

Interactive comment on “Uptake of NO₃ and N₂O₅ to Saharan dust, ambient urban aerosol and soot: a relative rate study” by M. J. Tang et al.

Anonymous Referee #2

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General comments

Tang et al. present a study of the relative heterogeneous uptake of N₂O₅(g) and NO₃(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 NO₃ on mineral dust, which has only been presented in one previous publication. The reactive uptake for NO₃ on Saharan dust reported here is 10 times smaller than reported in the one other study by Karagulian and Rossi (2005), however possible

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reasons for this large difference are not discussed here.

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. 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.

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.

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.

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Specific comments

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 NO_y 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).

Page 393, line 13: Also include the study of N₂O₅ uptake by Mogili et al (2006). Geoff Smith has used relative rate techniques to study heterogeneous kinetics, this should be mentioned in the Introduction (Hearn and Smith, 2006). 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? Was the absorption cross section used, as in Eqn. (E1)?

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).

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

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aerosol size, while the filter-based method used here does not.

Page 4500, line 19: 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.

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

Page 402, line 12: The factor of 10 difference between your determined gamma for NO₃ 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.

Is the gamma(N₂O₅) used from Wagner et al. the initial or steady-state value? 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.

Page 406, line 8: Can you be more specific in comparing the concentrations and reaction rates of HNO₃ compared to N₂O₅ and NO₃ with mineral dust? You do not compare N₂O₅ with HNO₃. Please cite some of the specific HNO₃ and other kinetic studies, in addition to the IUPAC report.

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

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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.

On a related topic, 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 N₂O₅ 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 NO₃/N₂O₅ source, and what magnitude of uncertainty does it introduce? You stated on page 399, line 2 that only data where the N₂O₅ and NO₃ source signals from the blank path remained stable were used, shouldn't that eliminate this issue? Same question for the noise in the N₂O₅ channel, and why does the NO₃ channel not suffer from this?

Fig. 3: 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?

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