

## ***Interactive comment on “Kinetics and mechanism of the uptake of N<sub>2</sub>O<sub>5</sub> on mineral dust at 298 K” by S. Seisel et al.***

**S. Seisel et al.**

Received and published: 27 October 2005

We thank the referee for the critical review of the manuscript. He/she raised a number of interesting points which we will respond to.

### Major Comments

A. We agree with the referee that the role of HNO<sub>3</sub> during the uptake of N<sub>2</sub>O<sub>5</sub> has to be discussed. In order to do this, we re-analysed a number of KC experiments of the uptake of N<sub>2</sub>O<sub>5</sub> where HNO<sub>3</sub> at its parent mass m/e 63 has been additionally monitored. Figure 3 and 6 have been replaced by figures showing one of these experiments The influence of HNO<sub>3</sub> on nitrate formation and uptake coefficients is now discussed in the manuscript.

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As a result it is shown that the MS-signal for  $\text{HNO}_3$  ( $m/e$  63) is slightly increasing from less than 7% with respect to the MS-signal  $m/e$  46 to approximately 20% during the course of the experiment. The evaluation of the kinetic data may be hindered by the formation of gas phase nitric acid which is a possible reaction product as well as a product of the hydrolysis of  $\text{N}_2\text{O}_5$  inside the cell and the gas mixing system. In addition, it interacts with mineral dust to a similar extent as  $\text{N}_2\text{O}_5$  (Seisel et al., 2004). Under these conditions it is not possible to entirely correct the MS-signal  $m/e$  46 for the  $\text{HNO}_3$ -contribution. Nevertheless, a rough estimate of the effect of  $\text{HNO}_3$  on the MS-signal  $m/e$  46 and the derived uptake coefficients is given by simply subtracting the contribution of  $\text{HNO}_3$  as monitored in the gas phase from the MS-signal  $m/e$  46 (also shown in Figure 3 and 6). During the first 5 min of reaction no significant influence of  $\text{HNO}_3$  is observed. At longer reaction times the formation of  $\text{HNO}_3$  leads to a faster saturation of the MS-signal  $m/e$  46. This "full" correction procedure represents the "worst case". If  $\text{HNO}_3$  is also interacting with the mineral dust surface, the derived uptake coefficients for  $\text{N}_2\text{O}_5$  would be lower as the one derived from the "full" corrected signal, even a few percent below the uncorrected values.

A reference experiment with  $\text{N}_2\text{O}_5$  flowing through the cell while the sample compartment is closed showed that  $\text{HNO}_3$  is formed to similar extent as in an uptake experiment. This result suggests, that a significant amount of  $\text{HNO}_3$  is formed by the decomposition of  $\text{N}_2\text{O}_5$  inside the cell and the gas mixing system.

The initial uptake coefficient of  $\text{N}_2\text{O}_5$ , which is determined from the minimum MS-signal just after lifting the plunger, is not influenced by the formation of  $\text{HNO}_3$ . Even if an impurity of  $\text{HNO}_3$  of 7% is assumed which is interacting with the mineral dust surface (uptake coefficient of 0.1) the determined uptake coefficient of  $\text{N}_2\text{O}_5$  is 1% lower.

a) In the DRIFTS experiments it is not possible to monitor the amount of  $\text{HNO}_3$  during an uptake experiment. In addition, nitrate as a product is formed during the uptake of  $\text{HNO}_3$  as well as of  $\text{N}_2\text{O}_5$  and therefore the two reactions may not be distinguished. However, as the referee already mentioned, in the case of  $\text{HNO}_3$  the formation of free

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water is observed on the surface and in the gas phase in contrast to the uptake of  $\text{N}_2\text{O}_5$  where only strongly hydrogen bonded water has been found to form. In addition, the derived uptake coefficients during the uptake of  $\text{N}_2\text{O}_5$  are significantly lower than the one for  $\text{HNO}_3$  (Seisel et al., 2004). If  $\text{HNO}_3$  would be the major compound in the gas mixture, we would expect to determine much higher values for the uptake coefficient.

In summary, we conclude that the  $\text{HNO}_3$  impurity inside the DRIFTS cell is formed to a similar extent as in the KC which seems reasonable in view of the fact the concentrations used were only one order of magnitude higher but the residence of  $\text{N}_2\text{O}_5$  roughly a factor of 10 lower (see under B) in the DRIFTS experiment compared to the KC experiment. Therefore the formation of nitrate and the derived uptake coefficients (DRIFTS) may be overestimated by roughly 20% due to the  $\text{HNO}_3$  impurity, what is now stated in the manuscript. In addition, we changed Figure 1 in a way that only the first 60 min of the uptake are shown. In view of the increasing amount of  $\text{HNO}_3$  in the  $\text{N}_2\text{O}_5$  gas mixture no reliable results can be obtained from longer reaction times.

b) We calculated the ratio of the fragments  $m/e$  30 and  $m/e$  46 for the experiment shown in the original as well as for the experiment shown in the revised version. In both cases the ratio is constant except for the first minutes of the experiment, where a large scatter is observed. In the revised version of the manuscript MS-signal  $m/e$  30 has been replaced by that ratio. The constant ratio indicates that nitrogen oxides like NO or  $\text{NO}_2$  are not formed. The formation of  $\text{HNO}_3$  does not affect the MS-signal ratio  $m/e$  30 to  $m/e$  46 since the fragmentation patterns of  $\text{HNO}_3$  and  $\text{N}_2\text{O}_5$  are very similar under the QMS settings used.

B. We estimate the residence time of  $\text{N}_2\text{O}_5$  inside the DRIFTS cell to be 0.03 s, which is a factor of 10 lower than in the KC. Both  $\text{N}_2\text{O}_5$  samples had comparable impurities of  $\text{HNO}_3$  at the beginning of an uptake experiment what was routinely checked by means of MS (Essen) and FTIR (FFZA). The concentrations used in the DRIFTS experiments have been slightly larger because of the less sensitive method (FTIR).

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C. This comment is essentially the same as one made by referee 2. Therefore the same answer is applicable.

Although the experiments were performed under similar conditions some differences between the two methods exist:

a) The geometric surface area as well as the mineral dust masses used in the DRIFTS experiments are approximately 20 times smaller than in the KC experiment, resulting in a lower absolute number of reactive surfaces sites at the top layer of the sample as well as in the entire sample.

b) Although there is a certain overlap in the gas phase concentrations used in both studies the ones in the DRIFTS experiment are usually higher due to the lower sensitivity of the technique.

c) In the KC experiments a time-resolved uptake coefficients have been determined whereas mean uptake coefficients are obtained from the DRIFTS experiments, which are less sensitive to variations (Seisel et al., 2004). These differences lead to the assumption that under our experimental conditions different processes were measured in the KC and in the DRIFTS experiment. The initial period of the uptake where the surface reaction (reaction 1a-c) is dominating, is observed in the KC experiments. In contrast, the hydrolysis of  $\text{N}_2\text{O}_5$  is measured in the DRIFTS experiments and in this case the saturation of the uptake is due to the vanishing amount of water and not of S-OH. For both processes the rate is constant and the derived rate constant is independent of the  $\text{N}_2\text{O}_5$  gas concentration as long as the number of surface site (S-OH or water) is large enough to establish pseudo-first order condition. In addition, it has to be noted that the concentrations given in Figure 2 are the  $\text{N}_2\text{O}_5$  concentrations at the time where the uptake coefficient has been determined. In this sense the concentration given for the DRIFTS data are also mean concentrations during uptake and not initial ones.

D. As the referee mentioned,  $\text{N}_2\text{O}_5$  is not easy to handle. Therefore we decided to per-

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form our experiments with the largest escape aperture and the lowest residence time of  $\text{N}_2\text{O}_5$  inside the cell. However, we performed a few experiments with a smaller escape aperture (diameter 4 mm,  $k_{esc} = 0.32 \text{ s}^{-1}$ ). The initial loss rates of  $\text{N}_2\text{O}_5$  obtained from these experiments are in agreement with a first order rate law and are included now in Figure 2.

The first order rate law in  $\text{N}_2\text{O}_5$  is only observed at two points during the course of the experiment. First, at the beginning of the uptake the number of reactive sites on the surface is high enough to establish pseudo-first order condition and consequently the initial uptake of  $\text{N}_2\text{O}_5$  follows a first order rate law according to equation 2 (see manuscript). These initial loss rates were measured using the KC experiment and are shown in Figure 2. Second, if the S-OH groups have been consumed but enough water is available on the surface to ensure pseudo-first order conditions with respect to the hydrolysis of  $\text{N}_2\text{O}_5$  the rate of nitrate formation increases linearly with the  $\text{N}_2\text{O}_5$  gas concentration according to equation 3 (see manuscript). The nitrate formation rates measured under these conditions with the DRIFTS experiment are also shown in Figure 2.

E. The statement has been rewritten: Recent model calculations used uptake coefficients of  $\gamma < 5 * 10^{-2}$  (Bauer et al., 2004) and  $\gamma = 1 * 10^{-3}$  (Bian and Zender, 2003) for the uptake of  $\text{N}_2\text{O}_5$  on mineral dust and calculated a significant decrease in the atmospheric  $\text{N}_2\text{O}_5$  as well as  $\text{O}_3$  concentration. They experimental results reported in this paper suggest, that the uptake of  $\text{N}_2\text{O}_5$  is indeed fast enough to influence the photo-oxidant budget of the atmosphere to an extent estimated in the recent model calculation by Bauer et al. (2004) and Bian and Zender (2003).

Minor comments:

The doses were varied between  $5 * 10^{14}$  and  $2 * 10^{15}$  molecules, given now in the Figure caption 4.

Included.

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S-OH groups can be regenerated by exposing the surface to 100 % RH for several hours (Little, 1966)

corrected

## References

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