# Reviewer 2

## General Comment 1

Tang et al. present a study of the relative heterogeneous uptake of $N_2O_5$(g) and $NO_3$(g) on the surface of Saharan mineral dust as a function of relative humidity, using cavity ring down spectroscopy to measure relative changes in the gas phase reactants. The nature of the relative rate technique precludes the direct determination of absolute rate constants or uptake coefficients, but the authors derive these from comparison to absolute kinetics from previous studies. Through this comparison this new study provides some valuable new information regarding the heterogeneous uptake coefficient of $NO_3$ on mineral dust, which has only been presented in one previous publication. The reactive uptake for $NO_3$ on Saharan dust reported here is 10 times smaller than reported in the one other study by Karagulian and Rossi (2005), however possible reasons for this large difference are not discussed here.

**Reply**

In the introduction we alluded to the fact that the use of bulk substrates to derive absolute uptake coefficients is precarious as the estimation of the surface area involved is non-trivial. The values measured by Karagulian and Rossi must be regarded as upper limits as they used the geometric sample area to calculate gamma. The fact that our uptake coefficient derived from the relative study here and our absolute study using a dispersed sample gives a lower result is thus hardly surprising. The following text has been added to explain this. "This value is ≈ a factor of 10-20 lower than the uptake coefficient of 0.1-0.2 reported by (Karagulian and Rossi, 2005) using bulk samples of Saharan dust. The large difference in these results is most likely related to the use of Karagulian and Rossi (2005) of the geometric surface area of the sample to calculate the uptake coefficient, which must result in an upper limit."

## General Comment 2

The experiments presented here are not very thorough. There also appear to be significant limitations from the (new?) experimental method used here. The amount of sample mass and surface area actually involved in the reaction is unknown. While this is not required for measuring relative rates, it is important for the derivation of absolute rate constants and uptake coefficients, which the authors do derive from their relative rate data. Without knowledge of particle size and surface area the correct absolute kinetics to compare to cannot be properly selected.

**Reply**

The underlying concept of the relative rate method when applied to a heterogeneous process is that the surface area and the particle morphology do NOT need to be known. We do NOT compare our result to absolute values we USE an absolute value (obtained using the same sample but dispersed in an aerosol flow tube) to convert the relative uptake rate to an absolute one for $NO_3$. Ignorance of the particle mass, surface area and morphology is NOT a limitation in deriving the relative uptake coefficient.

## General Comment 3

The uncertainty reported for the measured relative kinetics seems to preclude the conclusive determination of the effect of relative humidity on the observed kinetics. The data presented here can really only say with confidence that there is not a large effect from relative humidity on the kinetics. To say that there is NO effect ignores the large degree of scatter and uncertainty in the reported data.

**Reply**

In any experimental study, measuring the dependency of the extracted result on an experimental variable will be limited by factors such as signal stability, noise etc and (obviously) will depend on the size of the effect. In this case we observe no (significant) change in the relative uptake coefficient when the relative humidity is varied between 0 and 70 %. Our data indicates that the relative uptake coefficient does not vary more than ≈ 50 % in this range. If the uptake had been as sensitive to RH as e.g. found for organic aerosols where it may vary by up to a factor of 10 between 10 and 70 % RH (Thornton et al., Phys. Chem. Chem. Phys. 5, 4593-4603, 2003) we would have observed an effect. We shall modify the text and refer to upper limits to the observed affect rather than stating that there is no effect. "Within our experimental uncertainty, we can state that the uptake coefficient does not change by more than 50 % within this RH range."

**General Comment 4**

The authors also present a limited set of experiments performed on wax soot and collected ambient particles. Unfortunately, very little can be concluded from these results since the physicochemical properties of the particles used were not determined. As these results are preliminary in nature I recommend they be omitted from the revised manuscript.

**Reply**

These experiments were not carried out to provide detailed data sets describing the interactions of $NO_3$ and $N_2O_5$ with soot or "ambient" aerosol. Their purpose (as stated in the introduction) was simply to illustrate the range (and limitations) of the method and as such are qualitative (but useful) contributions to this work.

**General Comment 5**

The relative kinetics experiments for $NO_3$ and $N_2O_5$ conducted on the Saharan dust surface add some valuable new kinetic information for these systems. However, the experimental method used contains some serious experimental limitations that must be addressed in the manuscript; these limit what can be reliably concluded from the observed kinetics. This experimental method requires testing and validation before it can produce high quality kinetics data that can account for the important effects of surface area, particle size, and relative humidity. This data will be of interest to the readership of Atmospheric Chemistry & Physics. The revised manuscript might be acceptable for publication after major revisions and the following specific issues have been addressed.

**Reply**

The comment repeats the content of General Comment 2 and General Comment 3. Again, we would like to emphasise that knowledge of surface area and particle size is NOT necessary to extract the RELATIVE uptake coefficient. We have shown that there is not a LARGE change in the relative uptake coefficient with varying RH as found for example for other systems with $N_2O_5$ uptake (see above).

**Comment**

Page 393, line 5: The Introduction would benefit from some mention of observations of secondary nitrate products in ambient mineral dust particles (e.g. Laskin et al., 2005; Shi et al., 2008; Sullivan et al., 2007). Currently the abstract focuses on the importance of NOy uptake for gas-phase chemistry, but says little regarding the important changes it can induce in the aerosol phase (e.g. Bates et al., 2004; Gibson et al., 2006; Sullivan et al., 2009; Tang et al., 2004).

**Reply**

We already state that the reactions of $NO_3$ and $N_2O_5$ are important for the formation of aerosol nitrate and cited Zhang et al and Vrekoussis et al. in the text. Unfortunately, these references did not appear in the bibliography. The text (and bibliography) has been amended to state: "The heterogeneous reactions of $NO_3$ and $N_2O_5$ are important for the formation of aerosol nitrate (see e.g. Zhang et al., 1994; Tang et al., 2004; Vrekoussis et al., 2006; Sullivan et al., 2007), and also the aging of ambient organic aerosols (Rudich, 2003).." Dozens more references to this theme could be added, but we are no trying to be comprehensive and feel that citing a few exemplary papers is sufficient.

**Comment**

Page 393, line 13: Also include the study of $N_2O_5$ uptake by Mogili et al (2006).

**Reply**

Mogili et al will be added to the revised manuscript.

**Comment**

Geoff Smith has used relative rate techniques to study heterogeneous kinetics, this should be mentioned in the Introduction (Hearn and Smith, 2006).

**Reply**

This is a different approach. Hearn and Smith measure the relative rate of loss of a trace gas (X) to either a particle or to another (reference) trace gas. In this case, the concentration of the reference trace gas, its rate coefficient with X and the collision rate of X with the particles are required. The latter implies knowledge of particle surface area. We now emphasise that these approaches are different. "This approach is different to that used e.g. by Hearn and Smith (2006), who measured relative rates of loss of a target trace gas to either a reference trace gas or to particles, the surface area of which was thus needed to extract kinetic data."

**Comment**

Page 394, line 11: Synthesis of pure N2O5 is not trivial, and there are safety concerns related to its storage and handling. Please provide more details and related references here. How was the absolute concentration of N2O5 measured or estimated?

**Reply**

The synthesis of $N_2O_5$ is not trivial but it is also no great challenge and its production in gram amounts has been described many times in the literature. We will add the following "$N_2O_5$ crystals were generated as described previously in this group (Wagner et al., 2008). To reduce the danger of explosion, only small (~ 1g) amounts were prepared without further distillation."

**Comment**

How was the absolute concentration of $N_2O_5$ measured or estimated? Was the absorption cross section used, as in Eqn. (E1)?

**Reply**

The concentration of $N_2O_5$ was measured by quantitative, thermal conversion to $NO_3$, which was measured via its absorption cross-section. This is already described in the text. The literature sources for the cross section are now given. "$\sigma(NO_3)$ is the effective $NO_3$ absorption cross section at the laser wavelength and was calculated using temperature dependent cross sections from Yokelson et al. (1994), Orphal et al. (2003) and Osthof et al. (2007)."

**Comment**

Has this relative rate kinetics method on filter-loaded samples been previously reported, or validated against other methods? It is similar to the particle-on-substrate technique used by Alex Laskin's group (Liu et al., 2008).

**Reply**

The method we describe has not been validated. As a relative rate method it does not need to be "validated". though the good agreement with the relative uptake coefficient derived from the absolute studies of Karagulian indicates that it works. It is NOT similar to the method of Laskin.

**Comment**

The lack of control or measurement of the particle sizes deposited on the filters is a concern, as this can affect the kinetics (e.g. Thornton et al., 2003). Furthermore the mass or surface area of the sample that is actually exposed to the reactant gases could not be determined. These must be discussed further in the text in terms of the limitations of this method to accurately measure relative uptake coefficients. While bulk powder methods do suffer from the surface area and pore diffusion issues you discuss, entrained aerosol flow tube methods do not, yet you have not discussed this method for measuring absolute or relative heterogeneous kinetics on mineral dust or other particle surfaces. The flow tube method also has the advantage of controlling aerosol size, while the filter-based method used here does not. Page 4500, line 19.

**Reply**

The comment is a repeat of General Comment 2. Once again, we do NOT need to know the surface area to derive the relative uptake coefficient. There is little point comparing the flow tube method with the relative rate method as they have different goals. One measures an absolute uptake coefficient (based on measured surface areas) and one a relative uptake coefficient.

**Comment**

Regarding acidic gases reacting with the mineral particle bulk and not just the surface, Laskin et al. (2005) and Matsuki et al. (2005) are more appropriate references.

**Reply**

Carmichael et al was given as example. Laskin and Matsuki are also appropriate (as are many others). We shall add these two, as further examples.

**Comment**

Over what reaction time periods do you derive your initial and steady-state rates from?

**Reply**

There is no significant difference in the initial and "steady state" uptake coefficient ratios, hence both can be derived from the whole datasets, independent of exposure time. This is discussed on page 401.

**Comment**
Page 402, line 12: The factor of 10 difference between your determined gamma for $NO_3$ compared to that of Karagulian and Rossi (2005) warrants a detailed discussion of the possible reasons for this large difference. This is particularly important as you are using a new and far as I am aware unvalidated method to measure these rates. The previous study used bulk powder samples, which could impede the observed kinetics due to pore diffusion limitations. However, your observed gamma is 10 times smaller than theirs, so this explanation does not follow. Another obvious issue is the estimation of available surface area in the previous study.
**Reply**
The following text has been added:" This value is ≈ a factor of 10-20 lower than the uptake coefficient of 0.1-0.2 reported by (Karagulian and Rossi, 2005) using bulk samples of Saharan dust. The large difference in these results is most likely related to the use of Karagulian and Rossi (2005) of the geometric surface area of the sample to calculate the uptake coefficient, which must result in an upper limit."

**Comment**
Is the $\gamma$ (N2O5) used from Wagner et al. the initial or steady-state value?
**Reply**
Wagner et al used an aerosol flow tube, i.e. a steady state experiment.

**Comment**
Section 3.2 on the ambient particles really adds nothing valuable to the paper. Without a proper characterization of the aerosol sample the measured kinetics have little significance. Sect. 3.3: Similarly, the data presented for the soot samples is difficult to interpret without characterizing the soot surface itself. The few experiments conducted here on soot surfaces add little to the paper and their interpretation can only be speculated given the lack of information regarding the substrate.
**Reply**
This comment repeats General Comment 4. As mentioned in our reply above, these experiments were not carried out to provide detailed data sets describing the interactions of $NO_3$ and $N_2O_5$ with soot or "ambient" aerosol. Their purpose (as stated in the introduction) was simply to illustrate the range (and limitations) of the method and as such are qualitative (but useful) contributions to this work.

**Comment**
Page 406, line 8: Can you be more specific in comparing the concentrations and reaction rates of $HNO_3$ compared to $N_2O_5$ and $NO_3$ with mineral dust? You do not compare $N_2O_5$ with $HNO_3$. Please cite some of the specific $HNO_3$ and other kinetic studies, in addition to the IUPAC report.
**Reply**
That $HNO_3$ is (almost always) more abundant than $N_2O_5$ and $NO_3$ (which only exist at significant concentrations) at night is surely clear and need not be referenced. There are numerous studies on the uptake of $HNO_3$ to mineral dust. These are compiled and discussed in the IUPAC publication cited. It is not clear what benefit would be had from repeating this lengthy discussion here or selecting single studies for citation.

**Comment**

Table 1: The relative uptake values reported as a function of RH all lie within the stated experimental uncertainties. Given this, I do not think that this method is presently able to detect with confidence the effect of RH on the relative kinetics, unless the effect is quite large. The manuscript needs to be revised to more precisely state what difference in the relative uptake coefficients that this method can reliably determine. There is too much scatter in the data to really conclude anything about the possible effect of RH with any certainty, except that there is not a large effect. To say with confidence that there is no effect ignores the uncertainty of the method and scatter present in the data.

**Reply**

This is a repeat of General Comment 3. The text will be changed as outlined in our reply above.

**Comment**

On page 405, line 7 you state: "The maximum (or minimum) measurable change in concentration could be improved by increasing the stability of the NO3/N2O5 source and reducing the noise in the $N_2O_5$ channel." First, these importance issues should really be discussed in the experimental and results sections, not left for the conclusions. What is the cause of the instability in the $NO_3/N_2O_5$ source, and what magnitude of uncertainty does it introduce? You stated on page 399, line 2 that only data where the $N_2O_5$ and $NO_3$ source signals from the blank path remained stable were used, shouldn't that eliminate this issue? Same question for the noise in the $N_2O_5$ channel, and why does the $NO_3$ channel not suffer from this?

**Reply**

The discussion of possible improvements is not specific to any of the previous sections dealing with Saharan dust, ambient aerosol or soot. Hence, we prefer to keep it in the (renamed) section "Summary and atmospheric conclusions".

The cause of the instability in the $N_2O_5$ channel is non-homogeneous temperature distribution in the heated channel, as discussed in Schuster et al. The magnitude of uncertainty is already mentioned as it limits the smallest possible measurable change in concentration. The use of data where the $NO_3$ and $N_2O_5$ signal in the blank were stable refers to long-term stability (i.e. over the course of an experiment) and not signal noise. This is already apparent from the text.

**Comment**

Fig3: Why is there such a large difference between the 2.16 and 1.04 mg samples in Fig. 3a, but not for the 1.09 and 1.67 mg samples in Fig. 3c?

**Reply**

This reflects the reproducibility of the method. There is no systematic trend when varying the sample mass. This variability is the reason why we expand our error limits on the relative uptake coefficients to cover all data. This is already discussed on page 401, lines 18-22.