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Kinetics and mechanism of the uptake of N_2O_5 on mineral dust at 298 K

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Abstract. The heterogeneous reaction of N_2O_5 with mineral (Saharan) dust has been studied at T=298 K using a combination of Knudsen and DRIFTS cells for kinetic and product investigations, respectively. The initial uptake coefficient has been determined to be γ=(8.0±0.3)·10^{-2}. This uptake slowly saturates into a steady state uptake of γ=(1.3±0.3)·10^{-2} suggesting that reaction of N_2O_5 with the mineral dust surface and hydrolysis of N_2O_5 on the surface take place simultaneously. Both uptake coefficients have been calculated on the basis of the geometric (projected) surface area of the sample and must therefore be regarded as upper limits. In addition, the product investigations show that N_2O_5 is irreversibly taken up to form nitrate on the surface. Recent model calculations suggest that the uptake rates of N_2O_5 on Saharan dust which we measured may be large enough to influence the photo-oxidant budget of the atmosphere.

1 Introduction

The mineral aerosol represents one of the largest natural mass fractions of the global aerosol with an estimated global atmospheric burden of 14 to 41 Tg (Houghton et al., 2001). Mineral dust particles smaller than 10 μm may be transported over thousands of kilometers and are therefore found far away from their sources resulting in a global distribution (Husar et al., 2001). During dust storm events particle mass densities of up to 4650 μg m^{-3} are measured in the lower troposphere (Alfaro et al., 2003). Even at altitudes of 10 to 12 km, up to 500 ppt of mineral ions can be found in aerosol samples, indicating that these particles are also transported into the upper troposphere (Tabazadeh et al., 1998).

The impact of mineral dust particles on the Earth's atmosphere is manifold. They are believed to have a direct and indirect effect on the radiation budget of the atmosphere and therefore are expected to impact on climate (Cziczo et al., 2004; Tegen and Lacis, 1996). In addition, the surface of such aerosol particles represents a site for heterogeneous reactions, the potential role of which has been emphasized in several modelling studies (Bauer et al., 2004; Dentener et al., 1996; Phadnis and Carmichael, 2000; Zhang and Carmichael, 1999). It was found, that the interaction of NO_y (HNO_3+NO_3+N_2O_5) species with mineral dust particles may lead to a global ozone reduction of approximately 5% (Bauer et al., 2004). Evidence for the occurrence of such reactions comes from field experiments as well as from laboratory studies (Hanke et al., 2003; Usher et al., 2003; Putaud et al., 2004; Seisel et al., 2004a).

Roughly 1% ozone reduction is due to a heterogeneous loss of N_2O_5 on mineral dust aerosol assuming an uptake coefficient of N_2O_5 in the range of $5\cdot10^{-2}>\gamma>1\cdot10^{-3}$ depending on the relative humidity (Bauer et al., 2004). Bian and Zender (2003) used a smaller value for the uptake coefficient of γ=1·10^{-3} and calculated a reduction of the atmospheric N_2O_5 concentrations by up to 20%. Moreover, low NO_3 levels during dust storm events have been attributed to an enhancement of the heterogeneous removal of N_2O_5 due to the increased particle concentration (Shon et al., 2004). Although these studies suggest an impact of the heterogeneous reaction of N_2O_5 with mineral dust particles on the photo-oxidant budget of the atmosphere, laboratory studies are not yet available to confirm and quantify this process.

In the present study the uptake of N_2O_5 on Saharan dust samples has been investigated at 298 K using a Knudsen cell with mass-spectrometric detection to probe the gas-phase. In addition, the mineral dust surface has been probed by means of DRIFT spectroscopy. The experiments using the two techniques have been performed under similar conditions and therefore a comparison of the results is possible. From these investigations uptake coefficients for N_2O_5 as well as condensed-phase products could be determined for the first time.

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2 Experimental

2.1 Diffuse Reflectance Infrared Spectroscopy (DRIFTS)

Diffuse Reflectance FTIR Spectroscopy (DRIFTS) was used to probe the condensed phase during the heterogeneous reactions. The experimental set-up has been described in detail elsewhere, (Börensen et al., 2000; Seisel et al., 2004a) and only the most relevant features will be described here. The sample compartment of the FTIR-spectrometer houses the reaction cell equipped with a DRIFTS optic and a sample holder. The reaction cell was part of a flow system, where a mixture of N_2O_5 in Helium was added to a carrier gas stream of Helium. The flow was adjusted to a fixed value of 50 sccm resulting in a total pressure of 4 mbar and a gas residence time of 0.03 s in the cell. With the known mixing ratio and flow rate of the N_2O_5/Helium mixture the concentration of the reactive gas inside the reaction cell could be calculated. In order to make the experimental set-up suitable for fast heterogeneous reactions ($\gamma > 10^{-4}$) a glass plate placed into the focus of the DRIFTS optic served as a holder for the dust samples.

During the exposure of the dust sample to N_2O_5 vibrational spectra were recorded in the spectral range from 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1}. To improve the signal to noise ratio 100 scans were co-added for each spectrum resulting in a time resolution of 1 min. The mineral dust samples had a reflectivity similar to γ-alumina resulting in a sensitivity of approximately $1.2 \cdot 10^{17}$ nitrate ions g^{-1} corresponding $3 \cdot 10^{15}$ ions cm^{-2} in the spectral range from 4000 to 1100 cm^{-1}.

The integrated absorption bands of the products were calibrated absolutely by analysing the sample by ion chromatography after reaction (Seisel et al., 2004a). In order to account for a possible nitrate background in the mineral dust, reference samples have been analyzed where a nitrate background of $3.4 \cdot 10^{17}$ ions g^{-1} has been found. The number of nitrate found in the samples after background correction was linearly correlated to the integrated absorbance of the corresponding nitrate absorption band. Using this calibration the formation rate of nitrate and thus the uptake coefficients for product formation on mineral dust could be calculated according to Börensen et al. (2000).

2.2 Knudsen cell reactor (KC)

The experiments were performed in a Teflon coated Knudsen flow reactor operating in the molecular flow regime (10^{-3} mbar $> p > 10^{-5}$ mbar). The experiment has already been described in the literature (Seisel et al., 2004a). In the present paper we will therefore only describe the main features of the technique as pertinent to the present study.

The apparatus consists of a gas handling system, the Knudsen reactor (V=1950 cm^3) and a differentially pumped vacuum chamber housing the quadrupole mass spectrometer (QMS). N_2O_5 is introduced into the Knudsen reactor from the gas handling system and leaves the Knudsen reactor through an escape orifice of 12 mm diameter, which results in a residence time of N_2O_5 in the cell of τ=0.29 s. A few experiments have been performed using an escape orifice of 4 mm diameter, resulting in a residence time of τ=3.1 s. The effusive beam formed behind the exit of the cell is detected by QMS with a detection limit of $5 \cdot 10^9$ molecules cm^{-3}.

The Knudsen cell has been operated in two different modes. In the pulsed operation of the Knudsen cell a pulse of N_2O_5 of typically 5 ms duration is introduced via a solenoid valve. While the sample compartment is closed in a reference experiment the rate constant for effusive loss k_{esc} is obtained from the mono-exponential decay of the N_2O_5 concentration monitored by the QMS. By introducing a pulse of N_2O_5 while the sample compartment is open on the other hand the exponential decay is characterized by a different decay constant $k_{dec}=k_{esc}+k_{uni}$, where k_{uni} is the rate constant for the uptake of N_2O_5.

In the steady state operation a constant flow of N_2O_5 is introduced via a capillary while bypassing the reactive surface. After lifting the plunger, which separates the sample compartment from the reactor, N_2O_5 is exposed to the surface and the steady state MS-signal S^{in} decreases to a new value S^{out}. For a surface reaction first-order in gas phase concentration from the difference in the two MS-signals the rate constant for the uptake $k_{uni}=(S^{in}/S^{out}-1) \cdot k_{esc}$ can be inferred. By normalizing the rate constant k_{uni} with respect to the collision frequency ω (58.6 s^{-1}) of the gas with the geometric surface area of the sample holder, an upper limit for the dimensionless uptake coefficient ($\gamma=k_{uni}/\omega$) is obtained.

2.3 Sample preparation

Saharan dust collected at the Cap Verde Islands (Desboeufs et al., 1999) was used as mineral dust. The particles had a mean diameter of 15 μm and the BET-surface area was determined to be 50 $m^2\,g^{-1}$. The bulk density was found to be ρ_B=0.93 $g\,cm^{-3}$ whereas the true density was 2.86 $g\,cm^{-3}$. The solid samples were prepared by suspending the dust in approximately 5 ml de-ionized water and subsequent spreading of the suspension on the sample holder. Glass plates of 9×9 mm and 49 mm diameter, respectively, served as sample holders for the DRIFTS cell and the Knudsen cell. A reference experiment performed in the Knudsen cell showed that the uptake of N_2O_5 onto the plate itself is negligible with an uptake coefficient of $\gamma \leq 1 \cdot 10^{-3}$.

All samples were dried under vacuum before each experiment. The extent of dryness of the samples was controlled by monitoring the water desorbing from the surface in the Knudsen cell. Samples were defined as "dry" if water was no longer observed to desorb from the surface upon opening the plunger. Although we can not exclude the presence of strongly adsorbed water, a more efficient drying procedure

i.e. at higher temperatures has been rejected in order not to destroy the internal structure of the clay mineral.

N_2O_5 was synthesized by oxidation of NO_2 with O_3 described by Fenter et al. (1996). The quality of the produced N_2O_5 was checked routinely by means of mass spectrometry or FTIR-spectroscopy. Impurities of HNO_3 were less than 7%, NO_2 impurities have been found to be lower than 1%.

3 Results and discussion

3.1 Condensed-phase products

In order to identify the condensed phase products the interaction of N_2O_5 with mineral dust samples has been studied at T=298 K using the surface sensitive DRIFTS method. N_2O_5 gas phase concentrations have been varied between $4{\cdot}10^{11}$ and $5{\cdot}10^{12}$ molecules cm^{-3} and sample masses between 15 and 20 mg have been used, resulting in sample heights of several hundred microns. Under these conditions the sample height is always larger than the penetration depth of the ir-beam. In all uptake experiments the DRIFT-spectrum of the unreacted mineral dust sample has been used as a background spectrum.

In Fig. 1 a typical time series monitored during the exposure of N_2O_5 to Saharan dust is shown. The most prominent feature in the spectra is the appearance of two strong absorption bands at 1350 cm^{-1} and 1452 cm^{-1} which can be assigned to a split of the double degenerated asymmetric stretch vibration (ν_3) of the nitrate ion. The split of this degeneration has been observed before, especially for nitrate in an adsorbed state (Vogt and Finlayson-Pitts, 1994). It is caused by a non-symmetric environment (Nakamoto, 1997) and due to the observed small split of 100 cm^{-1} the two adsorption peaks at 1350 and 1452 cm^{-1} are clearly assigned to the nitrate ion (Seisel et al., 2004a). Evacuating the reaction cell as well as heating the reacted sample to 470 K did not change the intensity of the absorption bands, indicating that strongly bounded nitrate is irreversibly formed during the uptake of N_2O_5 onto Saharan dust.

The absorption band at 3756 cm^{-1} and the shoulder at 3725 cm^{-1} can be attributed to the stretching vibration of free OH-groups located on the surface of the mineral dust sample (Little, 1966). The observed decrease in the absorption intensity indicates therefore a loss of surface OH-groups.

The growth of a broad absorption ranging from 1650 to 3100 cm^{-1} with a maximum around 2500 $cm^{-1}$is assigned to adsorbed water. Such unusual red-shifted band positions have already been observed before for water adsorbed on mineral dust (Seisel et al., 2004a). The band positions as well as their shapes indicate the presence of strongly hydrogen bonded water assigning the broad absorption between 1800 cm^{-1} and 3100 cm^{-1} to the ν_1,ν_3-stretching vibration and the absorption at 1720 cm^{-1} to the ν_2-bending mode of H_2O (Geiseler and Seidel, 1977; Hair, 1967).

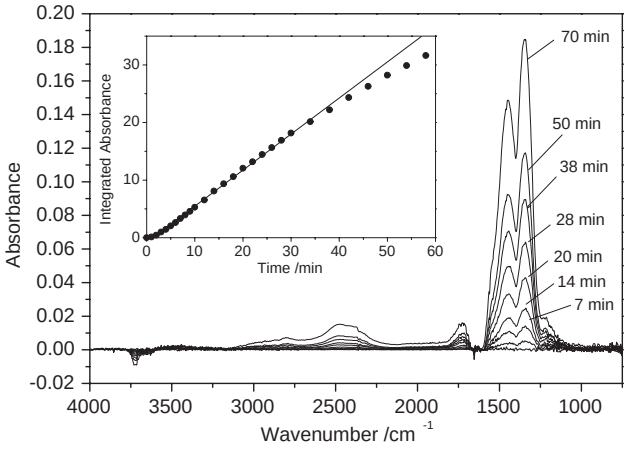

Fig. 1. DRIFTS experiment: Absorption spectra recorded during the reaction of N_2O_5 ($[N_2O_5]_0$=$1.7{\cdot}10^{12}$ molecules cm^{-3}) on Saharan dust. The insert shows the temporal evolution of the integrated absorbance of the nitrate absorption band (1600–1240 cm^{-1}).

The occurrence of strongly hydrogen bonded water may be explained by the fact that water is produced during the reaction of the mineral dust with N_2O_5 and remains attached to the surface. An additional contribution to the observed absorption bands may come from the stretching and bending vibrations of the hydronium ion (H_3O^+) which are observed around 2500 cm^{-1} and 1700 cm^{-1}, respectively, (Ritzhaupt and Devlin, 1991; Smith et al., 1991) and which may be produced by the hydrolysis of N_2O_5. It should be noted, that for solvated nitrate no split of the double degenerated asymmetric stretch vibration (ν_3) is observed (Castro and Jagodzinski, 1991; Seisel et al., 2004a) and consequently the formation of a liquid water layer on the mineral dust surface is excluded.

The formation of nitrate on the mineral dust surface has also been observed in the interaction of HNO_3 with mineral dust (Seisel et al., 2004a). HNO_3 is an impurity of N_2O_5 formed by hydrolysis with residual water. Although the HNO_3 impurity in the N_2O_5 gas mixture has been found to be less than 7% it may increase during the course of the experiment. However, under the assumption that HNO_3 is formed to a similar extent as in the Knudsen cell experiments discussed below no more than 20% of the absorptions at 1350 cm^{-1} and 1452 cm^{-1} is due to the HNO_3 impurity. In addition, the absence of free water on the surface in contrast to the case of HNO_3 indicates that the chemistry occurring on the surface is different.

3.2 Uptake coefficients

In addition to the study of the condensed products formed during the heterogeneous interaction, kinetic data can also be deduced from the DRIFTS experiments. In the insert in Fig. 1 the integrated absorbance of the ν_3 absorption band

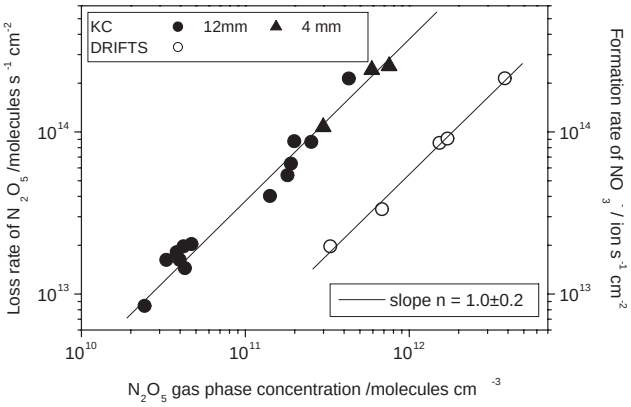

Fig. 2. Bilogarithmic plot of the loss rate of N_2O_5 and the formation rate of nitrate as a function of the N_2O_5 gas phase concentration. The solid lines have a slope of 1, indicating first order processes.

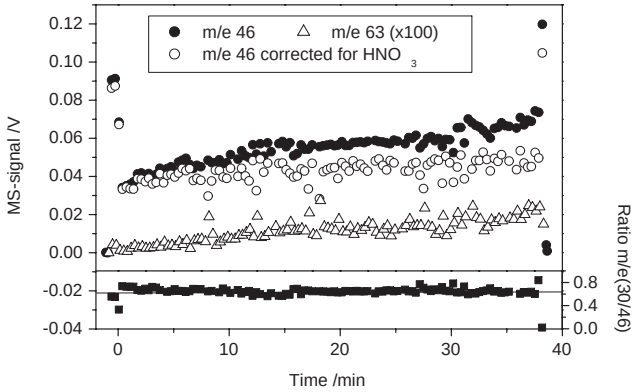

Fig. 3. KC experiment: Typical time profile for the gas phase concentrations of N_2O_5 (monitored at m/e 46) and HNO_3 (monitored at m/e 63) during the interaction N_2O_5 ($[N_2O_5]_0$=9·10^{10} molecules cm^{-3}) with mineral dust (m=139 mg). At t=0 min the plunger is lifted and at t=38 min the plunger is lowered. The corrected signal trace m/e 46 has been obtained by substracting the MS-signal m/e 63 (x100) from the original signal. In the lower part of the figure the signal ratio m/e 30 to m/e 46 is shown.

(1600–1240 cm^{-1}) of the nitrate formed during the reaction as a function of reaction time is shown. From the slope of that curve and the calibration factor derived by ion chromatography the rate of nitrate formation on the surface can be calculated. As can be seen from Fig. 1, the integrated absorbance increases linearly with time for the first 40 min. The linear region of this increase corresponds to a constant formation rate of nitrate ions on the surface, at longer reaction times the integrated absorbance starts to level off indicating that the formation rate slows down.

The reactive uptake coefficient can be calculated from the reaction rate, the order of the reaction and the rate constant for nitrate formation (Börensen et al., 2000). For a heterogeneous reaction of the type:

$$nN_2O_{5(g)} + mS \rightarrow 2nNO_{3\,(ads)}^{-}$$

with S=surface site, and m and n being stoichiometric coefficients of the reactants, the reaction order in N_2O_5(g) for nitrate formation can be determined via (Börensen et al., 2000):

$$\log\left(\frac{1}{2}\frac{d\left[NO_3^-\right]_{ads}}{dt}\right) = n\log\left[N_2O_5\right]_g + \log k + m\log\left[S\right] \quad (1)$$

where k is the rate constant for nitrate formation. In Fig. 2 the formation rate derived from the linear temporal increase of the integrated absorbance of experiments performed at different N_2O_5(g) concentrations has been plotted against the corresponding N_2O_5 concentration on a double-logarithmic scale. As can be seen, the uptake follows a first order rate law in N_2O_5. By dividing the reaction rate by the total number of collisions of N_2O_5 Z=(1/4·A·$[N_2O_5]_g$·c) with the geometric surface area A of the sample (c=mean speed), a reactive uptake coefficient of γ=(9.1±0.7)·10^{-3} is obtained. It has to be noted that the value may be overestimated by 10 to 20% due to the HNO_3 impurity of the N_2O_5 sample.

In addition, the uptake coefficients of N_2O_5 on Saharan dust have been determined at T=298 K using the Knudsen cell reactor. N_2O_5 gas phase concentrations have been varied between 3·10^{10} and 1·10^{12} molecules cm^{-3}. Mineral dust sample masses between 140 and 460 mg, have been used. Figure 3 shows a typical temporal concentration profile for the uptake of N_2O_5 followed at its MS-signals m/e 46. After lifting the plunger at t=0 s a steep decrease in the N_2O_5 concentration due to the uptake on the surface is observed. This initial uptake (MS-Signal S_i for m/e 46) is followed by slow saturation and a time-dependent uptake of N_2O_5. At the end of the uptake experiment, N_2O_5 has not been observed to desorb from the surface, indicating that the uptake is irreversible in agreement with the results of the DRIFTS experiments. The ratio of the MS-signals m/e 30 and m/e 46 remains constant during the course of the experiment, indicating that gaseous nitrogen oxides like NO_2 or NO are not formed during uptake.

However, during the experiment the MS-signal for HNO_3 (m/e 63) is slightly increasing from less than 7% with respect to the MS-signal m/e 46 to approximately 20%. The formation of HNO_3 does not affect the MS-signal ratio m/e 30 to m/e 46 since the fragmentation patterns of HNO_3 and N_2O_5 are very similar under the QMS settings used. Nevertheless, the evaluation of the kinetic data may be hindered by the formation of gas phase nitric acid. Nitric acid is a possible reaction product (see Sect. 3.3) as well as a product of the hydrolysis of N_2O_5 inside the cell and the gas mixing system. In addition, it interacts with mineral dust to a similar extent as N_2O_5 (Seisel et al., 2004a). Under these conditions it is not possible to entirely correct the MS-signal m/e 46 for the HNO_3-contribution. Nevertheless, a rough estimate of the effect of HNO_3 on the MS-signal m/e 46 and the derived uptake coefficients can be given by simply substracting

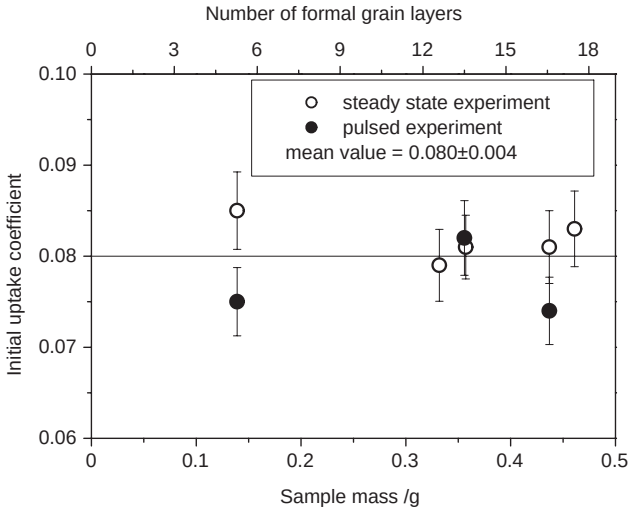

Fig. 4. Initial uptake coefficients of N_2O_5 on Saharan dust as a function of the sample mass. For the pulse valve experiment N_2O_5 doses between $5{\cdot}10^{14}$ and $2{\cdot}10^{15}$ molecules have been exposed to the surface.

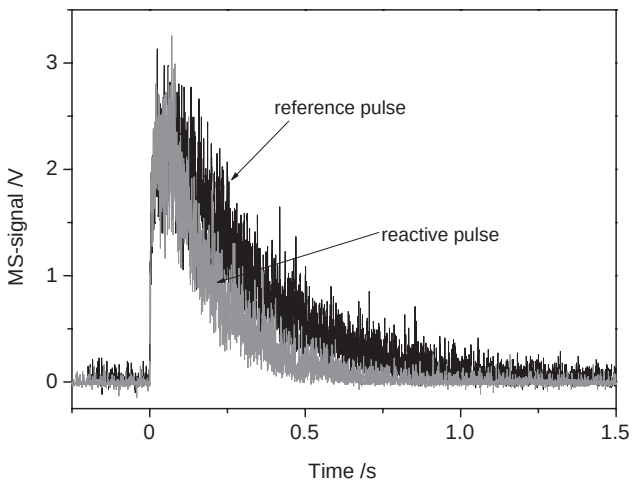

Fig. 5. Temporal traces for the uptake of N_2O_5 on mineral dust using the pulsed mode operation of the Knudsen cell (m(dust)=139 mg). N_2O_5 has been monitored at its mass fragment m/e 46. During the reference experiment the plunger is kept closed. During the reactive experiment the plunger is kept open and N_2O_5 is exposed to the surface the entire time.

the amount of HNO_3 monitored in the gas phase from the MS-signal m/e 46. The MS-signals m/e 46 and m/e 63 of HNO_3 have a ratio of 100; multiplying the MS-signal m/e 63 by 100 gives directly the HNO_3-contribution to the signal m/e 46. The corrected time profile has been added to Fig. 3. During the first 5 min of reaction no significant influence of HNO_3 is observed. At longer reaction times the formation of HNO_3 leads to a faster saturation of the MS-signal m/e 46. A reference experiment with N_2O_5 flowing through the cell while the sample compartment is closed showed that HNO_3 is formed to a similar extent as in an uptake experiment. This result suggests, that a significant amount of HNO_3 is formed by the decomposition of N_2O_5 inside the cell and the gas mixing system.

The initial uptake coefficient of N_2O_5, which is determined from the minimum MS-signal just after lifting the plunger, is not influenced by the formation of HNO_3, as can be seen from Fig. 3. Even if an impurity of HNO_3 of 7% is assumed which is interacting with the mineral dust surface with an uptake coefficient of γ=0.1 (Seisel et al., 2004a) the determined uptake coefficient of N_2O_5 is only 1% lower. The determined initital uptake coefficients are found to be independent of the N_2O_5 gas phase concentration that is the uptake follows a first order rate law in N_2O_5 (Fig. 2).

In addition to the concentration dependence the dependence of the initial uptake on the total mass of the dust sample has been investigated. Such studies are important in order to unravel whether or not the effectively available surface area is influenced by internal surface areas caused by interstitial voids between the individual dust grain particles. As can be seen in Fig. 4, the initial uptake coefficients determined are independent of the sample mass, which is proportional to the number of formal grain layers deposited on the sample holder. This number is calculated on the basis of the sample mass, the area of the sample holder, the mean particle diameter and the bulk density. The bulk density corresponds to the sample mass divided by the total volume that is the sum of the particle volume and the interstitial voids. Consequently, one formal grain layer is not sufficient to cover the sample holder completely. The lowest sample mass used has been 140 mg, corresponding to 5.3 formal grain layers. Using instead the true density of the mineral dust particles 140 mg would correspond to 1.7 layers and would therefore just cover the sample holder completely. The result indicates that diffusion of N_2O_5 into the bulk of the mineral dust sample is too slow to influence the initial uptake kinetics on the time scale of our experiments. It has to be noted, that this conclusion can only be drawn for the initial uptake coefficient because at longer exposure times diffusion into the bulk of the mineral dust sample may occur.

In order to support this conclusion, additional uptake experiments have been undertaken using the pulsed valve gas inlet with an improved response time (Seisel et al., 2005). Whereas in a steady state experiment the uptake coefficient can be determined after 1 s exposure time at the earliest, the pulsed gas inlet allows the determination of an uptake coefficient within one life-time that is under our conditions 200 to 300 ms. Consequently, the surface coverage as well the probe depth of the gas in the case of diffusion can be reduced by this experimental technique, leading to improved initial uptake coefficients. In Fig. 5 a typical time profile for the uptake of N_2O_5 on mineral dust using the pulsed gas inlet is shown. The decay is mono-exponential indicating again

that the uptake follows a first order rate law. Uptake coefficients obtained from pulsed and steady state experiments are in good agreement as shown in Fig. 4, indicating that the initial uptake coefficients determined represent indeed the uptake of N_2O_5 onto the uppermost layer of the mineral dust sample.

Consequently, at T=298 K the mean value for the initial uptake coefficient determined in the Knudsen cell experiments has been found to be of γ=(8.0±0.3)·10^{-2} on the basis of the geometric (projected) surface area of the solid samples. The geometric surface area represents the lower limit of the reactive surface area and the determined uptake coefficient has therefore to be regarded as an upper limit. In contrast, a complete coverage of the sample holder with mineral dust would need 81 mg of dust, resulting in a surface area of 2 m^2 using the BET surface area of 50 $m^2\,g^{-1}$. This value represents the upper limit of the reactive surface area for two reasons: i) Not all adsorption sites which are occupied by N_2 are reactive sites for N_2O_5 ii) A molecule colliding with the surface will "see" the projected surface area and not a BET surface area including e.g. pores.

In atmospheric models the surface area of aerosol particles are usually calculated on the basis of the particle diameter which results in a geometric surface area (e.g. Bauer et al., 2004; Dentener et al., 1996; Pöschl et al., 2005; Underwood et al., 2001). In order to make our uptake coefficients directly applicable to atmospheric models, we therefore decided to report all values on the basis of the geometric surface area. Although these values are upper limits, a possible surface roughness of our samples will only overestimate the uptake coefficient by a factor of 2 to 3. Nevertheless, the initial uptake coefficients obtained form the KC experiments are roughly one order of magnitude higher than the reactive uptake coefficients determined by the DRIFTS technique, the possible reasons of which will be discussed in the next section.

3.3 Mechanism

During the uptake of N_2O_5 on Saharan dust the most intense absorption bands have been observed for ionic nitrate. Along with the formation of nitrate the loss of surface OH-groups has been observed suggesting that N_2O_5 reacts with surface OH-groups to form nitrate via reactions 1a and 1b. The formation HNO_3 on the mineral dust surface could not be observed and the amount of HNO_3 found in the gas phase has mainly been assigned to the decomposition of N_2O_5 inside the gas mixing system and the cell. Consequently, HNO_3(ads) is assumed to readily react via reaction 1c as already shown by Seisel et al. (2004a).

$$N_2O_5(g) + S{-}OH \rightarrow N_2O_5 * S{-}OH \quad \text{(R1a)}$$

$$N_2O_5 * S{-}OH \rightarrow HNO_3(ads) + S{-}NO_3 \quad \text{(R1b)}$$

$$HNO_3(ads) + S{-}OH \rightarrow H_2O(ads) + S{-}NO_3 \quad \text{(R1c)}$$

On the surface as well as in the gas phase free water molecules have not been found in contrast to the reaction of HNO_3 with mineral dust (Seisel et al., 2004a). Instead, water was observed in a strongly hydrogen-bonded form or as hydronium ions which leads to the conclusion that it is consumed in a hydrolysis of N_2O_5 (Reaction 2a) followed by dissociation of nitric acid (Reaction 2b).

$$N_2O_5(g) + H_2O(ads) \rightarrow 2HNO_3(ads) \quad \text{(R2a)}$$

$$HNO_3(ads) + H_2O(ads) \rightarrow H_3O^+ + NO_3^- \quad \text{(R2b)}$$

By taking into account that mineral dust consists of clay minerals with interlamellar water the actual amount of water present in the mineral dust samples even under dry conditions may be large enough to induce an efficient hydrolysis of N_2O_5. Consequently, the uptake of N_2O_5 on mineral dust surfaces proceeds simultaneously via reaction with surface OH-groups as well as hydrolysis, both channels leading to the formation of nitrate ions on the surface.

The simultaneous occurrence of surface reaction and surface hydrolysis is also reflected by the uptake coefficients. The loss rate of N_2O_5 is given by:

$$\frac{d\,[N_2O_5]_g}{dt} = -\left(k_{1a}\ [S\text{-}OH] + k_{2a}\,[H_2O]_{ads}\right)[N_2O_5]_g \quad (2)$$

with the units of all compounds in number of molecules. In agreement with the experimental observation (Fig. 2) this loss rate follows a first order rate law in N_2O_5 as long as pseudo-first order conditions with respect to [S-OH] and $[H_2O]_{ads}$ prevail in the beginning of the uptake, where the initial uptake coefficient is derived. Dividing this expression by the collision number Z of N_2O_5 with the surface yields the overall (observed) uptake coefficient, which according to Eq. (3) is the sum of two terms:

$$\gamma_{obs} = \gamma_{reac} + \gamma_{hydr} \quad (3)$$

Whilst the reaction proceeds the number of surface-OH groups decreases and consequently a time-dependent uptake is observed. At longer exposure times the uptake is dominated by the hydrolysis of N_2O_5 and the determined uptake coefficient corresponds to γ_{hydr}. In Fig. 6 the temporal evolution of the uptake coefficient for N_2O_5 on mineral dust determined in a KC experiment is shown. It can be seen that the uptake coefficient decreases within 30 min to a value of approximately γ=2·10^{-2}. The uptake coefficients calculated from the corrected MS-signal m/e 46 (Fig. 3 and Sect. 3.2) are also shown. The decay of the corrected values leads to a limiting value approximately a factor of two higher. It has to be noted, that the correction procedure considers the case where HNO_3 is not reacting with the surface. If HNO_3 is taken up as well, the corrected values will be lower, even a few percent below the uncorrected uptake coefficients.

Analysing the experiments performed in more detail, the decay of the uptake coefficient can be described by the following mono-exponential expression:

$$\gamma = (1.7 \pm 0.3) \cdot 10^{-2} + (6.2 \pm 0.5) \cdot 10^{-2} \exp(-(1.8 \pm 0.5) \cdot 10^{-3} s^{-1} t)$$

where t is the exposure time of N_2O_5 to the mineral dust. Following the arguments above, the first term corresponds to the hydrolysis of N_2O_5 (γ_{hydr}=(1.7±0.3)·10^{-2}). The exponential term describes the time dependence of the surface reaction and gives an initial uptake coefficient for N_2O_5 of γ_{reac}=(6.2±0.5)·10^{-2}. It has to be noted again, that these values are upper limits, since they are derived on the basis of the geometric surface area of the sample.

Taking into account the complex structure and composition of mineral dust the proposed mechanism may be an oversimplification, neglecting the heterogeneities of the surface. Nevertheless, the temporal evolution of the uptake coefficient clearly shows that two different processes are operating. A slow time-independent (on the time scale and conditions of the KC experiment) uptake superimposed by a faster time-dependent process which suggest that N_2O_5 is reacting with two different surface sites. Long time experiments have been performed with different sample masses and no significant difference in the temporal evolution of the uptake coefficient is observed, indicating, that diffusion of N_2O_5 into the bulk is not a dominating process under those conditions. The so-called nitrate effect, which leads to a decrease of the N_2O_5 uptake due to the build up of nitrate, has only been observed at nitrate concentrations of more than 20 wt% nitrate of aqueous aerosol particles (Hallquist et al., 2003; Mentel et al., 1999; Wagner et al., 2005). During the first 5 min of N_2O_5 exposure approximately 2·10^{17} nitrate ions accumulate on the dust surface under our experimental conditions. Although the water content of our dust samples is considerably lower than the one of aqueous aerosol particles the nitrate concentration built up during the first minutes of the reaction would not suffice to induce a significant nitrate effect as observed by Wagner et al. (2005) and Mentel et al. (1999).

Mineral dust consists of clay minerals which are able to store large amounts of water. Upon heating our mineral dust sample to up to 600 K more than 1·10^{20} molecules g^{-1} water are released into the gas phase. In addition, it is known that the surface of mineral oxides is terminated by OH-groups which can only be recovered after loss by exposing the mineral oxides to 100% *RH* for several hours (Little, 1966). Consequently, the assumption of surface OH-groups and adsorbed water molecules as reactive species on the surface is a realistic possibility.

Moreover, the value of γ_{hydr}=1.7·10^{-2} is close to literature values for the hydrolysis of N_2O_5 on solid and liquid water surfaces (Atkinson et al., 2001). Our measurements have been performed under dry conditions. Recent studies on liquid and solid aerosol particles show a strong dependence of the uptake coefficient on the *RH* with values ranging from

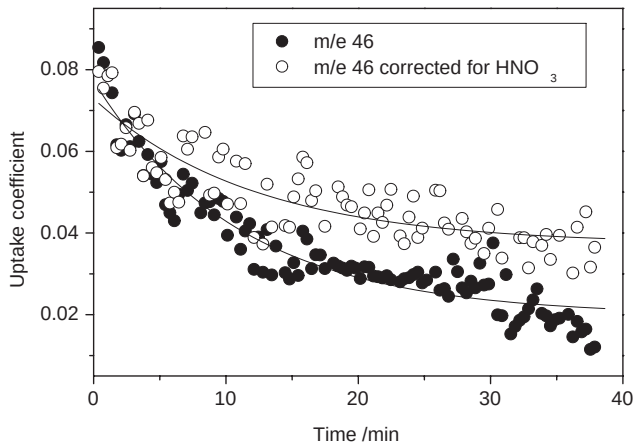

Fig. 6. Temporal evolution of the uptake coefficient of N_2O_5 ($[N_2O_5]_0$=9·10^{10} molecules cm^{-3}) on mineral dust (m=139 mg).

γ=1·10^{-3} at low *RH* to up to γ=7·10^{-2} at *RH*>70% (Hallquist et al., 2003; Kane et al., 2001; Stewart et al., 2004; Thornton et al., 2003). In view of these results the value of $\gamma_{hydr} \leq 1.7 \cdot 10^{-2}$ seems to be high. However, in contrast to this work, the studies mentioned above have been performed with sub-micron aerosol particles. The liquid phase volume of the particles decreases with decreasing *RH* and the uptake rate becomes volume dependent at low *RH* resulting in an apparent humidity dependence (Hallquist et al., 2003; Stewart et al., 2004; Thornton et al., 2003). Therefore, bulk samples of mineral dust with interlamellar water layers as used in this study may promote a high uptake of N_2O_5 even at low *RH*.

In contrast to the KC experiment the uptake rate determined from the DRIFTS experiments remains time independent over a certain time (e.g. 40 min for the experiment shown in Fig. 1) and then slowly decreases. The time where the saturation is observed to start decreases with increasing N_2O_5 gas phase concentration, suggesting that it may be due to a decrease in the number of reactive surface sites. Although the experiments were performed under similar conditions some differences between the two methods exist:

– 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.

– 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.

– In the KC experiments 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., 2004a).

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 surface reaction (Reactions 1a–c) dominates, is observed in the KC experiments. In contrast, hydrolysis of N_2O_5 is measured in the DRIFTS experiments and in this case the saturation of the uptake is due to the vanishing amount of water along with an increasing amount of nitrate ions which may lead to a nitrate effect (Hallquist et al., 2003; Mentel et al., 1999; Wagner et al., 2005) and a decrease of the uptake rate.

The uptake coefficients derived in the KC experiments have been implemented into a simple kinetic model including Reactions (R1) and (R2). With a number of S-OH groups of $2{\cdot}10^{16}$ cm^{-2} the time profiles observed in the KC experiments could be reproduced. This value is 10 times higher than the value expected from the geometric surface area but 3 orders of magnitude lower than expected from the BET surface area of the upper-most layer. This finding strengthens again the argument given in Sect. 3.2 that the geometric surface area represents a lower limit for the reactive surface and the BET surface area an upper limit for the surface area. In addition, the number is similar to the number of reactive sites estimated for the uptake of water on mineral dust (Seisel et al., 2004b).

Under the conditions of the DRIFTS experiment, a number of $2{\cdot}10^{16}$ S-OH groups cm^{-2} is consumed within 1 min reaction time and the uptake was controlled by Reaction (R2), supporting the arguments given above. Consequently, the observed nitrate formation is assumed to be caused by the hydrolysis of N_2O_5 (Reactions 2a and b) rather than surface reaction (Reactions 1a–c). Under this assumption the formation rate of nitrate can be described by:

$$\frac{d\left[NO_3^-\right]}{dt} = 2\ k_{2a} \cdot [H_2O]_{ads} \cdot [N_2O_5]_g \qquad (4)$$

According to this expression the formation rate of nitrate is first order in $[N_2O_5]_g$ as observed (Fig. 2) and constant as long as enough water is available. The uptake coefficient of $(9.1{\pm}0.7){\cdot}10^{-3}$ derived from the DRIFTS experiments corresponds then to γ_{hydr}, in agreement with the value determined from the KC experiments. From both experiments an upper limit for the surface hydrolysis of N_2O_5 of $\gamma{=}(1.3{\pm}0.3){\cdot}10^{-2}$ is determined.

3.4 Atmospheric implications

According to model calculations roughly 1% ozone reduction is due to a heterogeneous loss of N_2O_5 to mineral dust, which reduces thereby the atmospheric N_2O_5 concentrations by up to 20 % (Bauer et al., 2004; Bian and Zender, 2003). However, these results have been obtained for assumed values for the uptake coefficient of $5{\cdot}10^{-2}{>}\gamma{>}1{\cdot}10^{-3}$ (depending on the relative humidity, Bauer et al., 2004) and $1{\cdot}10^{-3}$ (Bian and Zender, 2003) due to the fact that kinetic data for the reaction have not been available. Although the uptake coefficients of $8.0{\cdot}10^{-2}{>}\gamma{>}1.3{\cdot}10^{-2}$ determined in this study are upper limits and may be overestimated by a factor of 2–3, they are as large as the values used in the above mentioned modelling studies. Consequently, the heterogeneous reaction of N_2O_5 with mineral dust should indeed have an impact on the photo-oxidant budget of the atmosphere. However, two important aspects have to be discussed concerning the application of our results to atmospheric condition, namely the time-dependent uptake of N_2O_5 and the influence of water on the uptake coefficient.

As has been discussed in the previous section, for the uptake of N_2O_5 on mineral dust these two aspects are closely related. The uptake of N_2O_5 proceeds via two reaction channels. The first one, the reaction of N_2O_5 with surface-OH groups has an high initial uptake coefficient of $\gamma_{reac}{\leq}(6.2{\pm}0.5){\cdot}10^{-2}$ and causes the time-dependence of the uptake by the depletion of surface-OH groups during uptake. The second reaction channel, the hydrolysis of N_2O_5, however, operates with a constant uptake coefficient of $\gamma_{hydr}{\leq}(1.3{\pm}0.3){\cdot}10^{-2}$ as long as enough water is available. Under atmospheric conditions the mineral dust particles are always in a humid environment compared to the experimental conditions used in this study. In addition, besides N_2O_5 a number of gas phase species may compete for the uptake on these aerosol particles. Therefore, it is unlikely that the surface reaction (Reactions 1a–c) is a dominant process. Consequently, it is concluded that under atmospheric conditions N_2O_5 is mainly hydrolysed on the mineral dust surface with an upper limit for the uptake coefficient of $\gamma{\leq}1{\cdot}10^{-2}$. However, this value has been derived under dry conditions and the actual dependence on the relative humidity has to be addressed in future studies.

In addition, the observed formation of H_3O^+ ions on the surface will lower the pH-value of the mineral dust particles upon uptake of N_2O_5. This might have consequences for other heterogeneous processes like the oxidation of SO_2, which should be addressed in a detailed modelling study.

4 Conclusions

In the study presented the heterogeneous reactions of N_2O_5 with mineral dust has been studied using DRIFT spectroscopy as surface-sensitive method and a Knudsen-cell coupled to a QMS for the analysis of the gas phase. It was found that N_2O_5 is readily and irreversibly taken up on Saharan dust with an upper limit of the initial uptake coefficient of $\gamma_{ini}{=}(8.0{\pm}0.3){\cdot}10^{-2}$ forming nitrate on the surface. In addition, water and hydronium ions have been observed to be produced on the mineral dust surface, which suggests that surface reaction and hydrolysis take place simultaneously.

For the two reaction channels upper limits of the uptake coefficients of γ_{reac}=(6.2±0.5)·10^{-2} and γ_{hydr}=(1.3±0.3)·10^{-2} have been derived.

Recent model calculations used uptake coefficients of $\gamma<5\cdot10^{-2}$ (Bauer et al., 2004) and $\gamma=1\cdot10^{-3}$ (Bian and Zender, 2003) for the uptake of N_2O_5 on mineral dust and calculated a significant decrease in the atmospheric N_2O_5 as well as O_3 concentration. They experimental results reported in this paper suggest, that the uptake of N_2O_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).

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