

Interactive comment on “Kinetics and mechanism of the uptake of N₂O₅ on mineral dust at 298 K” by S. Seisel et al.

Anonymous Referee #1

Received and published: 7 September 2005

Referee Report on “Kinetics and mechanism of the uptake of N₂O₅ on mineral dust at 298 K” by S. Seisel, C. Börensén, R. Vogt and R. Zellner Submitted to Atmos. Chem. Phys. Discuss. 5, 5645-5667, 2005.

This paper is the first study of the heterogeneous chemistry of N₂O₅ on a specific mineral dust sample (Cape Verde dust deposits) and examines its kinetics and certain aspects of its reaction mechanism. The kinetic and spectroscopic results should be interesting to both physical chemists and atmospheric scientists alike, and the atmospheric relevance is established at the end of the report. The experiments have been performed with due care given the difficulties in the handling of the title compound. However, a few important questions remain unanswered as outlined below. I recom-

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

mend publication of the present work in Atmospheric Chemistry and Physics once the authors have answered the listed questions in a satisfactory manner in the interest to clarify certain quantitative aspects of their work.

A. The role of HNO₃ in both the DRIFTS and kinetic results is not made sufficiently clear. HNO₃ is an unavoidable impurity in any N₂O₅ sample and must be accounted for in separate experiments. It appears that these experiments have been published in Seisel et al. (2004) using an identical technique so that no additional experiments are necessary, but little quantitative reference is made to their previous work throughout the present paper. In my opinion, a stronger tie needs to be established in order to help interpret the present data. It would be helpful to underline the difference between both HNO₃ and N₂O₅ systems and their mechanistic consequences. Two examples may be cited:

(a) The DRIFT spectrum in Figure 1 is nearly identical to the one obtained in Seisel et al. (2004) for the interaction of HNO₃/Saharan Dust except for the presence of free H₂O in the latter spectrum. Could the spectrum shown in Figure 1 originate from the HNO₃ impurity in the N₂O₅ sample? If not, why not? The only difference between the present N₂O₅ and the HNO₃ work is the different saturation behavior (50 minutes for N₂O₅, 30 minutes for HNO₃ in Figure 1 of Seisel et al. (2004)). This, however, may be due to different N₂O₅(+HNO₃) concentrations used in both experiments. In the text I could not find any mention regarding a possible interference of HNO₃ with the present results on N₂O₅.

(b) It is fairly clear from Figure 3 that the shapes of the uptake curves measured at m/e 30 and 46 are different, perhaps owing to the interference of HNO₃ that remains unaccounted for in the present work. The ratio of MS signals is not constant and therefore leads one to believe that there may be more than one parent responsible for the measured MS amplitudes whose relative ratio changes with exposure time.

B. What is the gas phase residence time in the DRIFTS cell? This parameter may be

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

important to assess the external impurity flow of HNO_3 generated somewhere in the inlet system as opposed to the production of HNO_3 inside the DRIFTS cell. Are the N_2O_5 samples and concentrations (including HNO_3 impurity) for the Knudsen reactor (Essen) and the DRIFTS cell (FFZA) comparable, assuming that both experiments were most probably performed in two different laboratories?

C. I believe that there is a certain inconsistency in the proposed mechanism (R1a-c, pg. 5654). The insert of Figure 1 conveys incipient saturation behavior of the rate of N_2O_5 (and/or HNO_3 ?) uptake after 50 minutes owing to hydrolysis reaction R1b which seems to be the rate-limiting step. How come you don't see any indication of this beginning saturation in Figure 6 after 45 minutes of exposure despite the claim that after the initial exponential drop of the uptake coefficient one measures the same hydrolysis reaction on this time scale? Granted, one does not observe the surface nitrate formation in the DRIFTS, probably because of lacking sensitivity. However, wouldn't you expect to see the same kinetic behavior in both experiments after 50 minutes?

D. I fully agree with the evaluation of the initial and steady-state uptake coefficients and the justification for the geometric surface area. What I do not agree with is the statement that the linearity observed over a factor of 10 change in N_2O_5 concentration (Figure 2) indicates a rate law first order in N_2O_5 unless the authors show that the uptake coefficient is independent of the chosen escape aperture. However, the authors report results for only a single (the largest) escape aperture. What were the results for the smaller aperture Knudsen flow reactors? How does one reconcile a first-order rate law in view of the complex reaction mechanism displayed in Reactions R1a-c knowing full well that adsorption (R1a) is NOT rate-limiting!

E. The last statement in the Conclusions (pg. 5658) regarding the magnitude of the uptake coefficient and its effect on the composition of the atmosphere is essentially given without any explanation. Please expound!

Some points of minor importance: - What is the dose of N_2O_5 for the experiment in

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Figure 5 (pg. 5666) and the ones in Figure 4 mentioned in the text on pg. 5654, lines 1-4? - I propose to include a reference by Finlayson-Pitts and coworkers for the evidence of surface nitrate (pg. 5661, line 5) - Pg. 5654, line 16: Seisel et al. (2004) - The S-OH groups must be basic: any idea if S-OH regenerates upon exposure of the mineral dust samples to H₂O? Any idea about the time scale? - The author list of the second reference is incomplete.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 5645, 2005.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper