

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

Anonymous Referee #2

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Manuscript title: Kinetics and mechanism of the uptake of N₂O₅ on mineral dust at 298 K

This paper describes laboratory experiments of the uptake and reaction of N₂O₅ on Saharan dust aerosol collected in the Cape Verde Islands. Reactive loss on dust represents a key uncertainty in describing the atmospheric fate of N₂O₅ due to a lack of experimental information. The heterogeneous loss of N₂O₅, in general, is one of the most important heterogeneous processes in terms of affecting global tropospheric O₃ production chemistry. Thus, the study described in this paper represents an important and relevant topic for ACPD readers.

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N₂O₅ loss to bulk dust samples was monitored in a Knudsen Cell with electron-impact mass spectrometry. NO₃- production was monitored using a Diffuse Reflectance Infrared Spectroscopy (DRIFTS) setup, and ion chromatography was used to calibrate the DRIFTS signal. Several studies of heterogeneous chemistry have employed Knudsen Cells, though not to the study of N₂O₅ reaction on dust, and few studies have employed DRIFTS. The experiments appear to have been carefully conducted, and the authors make an interesting mechanistic interpretation of the data.

I feel this paper should be published, but only after the authors address some key points described in detail below. The issues of greatest concern are related to how the authors calculate and report the reactive uptake coefficient, γ . It is important that they be more explicit in how it is derived from their measurements and that they provide more caveats for the degree to which their laboratory experiments are representative of the atmosphere. The authors do provide some caveats, but not enough in my opinion.

Major Comments (in no particular order)

1. The authors should stipulate that both the initial and steady state gammas reported are upper limits. This stipulation should appear in the abstract, results and discussion, and conclusion sections. For example on line 5 of page 5658, the authors imply $\gamma > 0.013$. My reasoning is below.

Due to the apparent lack of a mass dependence in γ , derived from Knudsen Cell (KC) experiments, the authors rule out use of BET surface areas. Instead, the authors use geometric surface area to convert measured rate constants into γ , which likely underestimates the true surface area. By how much it underestimates the surface area is open to discussion. The reaction may indeed be occurring so fast that the entire BET surface area is not accessible, but neither do their experiments show “that only the top layer of particles is involved”. This last statement appears on page 5653 lines 24-25, and I don’t see how the data supports such a conclusion since experiments always had more than 4 layers (Figure 5).

Even if the top layer were the only layer involved, wouldn't the available surface area still be greater than the geometric surface area given the roughness of a dust layer? See, e.g. SEM images of dust samples.

Is it possible a mass dependence wasn't observed because the masses used in the KC were not less than ~ 100 mg? Or did the range of sample mass extend lower than that? If 5 layers corresponds to 140 mg, then experiments with a factor of 3 lower mass could have been performed with multiple layers present. Underwood, et al [2000] and other papers from that group, generally show a mass dependence only at sample masses much lower than 100 mg. Granted these studies were for different gases and a different setup, but the authors should mention that a mass dependence may exist for lower sample masses than studied.

Perhaps most relevant, Underwood, et al [2000] argue that if a sample mass dependence can't be shown, then the gamma obtained in a KC experiment must be reported as an upper-limit. I don't think the data is presently capable of refuting this point, but the authors are encouraged to present an alternate argument.

2. The DRIFTS expt. shows that NO_3^- is produced at a constant rate for at least 50 min (the authors say 100 min on line 9 of page 5656, but Figure 1 seems to show deviation by 50 min). The KC results show that gamma decreases by a factor of 4 within 20 minutes. The authors rationalize the lack of a similar time dependence in the DRIFTS experiment by the fact that much lower geometric surface area and sample masses were used in the DRIFTS, leading to a lower number of surface sites for a specific reaction between N_2O_5 and "surface-OH groups". I comment more on this aspect of the mechanism later, but doesn't this explanation itself (on pg 5656) imply a sample mass dependence and/or an N_2O_5 concentration dependence to the gamma? There should be the same number of S-OH per cm^2 of geometric surface area. If the same time dependence is not observed because there's fewer S-OH in an absolute sense, doesn't that mean the amount of N_2O_5 could be lowered, and a larger initial gamma be observed at short reaction times? The authors may need to better qualify

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their statements about gamma being independent of the initial N₂O₅ concentration in the DRIFTS experiment.

Judging by the data in Figure 6, and given that the authors state the DRIFTS has a time resolution of 1 minute, I would expect some curvature to be detectable in the DRIFTS data at short times (i.e. first 10 minutes). Perhaps a simple kinetics model could illustrate if curvature is to be expected in the DRIFTS data based on extrapolation of the time-dependence derived from the KC results. It seems to me such a modeling effort would impact the paper's conclusions, either strengthening or weakening depending on the results. I don't think that modeling effort should be required for publication as long as the authors qualify their conclusions accordingly.

3. There has been a significant amount of work on N₂O₅ hydrolysis on aerosol of several types since the Atkinson 2001 reference, which is the only reference the authors cite in this regard. It would be useful to discuss their results in terms of more recent work on the subject [Hallquist, et al., 2000; Kane, et al., 2001; Folkers and Mentel, 2003; Hallquist, et al., 2003; Thornton, et al., 2003; Stewart, et al., 2004]. Of interest is that most of these studies show a dependence on aerosol phase (aqueous or solid), i.e. amount of liq. H₂O. Most studies show that on aqueous aerosol, the gamma plateaus at high RH to a value of gamma ~ 0.02 - 0.04 for a range of aerosol compositions. The upper-limit gammas reported in this paper (0.01 - 0.08) seem high given that the mass fraction of H₂O available for hydrolysis is probably quite low in mineral dust where residual water has been pumped away. How do the authors rationalize this issue?

4. Could an alternative mechanism to explain the time dependence observed in the KC experiments be that there is a fast initial hydrolysis reaction in the absence of NO₃-, but as the product builds up, the gamma decreases due to a "nitrate effect" [see, e.g., Wahner, et al., 1998; Mentel, et al., 1999; Thornton, et al., 2003]? That is, do the authors need to invoke two different N₂O₅ reactions, one with "S-OH" and the other with "H₂O(ads)"?

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5. The authors argue that the agreement between the gammas obtained in the pulsed and steady state operation of the KC means that “the initial uptake coefficients are not influenced by saturation effects.” (pg 5654 lines 3-4). What is the expected time scale for saturation of the surface area participating in the reactive process? The decays in the pulsed experiment don’t appear to begin until ~ 100 ms after the initial rise in N₂O₅ signal, and extend out to ~ 750 ms. Is saturation not possible on this time scale? Basically, a simple justification for the statement on pg 5654 is needed and the statement needs to be clearly connected to the KC data only.

6. Overall, I feel the authors could be a bit more illustrative in the calculations performed to obtain gammas. For example what was “Z” on page 5652 line 24? What is the exact relationship between “formal layers” and sample mass, how was this relationship derived, and is it truly constant with sample mass? If there’s a reference to consult for such numbers or calculations, that will suffice.

Minor Comments

1. Pg 5646 lines 6-10: I find this paragraph confusing. I assume the first sentence means that 20% (i.e. 1 out of 5) of the total reduction in O₃ calculated with the model was due to a heterogeneous loss of N₂O₅. The model must have assumed a gamma for N₂O₅ on dust, what was it? See also, page 5657 line 12-15. On pg 5646 line 7, what does “additional heterogeneous sinks of N₂O₅” refer to? Additional to what?

2. Pg 5648 lines 9 and 14: Is it possible to put the sensitivity and typical NO₃- background in the same units? Is the sensitivity referenced to cm² of geometric surface area?

3. Pg 5649 lines 18-19: “From a comparison of the two decay constants”, do the authors mean a simple difference between k_{esc} and k_{dec} ? What is the nature of this “comparison”? This gets back to showing exactly how g was determined.

4. Pg 5649 line 20 should read: "sample holder, an upper limit to the dimensionless

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initial uptake”

5. Pg 5651 lines 24-26: Can the authors specify a minimum detectable limit for solvated nitrate ions? What would be the spectral indications of solvated nitrate ions?

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