point out in the revised version that we can but attribute a large value to  for N2O5/mineral dust because of the numerical value listed for instance in synoptic Table 5 at the low [N2O5] of 4x10-11 cm-3 (0 = 0.12 for CaCO3) which effectively prevents the application of pore diffusion theory because reaction is much faster than Knudsen diffusion into the bulk. In view of the small atmospheric concentration of N2O5 of typically 5x109 cm-3 which is roughly two orders of magnitude lower than the lowest concentration used in the present experiments and the displayed inverse concentration dependence of both 0 and ss (Table 3 and 5, except for Kaolinite, see Figure 8) the rate of uptake under atmospheric conditions will correspond to #61543; > 0.12 such that we feel justified to take the external surface as a basis to extract the  values from the measured rates. It is not our intention at all to "reject the steady-state value of ". In view of the low atmospheric [N2O5] we confer more weight to :0 because it is mostly free of saturation effects that lower 0 to ss values under the chosen experimental conditions as displayed in Figure 1. Because we cannot attain concentration values of [N2O5] = 5x109 cm-3 in the present experiment we simply attribute more weight to 0 than to ss in that we believe that 0 more accurately describes the atmospheric value in view of the inverse concentration dependence. However, we point out that we always list both 0 as well as ss values in all presented Tables.

P10371, L10-15: we agree with the referee and will emphasize the main assumption of the model subject to which the present conclusions were drawn.

P10372, L19: agreed. The text will point out that Seisel et al.'s study on N2O5 + Saharan dust is the only experimental study published so far. At the time of submission of the present paper Seisel's paper was in open discussion in ACPD. Saharan dust of course is a surrogate for airborne mineral aerosol!

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P10372, L25: it should say "material" instead of sample. "Authentic" means that the properties of the material have been investigated by a previous study that has passed peer review and is therefore accepted as certified for the present purpose.

P10373, L23: We had removed the relevant Table from the text in the present version. However, we will add the Table describing the properties of the used mineral dust surrogates in the revised version in order to provide the properties of the dust surrogates.

P10374, L23: Correct. The MS fragment m/e = 46 was corrected for the contribution of HNO3 in order to calculate [N2O5]. The revised text will say so.

P10375, L7: The implication and what we wanted to say is that no species OTHER than HNO3 is released into the gas phase that may contribute to m/e 46. Not every HNO3 impinging onto mineral dust is taken up as  is not unity for this system, and conversely, not every HNO3 "born" on the surface from heterogeneous hydrolysis of N2O5 remains adsorbed on the substrate.

P10376, L24: We will add a curve in Figure 1 showing the corrected signal at m/e 46 for the presence of HNO3 at later times as an example. From the evaluation of many uptake signals such as shown in Figure 1 for m/e 46 we have concluded that the uptake tends to steady-state for reaction times t > 500s rather than to zero. The referee raises an important point that is exceedingly difficult to tackle in view of the kinetic instability of N2O5, especially towards the vessel walls, over long observation periods. This question may only be answered in the context of many kinetic observations performed over several months which is the case for this work. We think it is useful to present raw data in the present context in order to convey an impression for the quality of the data.

P10378, L13-17: This sentence is in fact not relevant in the present context and will be taken out.

P10378, L20-25: The sentence on P10379, L3-6 has been taken out as it is in fact misleading. It now appears that reaction (5) is much too slow under flow reactor conditions

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such that the surface intermediate Ca(OH)(HCO3) may only be formed under ambient conditions and at long reaction times according to Santschi et al. (2006). Once the surface intermediate is consumed, the surface reaction will saturate. Therefore, the rate and the extent of the heterogeneous reaction depend on the abundance of the preexisting surface intermediate.

P10379, L26: Two different CaCO3 samples have been used: a high-ordered sample from Aldrich (P10377, L14, 3.7 m2/g) and a low-ordered sample from Fluka which has been mostly used in the present study (5.06 m2/g). We believe that both samples are very similar in their H2O uptake/storage capabilities.

P10380, L1-15: The reactivity of N2O5 in no way precludes an estimate of the surface coverage at steady-state such as performed here. This semiquantitative estimate has been introduced in order to show that less than a formal monolayer of Ca(OH)(HCO3) is required to enable the reaction. At steady-state (time scale of hundred's of seconds) the entire internal surface area is accessible to N2O5 through slow surface diffusion because once adsorbed N2O5 diffuses into the bulk of the sample in search for a reactive site. However, the gas species does not "see" the total internal and external (BET) surface area within the gas lifetime (lifetime of a fraction to several seconds) which is the reason that  is based on the geometric (= projected) rather than on the BET surface area. As explained above, the corresponding  values are too high in order to allow competitive pore diffusion, at least at the start of the reaction.

P10381, L25: The residence time  (= 1/kesc) and the species concentration are interconnected at constant inflow of N2O5. However, the trend displayed in Figure 3 is preserved (not shown) even at constant [N2O5], that is when the flow rate is lowered concomitantly with an increase in .

P10383, L25 - P10384, L21: As discussed at the beginning our argument in favor of taking the geometric surface area as a basis for the conversion of the heterogeneous loss rate constant is the magnitude of the uptake coefficient, both 0

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and ss, that makes diffusion into the interstitial space non-competitive with reaction. This will be even more the case at atmospheric concentrations owing to the observed inverse concentration dependence which has been observed on numerous occasions, for instance for NO3 free radical. In addition, pulsed valve experiments have firmly established the values of 0 which decrease to a steady-state value owing to saturation of the surface intermediate. The mass dependence from 0 to 0.33 g displayed in Figure 4 is trivial as it is connected to incomplete coverage of the sample holder: the rate constant kobs is proportional to As/Vcell (P10376, L4-9). Please note that 0 and (pulsed valve) are identical within experimental uncertainty.

Additional questions:

Figure 5 (SEM of the used CaCO3 material) shows that the effective grain size is significantly larger (on average) than the 3.5 microns claimed by the manufacturer. Presumably, the individual grains of 3.5 micron each form grains of larger size with interstitial spaces that are not resolved in this SEM image.

We assert that one complete sample layer is attained at 330 mg of CaCO3 which determines the diameter of 57 microns (please read from P10383, L 27 onwards). We think that the pore diffusion model of Keyser, Leu and Moore is not applicable to polydisperse samples such as the present one. Many parameters such as penetration depth and tortuosity are ill defined in such a case.

The good agreement between 0 from pulsed valve and continuous flow experiments gives us confidence in the large numerical value which precludes pore diffusion. In the past we have performed real-time diffusion tube experiments using NaCl grains for which pore diffusion applies owing to their quasi-monodisperse nature. The arrival time of a non-interacting gas such as N2 or Ar was indistinguishable compared to a Teflon-coated tube (A Molecular Diffusion Tube Study of Dinitrogen Pentoxide and Nitric Acid interacting with NaCl and KBr at ambient Temperature, Th. G. Koch and

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M. J. Rossi, Phys. Chem. Chem. Phys. 1999, 1, 2687-2694.). We take this as proof that on a time scale of a few seconds the gas does not explore the interstitial space of the sample. However, on a much longer time scale slow diffusional processes will transport N2O5 into the bulk. Therefore, ss is controlled both by saturation as well as by mass transport.

The field experiment used as an example is consistent with the results of the laboratory study. We continue to believe in the necessity of performing laboratory work.

P10385, L26: As explained above the fast rate of initial uptake that is sustained over time is not in contradiction to the geometric surface area-based  values. There is simply no way that for a value of #61543;ss = 0.3 (Saharan dust) the diffusion into the interstitial space can be competitive with reaction.

P10386, L15: We do not understand this question. The water content of CaCO3 is an intensive parameter, independent of mass. A typical value for CaCO3 is 3.5 formal monolayers at ambient temperature and 33% rh, 5.4% and 1.4% of a monolayer after 6 minutes and 24h of pumping, respectively.

P10388, L1: This will be fixed in the revised manuscript as indicated above.

P10390, L9: As pointed out above the comparison with Wood et al. is only taken as a consistency test for an uptake coefficient that is of similar magnitude. With  = 0.1 Wood et al. derived an aerosol loading of 150 microgram m-3 from the measured N2O5 lifetime. The 0 value of 0.2 for "mineral dust" measured in this work is consistent with the field measurement in the presence of an "urban aerosol". Quite clearly, a quantitative comparison is not possible owing to lack of data. However, with an uptake coefficient three orders of magnitude lower (pore diffusion corrected) the aerosol loading would have to be higher by the same factor at constant N2O5 lifetime which may be excluded on experimental grounds as it is already quite high in a suburban environment.

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We are grateful to the referee for pointing out minor points and typographical errors which will be taken into account in the revised version.

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