# Referee Report (Michel J. Rossi) on manuscript acp-2013-721 „Heterogeneous reaction of $N_2O_5$ with Illite and Arizona Test Dust particles“ by M.J. Tang, G. Schuster, and J.N. Crowley submitted to Atmospheric Chemistry and Physics Discussions (acpd)

The presented work deals with experimental aspects of an important interfacial reaction of a $NO_y$ species for which considerable experimental backlog and remaining necessity exists regarding its role in numerical modeling of the troposphere. Definitive experimental results regarding the fundamental reactivity of "mineral dust" under tropospheric conditions are still outstanding and impatiently expected. The authors have investigated the reactions of $N_2O_5$ on the mineral dust proxies Illite and Arizona Test Dust (ATD) as a function of relative humidity at ambient temperature in order to discover a potential systematic trend of the uptake coefficient $\gamma$ with the goal to extract fundamental chemical kinetic laws applicable to mineral dust of a given provenience. The authors have developed a superb, extremely sensitive and simple optical monitor of $N_2O_5$ and/or $NO_3^{\bullet}$ free radical, namely cavity ring-down spectroscopy at 662 nm, that they have successfully applied to this laboratory study. I generally concur with the results and discussion by the authors but have a few remarks that I would like to see answered to the benefit of the readership of Atmospheric Chemistry and Physics.

The following are the points I would like to raise in decreasing order of importance:

- Pg. 24864, lines 9 to 16, and pg. 24865, lines 21 and following: authors claim an exponential rate law for the sum of $k_d + k_w$ as a consequence of the correlation between $[N_2O_5]$ and $N_d$ displayed in Figure 4, both for Illite and ATD. However, at a closer look, $[N_2O_5]$ visibly droops below the straight line that is heavily weighted towards the high values of $[N_2O_5]$ at the beginning (origin) of the plot (Figure 4). This is unusual, because in general the opposite is true owing to the increasing importance of the background as the signal decreases in amplitude. The measurement precision being what it is, and surmising that the authors do the best job they can, a slightly different interpretation may be proposed. One may claim that at these fairly large values of $[N_2O_5]$ partial saturation of uptake may occur at steady-state which would make the uptake rate constant $k_d$ faster at lower values of $[N_2O_5]$ under conditions of reversible and partial saturation of reactive surface sites. This "fall-off" effect of the apparently increasing value of $k_d$ with decreasing $[N_2O_5]$ may also be observed for $N_2O_5$/Saharan Dust in Figure 4 of the cited paper Tang et al. 2012 (PCCP, 2012, 14, 8551-85561). The authors gloss over the single-exponential rate law a bit fast for my taste in order to arrive at the probable, but perhaps debatable conclusion of "first-order" rate law for uptake. Knudsen flow reactor studies have shown over and over again that the rate constants generally do not follow first-order behavior, but the authors are a bit quick to dismiss these studies as not "atmospherically relevant". I in part agree – surprisingly - with this statement because the evidence is subtle. However, these studies teach one a lot about rate laws and reaction products that are not (yet) accessible using AFT's owing to experimental complexities. I am not so sure about the statement on top of pg. 24864 that $\gamma$ is "in any case not dependent on the initial $N_2O_5$ concentration". This rate law check is rarely performed, if at all, by flow tubers, more frequently by proponents of Knudsen flow reactor studies.

- A case in point related to the subject is made by Karagulian et al. (2006) cited by the authors where $k_d$ (or $\gamma_{ss}$) decreases by a factor of three upon increasing $[N_2O_5]$ by a factor of ten at $N_2O_5$ concentrations equal to or lower than used by the present authors. The same behavior of partial saturation of reactive surface sites has been observed for $NO_3$ interacting with mineral dust (Karagulian et al., PCCP 2005, 7, 3150). Over the years I have not come across a single uptake process that was independent of the concentration of the gas phase species, with the exception of unitary systems, such as $H_2O$ vapor on $H_2O$ ice.
- The gas-kinetic parameter $Z_{11}$ (gas-wall collision rate) of a gaseous ensemble of molecules is proportional to the total surface area of the particles present. Figure 2 displays the distribution of the number concentration as a function of the aerodynamic diameter. A more appropriate display would be to plot the surface distribution as a function of Stokes (= geometrical) diameter in order to obtain an appropriately surface-weighted average value for $A_d$ rather than the number concentration-weighted value. I assume that the authors have taken Figure 2 in order to deduce the "average surface area of dust particles" (pg. 24864, line 7). It would be instructive to compare the absolute values of the so-derived $\gamma$ with the procedure presented by the authors. I am sure that the surface-weighting of the distribution of Figure 2 leads to the inverse shown: large particles are more important than the smaller ones, which leads to the suppression of the mode at 1.8 mm and the emphasis of the mode at 8 mm for ATD. For illite there will be a shift of the mode towards higher values. As a result $\gamma_{exp}$ may become smaller if $A_d$ shifts to higher values owing to surface-weighting.
- It is not quite clear how absolute concentrations of $N_2O_5$ have been obtained by the authors. Although this knowledge is not necessary in the present context if first-order behavior of the rate law is postulated, this question triggered my curiosity as the authors reveal the $N_2O_5$ concentration, on the order of (8-24) $10^{12}$ molecule $cm^{-3}$ (Table 1). A first-order rate constant for disappearance of $NO_3$, $k_l = 0.6 \pm 0.27\ s^{-1}$, was measured at ambient temperature by Karagulian et al. (2005, see above) for a FEP-coated Knudsen flow reactor. The authors measure $k_w$ that is approximately a factor of six lower than this value (Schuster et al., 2009) at ambient temperature. However, caution needs to be exercized because $N_2O_5$ is undergoing dissociation at roughly 100°C such that the $NO_3$ disappearance may be faster. We routinely "sacrificed" about 50% of $NO_3$ in favor of $NO_2$ in our studies when we generate $NO_3$ from thermal dissociation of $N_2O_5$. What is the $HNO_3$ level in your experiment? This is another pegpoint for the quality of the used $N_2O_5$.
- Pg. 24860, lines 13 to 18: Figure 2 conveys a fairly moderate aerosol number concentration for small diameters, and a reasonable one for larger particles. Nevertheless, the surface area of suspended particles is much smaller than the surface area of the vessel walls. I do not get a feeling for the importance of $k_w$ vs. $k_d$ while reading the paper, which would be useful in view of the highly reactive

nature of the dust-laden walls of the flow tube. It is a clever idea by the authors to make the wall-loss rate independent of fluctuations, but I am left with the question of the absolute values of both contributions to the total rate of $N_2O_5$ disappearance. Is it the extremely sensitive detection of $NO_3$ that enables the successful separation of $k_w$ and $k_d$? This point should be belabored a bit more by the authors.

- Pg. 24866, lines 24 and following regarding surface OH-groups and pg. 24868, line 26 and following: What are the alternatives between reaction of $N_2O_5$ with surface OH-groups and heterogeneous hydrolysis? It would be instructive to clearly formulate the different reaction paths. First remark: $N_2O_5$ hydrolysis like any other organic or inorganic hydrolysis is either general acid- or base-catalyzed because both $H_2O$ and $N_2O_5$ are closed shell compounds and react only slowly in the absence of a catalyst. A second remark concerns the surface OH-groups which either behave as acids or bases. In the presence of adsorbed $H_2O$ (which is seldom absent) it is probably immaterial (and impossible) to distinguish between hydrolysis and acid/base-catalyzed (hydrolysis) reaction. For instance, $TiO_2$ (rutile, boehmite or anatase) have surface OH-groups ranging from very acidic to very basic all at once! I can think of the following in this regard:

  acidic OH group: $M^+OH^- + NO_2^+NO_3^- \rightarrow MO^- + HNO_3$ (or nitrate after neutralization) + $NO_2^+$

  basic OH group: $M^+OH^- + NO_2^+NO_3^- \rightarrow M^+ + HNO_3 + NO_3^-$

  In my view the basic pathway is favored because it generates the stable nitrate anion compared to the unstable nitronium ion. But surprises do happen: remember the heterogeneous reaction of $N_2O_5$ on deliquescent sea salt particles…There the nitronium ion was surprisingly stable.
- Pg. 24867, line 14 and following: This is the first time I hear that quartz does not have (intrinsic? What is that?) surface OH-groups. Fused and crystalline quartz and Pyrex (75% fused $SiO_2$) are slightly acidic just because of surface OH-groups. You may even titrate them as a function of rh. All inorganic oxide surfaces have surface OH-groups capping (terminating) the surface. But perhaps the authors address a distinctly different point that I did not get.
- The equilibrium between $N_2O_5$, $NO_3$ and $NO_2$ should perhaps make reference to the additional and irreversible pathway $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$ which is responsible for the slow $N_2O_5$ degradation to $NO_2$ in static or long-residence time (= slow flow) laboratory experiments, especially at elevated temperatures where the forward reaction of $N_2O_5$ decomposition is fast.

Some of the minor points are the following:

- Pg. 24857, line 15 and following: laboratory experiments established the existence and properties of $ClNO_2$ long before they were detected in the field!
- Pg. 24861, line 24: “bin” instead of “pin” (probably)
- Pg. 24867, line 3: “…uptake coefficient (0.04) on illite is similar to….”
- Pg. 24867, line 26: “Bulk samples”…
- Pg. 24868, line 12: “studying”; line 26: “…that under these….”
- Pg. 24869, line 24: “deserts”