



# The heterogeneous chemical kinetics of N<sub>2</sub>O<sub>5</sub> on CaCO<sub>3</sub> and other atmospheric mineral dust surrogates

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**Products and kinetics  
of  $\text{N}_2\text{O}_5$  interaction  
on mineral dust**

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# The heterogeneous chemical kinetics of $\text{N}_2\text{O}_5$ on $\text{CaCO}_3$ and other atmospheric mineral dust surrogates

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## Abstract

Uptake experiments of  $\text{N}_2\text{O}_5$  on several mineral dust powder samples were carried out under continuous molecular flow conditions at  $298 \pm 2 \text{ K}$ . At  $[\text{N}_2\text{O}_5]_0 = (4.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$  we have found  $\gamma_{ss}$  values ranging from  $(3.5 \pm 1.1) \times 10^{-2}$  for  $\text{CaCO}_3$  to  $(0.20 \pm 0.05)$  for Saharan Dust with  $\gamma_{ss}$  decreasing as  $[\text{N}_2\text{O}_5]_0$  increased. We have observed delayed production of  $\text{HNO}_3$  upon uptake of  $\text{N}_2\text{O}_5$  for every investigated sample owing to hydrolysis of  $\text{N}_2\text{O}_5$  with surface-adsorbed  $\text{H}_2\text{O}$ . At high and low  $[\text{N}_2\text{O}_5]$  Arizona Test Dust and Kaolinite turned out to be the samples to produce the largest amount of gas phase  $\text{HNO}_3$  with respect to  $\text{N}_2\text{O}_5$  taken up. In contrast, the yield of  $\text{HNO}_3$  for Saharan Dust and  $\text{CaCO}_3$  are lower. On  $\text{CaCO}_3$  the disappearance of  $\text{N}_2\text{O}_5$  was also accompanied by the formation of  $\text{CO}_2$ . For  $\text{CaCO}_3$  sample masses ranging from 0.33 to 2.0 g, the yield of  $\text{CO}_2$  was approximately 42–50% with respect to the total number of  $\text{N}_2\text{O}_5$  molecules taken up. The reaction of  $\text{N}_2\text{O}_5$  with mineral dust and the subsequent production of gas phase  $\text{HNO}_3$  leads to a decrease in  $[\text{NO}_x]$  which may have a significant effect on global ozone.

## 1. Introduction

Dinitrogen pentoxide,  $\text{N}_2\text{O}_5$ , is part of the family of active nitrogen,  $\text{NO}_y$ , owing to its equilibrium with  $\text{NO}_2$  and  $\text{NO}_3$  according to Reaction (1), which releases photochemically active  $\text{NO}_3$  and  $\text{NO}_2$  free radicals.



Under atmospheric pressure and 298 K the thermal lifetime of  $\text{N}_2\text{O}_5$  is approximately 20 s and is a strong function of temperature (Atkinson et al., 1997; Wängberg et al., 1997). The observation of the buildup of the concentration of nitric acid,  $\text{HNO}_3$ , in the polluted urban PBL during the night could only be explained by the heterogeneous

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conversion of  $\text{N}_2\text{O}_5$  to  $\text{HNO}_3$  according to Reaction (2) (Hjorth et al., 1987; Tuazon et al., 1983)



The substrate for the heterogeneous Reaction (2) has not been unambiguously identified but is thought to be urban  $\text{H}_2\text{O}$ -containing aerosols or humid surfaces on the ground whose purpose is to make available adsorbed  $\text{H}_2\text{O}$  in order to enable Reaction (2).

Together with  $\text{HNO}_3$  and  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$  contributes to the formation of particulate nitrate on the dust particles by surface processes in the troposphere (Zhang et al., 1994). These processes represent an important sink for nitrogen oxide species, with decreases of daytime  $\text{NO}_y$  levels reaching up to 60% in the presence of dust at a loading of about  $1.8\text{--}11.5 \mu\text{g m}^{-3}$  corresponding to a particle surface area of  $(0.11\text{--}0.7) \times 10^{-6} \text{ cm}^2 \text{ cm}^{-3}$ . During the nighttime, the conversion of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  to particles dominates the overall nitrate formation accounting for 80% of total particulate nitrate formation while the heterogeneous hydrolysis pathway leading to  $\text{HNO}_3$  accounts for only about 20% (Zhang et al., 1994).

In addition, the present study shows that gas phase  $\text{HNO}_3$  is a potential reaction product formed by heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$  with adsorbed water present on mineral dust. Previous laboratory studies performed using a Knudsen cell flow reactor have extensively supported the reactivity of  $\text{HNO}_3$  on  $\text{CaCO}_3$ , marble, mineral dust surrogates and metal oxides (Fenter et al., 1995; Frinak et al., 2004; Hanisch and Crowley, 2001a; Underwood et al., 2001).

Mineral aerosols provide reactive surfaces in the atmosphere where heterogeneous chemical reactions may take place. Dentener showed how the interaction of  $\text{N}_2\text{O}_5$ ,  $\text{O}_3$  and  $\text{HO}_2$  radicals with dust will affect the photochemical oxidant cycle, with ozone concentrations decreasing by up to 10% in and nearby the dust source areas (Dentener et al., 1996).

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Field observations, laboratory (Hanisch and Crowley, 2001a, b, c, d; Usher et al., 2003) and modelling studies have established the interaction of trace gases with mineral dust aerosol as well as the quantitative impact of the latter on the composition of the atmosphere. Box, regional and global scale models have shown the importance of dust on both the photochemical rates of oxidant formation as well as the loss of trace gases regarding atmospheric composition (Bauer et al., 2004; Bian and Zender, 2003; Dentener et al., 1996; Tabazadeh et al., 1998; Zhang et al., 1994).

The comparison of the global scale models of Bian and Zender with the one presented by Bauer et al. reveals significant quantitative differences of the effect of mineral dust on  $O_3$  and several important trace gases such as  $HNO_3$ ,  $N_2O_5$  and  $H_2O_2$ . However, both studies agree that the direct interaction of  $O_3$  with mineral dust is of minor importance, whereas the uptake of its precursor  $HNO_3$  is responsible for most of the ozone decrease in the areas affected by dust. In the modelling studies of both Bian and Zender (2003) and Bauer et al. (2004) an uptake coefficient  $\gamma_{N_2O_5} = 10^{-3}$  at a relatively humidity ( $RH$ ) of 30% has been used. In the modelling simulation performed by Bauer et al. the uptake of  $N_2O_5$  resulted in a reduction of 11% of its mass in the gas phase whereas the simulations of Bian and Zender indicate a global reduction of 2%.

Despite the published results of field observations and modeling studies (Bauer et al., 2004; Bian and Zender, 2003; Bonasoni et al., 2004; de Reus et al., 2000), there are no reports on laboratory experiments that deal with the heterogeneous reactivity of  $N_2O_5$  on mineral dust aerosol surrogates. Only a very recent laboratory study has been performed with  $N_2O_5$  on Saharan Dust using a combination of Knudsen and Drifts cell (Seisel et al., 2005). We have therefore embarked on a laboratory program to measure some of the heterogeneous reactions involving  $N_2O_5$  and  $NO_3$  (Karagulian and Rossi, 2005) as relevant trace atmospheric gases. In the present work, we have used a Knudsen flow reactor in order to investigate the uptake and reaction of  $N_2O_5$  on selected authentic mineral dust samples such as Kaolinite, Saharan Dust from Cape Verde Islands, Arizona test dust and natural limestone as well as on samples of pure  $CaCO_3$ .

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## 2. Experimental set up and detection

All experiments were performed in a TEFLON<sup>®</sup> coated Knudsen flow reactor operating in the molecular flow regime. This technique has been described in detail in the literature (Caloz et al., 1997). Briefly, N<sub>2</sub>O<sub>5</sub> was introduced into the Knudsen flow reactor from the gas handling system using a fine needle valve as a flow control device. An isolation plunger allows the separation of the reactive surface of interest from the reactor volume. The gases leave the Knudsen reactor through an escape orifice whose diameters (1, 4, 8, 14 mm) determine the residence time ( $\tau_g = 1/k_{\text{esc}}$ ) and molecular concentration at a given flow rate  $F_0^M = I_M \cdot C_{(M)}$ , where  $I_M$  is the mass spectrometric signal amplitude (*MS*) and  $C_{(M)}$  is a calibration factor for the species *M* of interest that depends on instrumental parameters. The concentration  $[M]_{MS} = N/V_{\text{cell}} = \frac{F_0^M}{k_{\text{esc}} \cdot V_{\text{cell}}}$  is related to the flow of molecules leaving the reactor  $F_0^M$ . Mass spectrometry (*MS*) provides a direct measure of the flow rate  $F_0^M$  which is proportional to the concentration of a species escaping the Knudsen flow reactor. The rate constant for the effusive loss  $k_{\text{esc}}$  of N<sub>2</sub>O<sub>5</sub> is given by the kinetic theory of gases and was measured for every used orifice. The characteristic parameters and relevant kinetic expressions used in this work are reported in Table 1.

The samples we have used in this study are the following: Kaolinite, poorly ordered (KGa-2, Warren County, Georgia, USA), CaCO<sub>3</sub> (Fluka), Arizona Medium Test Dust (Powder Technology Incorporated, Burnsville MN, USA), natural limestone (Transmat, La Sarraz, Switzerland) and Saharan Dust from deposits on Cape Verde Islands (SDCV).

Two kinds of sample holders were used: one consisted of a TEFLON<sup>®</sup> coated Pyrex holder of available sample surface of 19.6 cm<sup>2</sup>, the other consisted of an internal reduction piece made out of DELRIN<sup>®</sup> leading to a sample surface of 4.9 cm<sup>2</sup>. Both TEFLON<sup>®</sup> and DELRIN<sup>®</sup> did not show any reactivity towards N<sub>2</sub>O<sub>5</sub> under the present

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experimental conditions.

$N_2O_5$  was synthesized by the oxidation of  $NO_2$  with excess ozone. The  $O_3/O_2$  mixture at the outlet of the ozonator (Fisher 502) is passed through a  $P_2O_5$  trap in order to eliminate residual moisture before being mixed with equally dried  $NO_2$ . The  $N_2O_5$  is collected in a methanol/dry-ice bath at 195 K and is subsequently analyzed for purity by *MS*. Hydrolysis of  $N_2O_5$  may occur on surfaces of the traps and of the line before admission into the Knudsen flow reactor generating  $HNO_3$  as an impurity ranging from 10 to 15% as studied by *MS* at *m/e* 63, its molecular ion peak.

$N_2O_5$  does not have a measurable parent and fragment peak at *m/e* 108 and 62, respectively, under the present experimental conditions; the most intense peaks are its fragment  $NO_2^+$  at *m/e* 46 followed by the less intense fragment  $NO^+$  at *m/e* 30. However, the  $HNO_3$  impurity also contributes to the *MS* signal at *m/e* 46 and 30. Under the experimental conditions used  $HNO_3$  has a detectable parent peak at *m/e* 63. Through a calibrated mass spectrum of pure  $HNO_3$  we have accurately determined the effective contribution of  $HNO_3$  at *m/e* 46 and 30 by using the fragmentation pattern expressed as the ratios  $f_{46} = \frac{I_0^{46(HNO_3)}}{I_0^{63(HNO_3)}} = 52 \pm 8$  and  $f_{30} = \frac{I_0^{30(HNO_3)}}{I_0^{63(HNO_3)}} = 33 \pm 4$ . In the absence

of a substrate,  $f_{46} \cdot I_0^{63(HNO_3)}$  and  $f_{30} \cdot I_0^{63(HNO_3)}$  have been subtracted from the total *MS* signals  $I_0^{46}$  and  $I_0^{30}$  at *m/e* 46 and 30, respectively, in order to assign the remaining *MS* amplitude to the  $NO_2^+$  and  $NO^+$  fragments to  $N_2O_5$ :  $I_0^{46(N_2O_5)} = I_0^{46} - f_{46} \cdot I_0^{63(HNO_3)}$  and  $I_0^{30(N_2O_5)} = I_0^{30} - f_{30} \cdot I_0^{63(HNO_3)}$ .

The ratio between the two most intense peaks of  $N_2O_5$  therefore was  $r = \frac{I_0^{46(N_2O_5)}}{I_0^{30(N_2O_5)}} = 1.4 \pm 0.2$ . Mixtures of  $N_2O_5$  and  $HNO_3$  may thus be monitored using *MS* signal intensities at *m/e* 46, 30 and 63. However, in order to quantify  $N_2O_5$  we chose its most intense peak corresponding to its fragment  $NO_2^+$  at *m/e* 46. The subscript 0 and *r* refer to continuous gas uptake experiments in the absence and presence, respectively, of the solid sample.

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### 3. Uptake coefficient of N<sub>2</sub>O<sub>5</sub> and identity of reaction products

When N<sub>2</sub>O<sub>5</sub> is exposed to the sample, it is taken up and undergoes a heterogeneous reaction on the mineral dust surface which results in a decrease of the N<sub>2</sub>O<sub>5</sub> concentration that is monitored using the *MS* signal  $I_r^{46(\text{N}_2\text{O}_5)}$ . As shown in previous studies on mineral dust, HNO<sub>3</sub> that is always present as an impurity, is taken up on the mineral dust surface without releasing any product that may contribute to the total *MS* signal  $I_r^{46}$  at m/e 46 (Hanisch and Crowley, 2001b). We therefore determined the rate constant  $k_{\text{obs}}$  for the disappearance of N<sub>2</sub>O<sub>5</sub> following Eq. (E.1), assuming that the rate law is first order in N<sub>2</sub>O<sub>5</sub>:

$$k_{\text{obs}} = \left( \frac{I_0^{46(\text{N}_2\text{O}_5)}}{I_r^{46(\text{N}_2\text{O}_5)}} - 1 \right) \cdot k_{\text{esc}} \quad (\text{E.1})$$

$I_0^{46(\text{N}_2\text{O}_5)}$  and  $I_r^{46(\text{N}_2\text{O}_5)}$  are the intensities of the NO<sub>2</sub><sup>+</sup> fragment of N<sub>2</sub>O<sub>5</sub> before and during heterogeneous reaction, respectively, and  $k_{\text{esc}}$  is the measured rate constant of effusion for N<sub>2</sub>O<sub>5</sub> out of the flow reactor (see Table 1). In order to determine  $I_r^{46(\text{N}_2\text{O}_5)}$ , the raw *MS* signal at m/e 46 was corrected for HNO<sub>3</sub> generated through hydrolysis of N<sub>2</sub>O<sub>5</sub> with water adsorbed on the substrate surface. Production of HNO<sub>3</sub> has in fact been observed at m/e 63 in every uptake experiment of N<sub>2</sub>O<sub>5</sub>. Figure 1 shows the raw *MS* signal at m/e 63 for a typical uptake experiment of N<sub>2</sub>O<sub>5</sub> on CaCO<sub>3</sub>. Therefore, we have corrected the *MS* signal of N<sub>2</sub>O<sub>5</sub> at m/e 46 for the presence of HNO<sub>3</sub> according to Eq. (E.2) when the sample is exposed to N<sub>2</sub>O<sub>5</sub>:

$$I_r^{46(\text{N}_2\text{O}_5)} = I_r^{46} - f \cdot I_r^{63(\text{HNO}_3)} \quad (\text{E.2})$$

The ratio  $r$ , reported above, turned out to be the same before and during the exposure of the mineral dust sample to N<sub>2</sub>O<sub>5</sub>. Therefore,  $I_r^{46(\text{N}_2\text{O}_5)}$  exclusively corresponds to N<sub>2</sub>O<sub>5</sub> for this experiment after correction of the *MS* signal at m/e 46 for the contribution of HNO<sub>3</sub> desorbing from the mineral dust substrate.

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In the Knudsen flow reactor, reactant gas molecules either exit through an aperture into the mass spectrometer or are lost on the reactive surface. The net observed uptake coefficient for  $\text{N}_2\text{O}_5$ ,  $\gamma_{\text{obs}}$ , is given by the following expression:

$$\gamma_{\text{obs}} = \frac{k_{\text{obs}}}{\omega} \quad (\text{E.3})$$

- Equation (E.3) is only valid if the rate law for uptake is first order in  $\text{N}_2\text{O}_5$ , where  $k_{\text{obs}}$  is the pseudo-first order rate constant at steady state conditions given in Eq. (E.1),  $\omega$  is the collision frequency of the average molecule with the reactive surface area of the sample defined as  $\omega = \frac{\bar{c}}{4V_{\text{cell}}} A_s$ ,  $\bar{c}$  is the mean velocity of the gas-phase molecule,  $V_{\text{cell}}$  is the volume of the reactor and  $A_s$  is the surface sample area. In our data analysis,  $\gamma_{\text{obs}}$  was calculated using the geometric surface area of the sample holder as will be justified below. In the following, we evaluate  $\gamma_{\text{obs}}$  at the initial and steady state values of the uptake rate leading to  $\gamma_0$  and  $\gamma_{ss}$ , respectively.

#### 4. Uptake of $\text{N}_2\text{O}_5$ on $\text{CaCO}_3$ : results and discussion

- Typical raw data from an uptake experiment of  $\text{N}_2\text{O}_5$  on 510 mg of  $\text{CaCO}_3$  are shown in Fig. 1 using the 14 mm diameter-orifice. After a steady state flow of  $\text{N}_2\text{O}_5$  has been established, the isolation plunger is lifted at  $t=92$  s and the substrate is thus exposed to the  $\text{N}_2\text{O}_5$  flow. *MS* signals of 18 ( $\text{H}_2\text{O}^+$ ), 30 ( $\text{NO}^+$ ), 44 ( $\text{CO}_2^+$ ), 46 ( $\text{NO}_2^+$ ), and 63 ( $\text{HNO}_3^+$ ) were simultaneously monitored during the uptake. Because of the uptake of  $\text{N}_2\text{O}_5$  on  $\text{CaCO}_3$ , the number of molecules exiting through the escape orifice into the *MS* immediately decreases which leads to a decrease of the *MS* signal  $I_r^{46(\text{N}_2\text{O}_5)}$  at m/e 46. During the exposure of the sample to  $\text{N}_2\text{O}_5$  both  $\text{HNO}_3$  and  $\text{CO}_2$  monitored at m/e 63 and 44, respectively, have been observed in the gas phase. As the exposure time increases, the *MS* signal at m/e 46 partially recovers, indicating a decrease in the rate of uptake that ultimately leads to steady state towards the end of the displayed uptake experiment. At  $t=1150$  s the sample compartment is sealed by lowering the plunger

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and the  $MS$  signal at  $m/e$  46 approximately returns to its initial steady-state value. The slight decrease of  $I_0^{46(N_2O_5)}$  over extended periods of time such as displayed in Fig. 1 can be explained by a slight decrease of the corresponding flow rate into the reactor.

An ancillary experiment was performed in order to estimate the amount of water adsorbed on the  $CaCO_3$  substrate surface after a given pumping time. In order to limit  $H_2O$  desorbing from the Pyrex sample holder it was replaced by a gold-coated all-metal sample holder. In this way most desorbing  $H_2O$  may be attributed to the mineral dust sample. Typically, a fresh sample of 1 g of  $CaCO_3$  was pumped for 30 min at  $T=298\pm 2$  K in the 14 mm-orifice reactor until the  $MS$  signal of  $H_2O$  at  $m/e$  18 dropped to the background level. Subsequently, the  $CaCO_3$  sample was heated up to 470 K and the  $MS$  signal at  $m/e$  18 recorded until it reached background as well indicating that no additional water desorbed at that temperature. The  $MS$  signal at  $m/e$  18 was integrated in order to calculate the number of adsorbed water molecules  $H_2O_{(ads)}$  using the measured BET surface area of  $3.7\text{ m}^2\text{ g}^{-1}$  for precipitated  $CaCO_3$ . A value of approximately  $3.0\times 10^{13}$  molecule  $\text{cm}^{-2}$  has been found for the surface density of strongly adsorbed  $H_2O_{(ads)}$  (Santschi, 2003).

When the  $CaCO_3$  substrate is exposed to  $N_2O_5$  at 92 s, we observed rapid formation of  $CO_{2(g)}$  and  $H_2O_{(g)}$  as displayed in Fig. 1 which were either generated in a chemical reaction or desorbing from a precursor state. In order to better understand the uptake of  $N_2O_5$  on solid  $CaCO_3$  powder, we will briefly digress to the description of the chemical nature of a carbonate surface. From experimental and theoretical surface science studies, (De Leeuw and Parker, 1998; Kuriyavar et al., 2000; Stipp et al., 1994) there is clear evidence that under ambient conditions of pressure, temperature, and relative humidity, the surface of  $CaCO_3$  is terminated by OH groups that persist even under ultrahigh vacuum conditions. The OH-terminated surface may be a result of the dissociative adsorption of water according to Reaction (3):



In a recent study (Al-Hosney and Grassian, 2004), the surface chemistry of  $CaCO_3$  with

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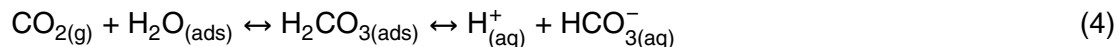
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trace atmospheric gases such as  $\text{HNO}_3$ ,  $\text{SO}_2$ ,  $\text{HCOOH}$ , and  $\text{CH}_3\text{COOH}$  was investigated using FTIR absorption spectrometry. This study has pinpointed adsorbed carbonic acid  $\text{H}_2\text{CO}_3$  to be involved in the surface chemistry of  $\text{CaCO}_3$  and was identified as a stable intermediate species on the  $\text{CaCO}_3$  surface in the presence of  $\text{H}_2\text{O}$  vapor.

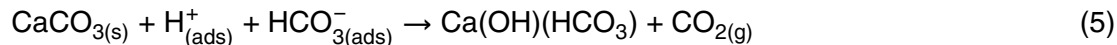
5 The vibrational spectrum of carbonic acid is well characterized by its  $\text{C}=\text{O}$  stretching frequency at 1685 and  $1705\text{ cm}^{-1}$  corresponding to the adsorbed and condensed phase, respectively. In the following, adsorbed  $\text{H}_2\text{CO}_3$  will occur as an intermediate in several instances.

10 Dissolution of  $\text{CaCO}_3$  in the system  $\text{H}_2\text{O}-\text{CO}_2-\text{CaCO}_3$  is controlled by three rate-determining processes: the kinetics of dissolution at the mineral surface, mass transport by diffusion, and the slow kinetics of Reaction (4):

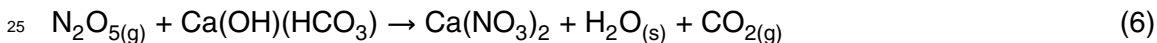


15 A theoretical model by Buhmann and Dreybrodt (1985) taking these processes into account predicts that, due to the slow kinetics of Reaction (4), precipitation rates on the surface of  $\text{CaCO}_3$  minerals critically depend on the ratio  $V/A$  of the volume  $V$  of the solution to the surface area  $A$  of the mineral in contact with it. They concluded that Reaction (4) is rate limiting (Dreybrodt et al., 1997).

20 Bicarbonate ion,  $\text{HCO}_3^-$ , may react with  $\text{CaCO}_3$  to yield a surface intermediate that is proposed to be the active surface reactant for the heterogeneous reactions discussed below according to the well-known “Karst dissolution” mechanism (Dreybrodt et al., 1996):



When the  $\text{CaCO}_3$  sample is exposed to  $\text{N}_2\text{O}_5$  the surface intermediate may react as follows:



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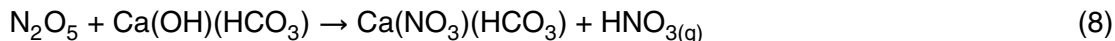
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and the net reaction resulting from Reactions (4), (5) and (6) will be:



It is evident that  $\text{H}_2\text{O}_{(\text{g})}$  and  $\text{CO}_2$  resulting from Reaction (6) could be used again to generate additional  $\text{Ca}(\text{OH})(\text{HCO}_3)$  according to Reactions (4) and (5) provided Reaction (5) is fast enough under flow reaction conditions. In this way  $\text{H}_2\text{O}$  is neither consumed nor generated and may therefore be viewed as a catalytic species.

On the time scale of the uptake experiments reported in Fig. 1 the calculated ratio  $\text{CO}_2/\text{N}_2\text{O}_5$  of the product yields was 0.42 which is significantly smaller than 1.0 that is stoichiometrically expected according to Reaction (7) (see Table 2). The mass balance between the adsorbed  $\text{N}_2\text{O}_5$  and the reaction product  $\text{CO}_2$  is therefore not satisfied. If Reactions (4) and (5) were fast and not rate limiting, the  $\text{CO}_2$  yield could be 100%. We therefore have to consider another possible pathway for Reaction (6) that does not result in release of  $\text{CO}_2$ :



In this case  $\text{N}_2\text{O}_5$  may directly be converted into gas phase  $\text{HNO}_3$  which is also observed at longer exposure times as displayed in Fig. 1. Reaction (8) may also help explain why the ratio  $\text{CO}_2/\text{N}_2\text{O}_5$  differs from 1.0 as no  $\text{CO}_2$  is released from Reaction (8). In addition,  $\text{HNO}_3$  may also react with  $\text{CaCO}_3$  as already observed by Hanisch and Crowley (2001). We routinely measure a yield of 51% of gas phase  $\text{H}_2\text{O}$  with respect to  $\text{N}_2\text{O}_5$  consumed which is comparable to the  $\text{CO}_2$  yield according to Eq. (6) and results from the uptake of  $\text{N}_2\text{O}_5$  on samples of different mass of powdered  $\text{CaCO}_3$ . In the wake of the observation of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{HNO}_3$  we propose that Reactions (7) and (8) compete with each other.  $\text{H}_2\text{O}$  is formed in Reaction (6) on  $\text{CaCO}_3$  that is in part pre-existing as a surface intermediate  $\text{Ca}(\text{OH})(\text{HCO}_3)$  from prior exposure to atmospheric  $\text{CO}_2$  and  $\text{H}_2\text{O}$  following Reactions (4) and (5).

Owing to the fact that  $\text{CaCO}_3$  has a specific surface area (BET) of  $5.06 \text{ m}^2/\text{g}$ , the 510 mg sample from the experiment displayed in Fig. 1 has a total surface area of

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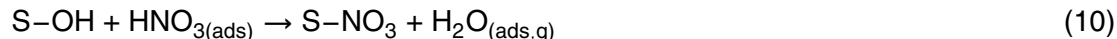
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$2.6 \times 10^4 \text{ cm}^2$ .  $\text{N}_2\text{O}_5$  may be represented as a sphere with a projected surface area of  $6.4 \times 10^{-15} \text{ cm}^2/\text{molecule}$  or  $1.56 \times 10^{14} \text{ molecules cm}^{-2}$ , assuming that  $\text{N}_2\text{O}_5$  has a characteristic diameter of approximately 9 Å and a density of  $2.93 \text{ g/cm}^3$ . After an exposure time of 1060 s  $2.2 \times 10^{18}$  molecules of  $\text{N}_2\text{O}_5$  are taken up on 510 mg of  $\text{CaCO}_3$  (Fig. 1) leading to a surface concentration of  $\frac{2.2 \times 10^{18}}{2.6 \times 10^4} = 8.4 \times 10^{13} \text{ N}_2\text{O}_5 \text{ molecule cm}^{-2}$  which corresponds to a coverage ( $\theta$ ) of approximately 54% based on the BET surface area after a reaction time of 1060 s. This assumes that at steady-state the total internal area of the powder sample is accessible to  $\text{N}_2\text{O}_5$  in contrast to the initial uptake where only the surface layer is interacting with the gas. After  $\text{N}_2\text{O}_5$  reacted on  $\text{CaCO}_3$  powder for 1060 s the substrate is apparently at steady state as displayed in Fig. 1. This means that there is a sufficient number of intermediate species  $\text{Ca}(\text{OH})(\text{HCO}_3)$  to allow Reactions (6) and (8) to occur. However, once reacted with  $\text{N}_2\text{O}_5$ , the intermediate species cannot regenerate because Reactions (4) and (5) are too slow. Therefore, we observe an amount of  $\text{CO}_{2(\text{g})}$  smaller than the maximum yield of 100% at steady state conditions. On the other hand,  $\text{N}_2\text{O}_5$  may react with adsorbed water  $\text{H}_2\text{O}_{(\text{ads})}$  that still remains on the  $\text{CaCO}_3$  substrate, thereby forming two molecules of nitric acid as follows:



In this case solid  $\text{CaCO}_3$  is just the support for the reactive adsorbed water  $\text{H}_2\text{O}_{(\text{ads})}$  and is not consumed in the chemical reaction. Initially,  $\text{HNO}_{3(\text{g})}$  is physically adsorbed on the surface to result in adsorbed  $\text{HNO}_3$  which reacts with a surface OH-group and slowly forms surface nitrates and  $\text{H}_2\text{O}$  according to Reaction (10):



where S represents a surface site for physical adsorption. This mechanism has been proposed by Seisel et al. (2004) in a DRIFTS study of the heterogeneous reaction of  $\text{HNO}_3$  on mineral dust where they observed the presence of free OH-groups located on the surface of mineral dust and the formation of surface nitrates.

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The fact that CO<sub>2</sub> is formed immediately after lifting the plunger (Fig. 1) whereas HNO<sub>3</sub> is formed later on after a certain delay clearly indicates that there are two competitive processes occurring during the reaction of N<sub>2</sub>O<sub>5</sub> with CaCO<sub>3</sub>. Immediately after the exposure of substrate, N<sub>2</sub>O<sub>5</sub> reacts with the intermediate species Ca(OH)(HCO<sub>3</sub>) on the CaCO<sub>3</sub> sample (Reactions (6) and (8)). At the same time heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub> may occur due to the presence of H<sub>2</sub>O<sub>(ads)</sub> on the substrate (Reaction (9)). However, the presence of a sufficient quantity of the intermediate formed in Reaction (5) may make Reactions (7) and (8) predominant at first with respect to Reaction (9). This explains the initial rapid formation of CO<sub>2(g)</sub> and the absence of any measurable trace of gas phase HNO<sub>3</sub> at  $t=92$  s in Fig. 1. Once the surface intermediate starts to be consumed owing to the initial fast reaction with N<sub>2</sub>O<sub>5</sub> the sample starts saturating and Reaction (9) becomes predominant compared to Reactions (7) and (8) which would explain the delayed formation of HNO<sub>3</sub> displayed in Fig. 1.

After having performed the uptake experiment shown in Fig. 1 on a substrate of CaCO<sub>3</sub>, we sealed the sample and halted the inlet flow of N<sub>2</sub>O<sub>5</sub> for approximately 10 min. Subsequently, we lifted the plunger again and observed small amounts of desorbing CO<sub>2</sub> (curve (a), Fig. 2) as well as a *MS* signal at *m/e* 30 without any measurable *MS* signal at *m/e* 46 (curve (b), Fig. 2). The total yield of desorbed CO<sub>2</sub> only represented 5% of N<sub>2</sub>O<sub>5</sub> taken up on the substrate of CaCO<sub>3</sub> during the reaction time of 1058 s (Fig. 1). The small intensity of the *MS* signal at *m/e* 30 strongly suggests formation of NO as a decomposition product of N<sub>2</sub>O<sub>5</sub>.

Uptake experiments of N<sub>2</sub>O<sub>5</sub> on 0.58 g of CaCO<sub>3</sub> powder were carried out at smaller orifice sizes, thus increased residence time  $\tau_g$  at constant flow of N<sub>2</sub>O<sub>5</sub> of  $2.3 \times 10^{15}$  molecule s<sup>-1</sup>. The values of  $\gamma_0$  and  $\gamma_{ss}$  decrease with increasing values of the residence time as displayed in Fig. 3 and Table 3. The strong dependence of  $\gamma_{ss}$  on  $\tau_g$  suggests that the mechanism of N<sub>2</sub>O<sub>5</sub> uptake is complex and does not correspond to a simple first order uptake reaction. These observations indicate that the reactivity of N<sub>2</sub>O<sub>5</sub> on CaCO<sub>3</sub> decreases for long residence times as the heterogeneous reaction rate not only depends on the gas phase concentration but apparently also on interme-

diates whose surface concentration depend on the extent of reaction that scales with  $\tau_g$  akin to an effective second order reaction. Apparently, the active surface intermediate  $\text{Ca}(\text{OH})(\text{HCO}_3)$  cannot regenerate sufficiently fast according to Reaction (5) so as to maintain the rate limiting Reaction (6) at higher partial pressure, that is at longer residence time  $\tau_g$ .

In order to unravel whether or not the effective available surface area for uptake is influenced by the internal surface area formed by interstitial voids between individual dust particles, the mass dependence of the  $\text{N}_2\text{O}_5$  uptake on  $\text{CaCO}_3$  was investigated in the Knudsen flow reactor at ambient temperature and at  $[\text{N}_2\text{O}_5] = (4.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$ . The mass of  $\text{CaCO}_3$  which is a non-porous material ranged from 0.11 g to 1.8 g and the results are shown in Fig. 4. Table 4 reports values of  $\gamma_{ss}$  and  $\gamma_0$  using the geometric surface area  $A_s = 19.6 \text{ cm}^2$ . The steady state and initial uptake coefficient  $\gamma_{ss}$  and  $\gamma_0$ , respectively, of  $\text{N}_2\text{O}_5$  were found to increase linearly at low masses of  $\text{CaCO}_3$ . Samples below 0.33 g were considered to be part of this linear mass-dependent regime. Increasing the sample mass further had a negligible effect on the amount of adsorbed  $\text{N}_2\text{O}_5$  because not the entire sample surface is apparently available for  $\text{N}_2\text{O}_5$  adsorption. This maximum value is attributed to the inability of  $\text{N}_2\text{O}_5$  to penetrate through all layers of the sample within the residence time of  $\text{N}_2\text{O}_5$  in the gas phase, thus resulting in a constant number of molecules taken up despite the increasing sample mass. The limiting  $\gamma_{ss}$  value therefore represents the maximum amount of  $\text{N}_2\text{O}_5$  able to interact with  $\text{CaCO}_3$  powder within the  $\text{N}_2\text{O}_5$  residence time.

In order to better define the saturation behaviour of  $\text{N}_2\text{O}_5$  on the substrate further uptake experiments were performed on  $\text{CaCO}_3$  employing a pulsed valve to admit  $\text{N}_2\text{O}_5$  into the reactor. The pulsed-valve experiments were carried out by using a solenoid valve, through which the gas was introduced in pulses with a duration of 5 *MS* and at a dose of  $2.5 \times 10^{15}$  molecules per pulse (Caloz et al., 1997) corresponding to  $[\text{N}_2\text{O}_5]_0 = 1.3 \times 10^{12} \text{ cm}^{-3}$ . We determined the total number of injected molecules per pulse and the value of  $k_{\text{esc}}$  in a reference experiment which was obtained by fitting the decaying *MS* signal to an exponential decay in the absence of reaction thereby

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obtaining  $k_{\text{esc}}$ . The “reactive pulse” was obtained by repeating the same pulsed experiment with the sample exposed to the gas. The total observed exponential decay in the presence of a reactive substrate was thus characterized by a new rate constant,  $k_{\text{dec}}$ , given by  $k_{\text{dec}} = k_{\text{obs}} + k_{\text{esc}}$  that is used to determine the number of interest given by  $\gamma_{\text{obs}} = k_{\text{obs}} / \omega$ . The pulsed valve uptake experiments on  $\text{CaCO}_3$  showed that there is a modest mass-dependence of the measured uptake  $\gamma_{\text{obs}}$  by approximately a factor of three to four. For a dose of about  $2.5 \times 10^{15}$  molecules per pulse we observed an unexpected increase of the uptake  $\gamma_{\text{obs}}$  with increasing mass of  $\text{CaCO}_3$  as reported for steady state experiments in Table 4 displayed in Fig. 4. The increase of  $\gamma_{\text{obs}}$  saturates at large sample mass because the number of layers exceeds the depth of diffusion of gas into the internal voids. For all series of pulses the measurements are identical, within the uncertainty, to those for steady state experiments.

Similar behavior has been observed in a recent study carried out by Seisel et al. (2005). In that study uptake experiments of  $\text{N}_2\text{O}_5$  on Saharan Dust obtained from pulsed and steady state experiments were in good agreement, indicating that the steady state uptake coefficients are not influenced by saturation effects under their experimental conditions.

In order to determine the number of layers, the total volume of the powder was calculated from its true density ( $\rho_t = 2.93 \text{ g/cm}^3$ ) and the mass of the sample spread out across the geometric area of the sample holder. The number of formal layers calculated for an average sample grain diameter of  $3.5 \mu\text{m}$  from the average particle size and the height of the sample is reported in Table 4. The typical grain diameter of  $3.5 \mu\text{m}$  has been obtained from the manufacturer’s specifications of the used  $\text{CaCO}_3$  powder.

Based on published microscopic images, it is reasonable to take into account a grain size diameter that is larger than  $3.5 \mu\text{m}$  as suggested by electron microscopy (SEM) displayed in Fig. 5. Figure 4 shows that a mass of 0.33 g corresponds to one nominal layer of  $57 \mu\text{m}$  diameter  $\text{CaCO}_3$  spread out over the geometric surface of the sample holder ( $19.6 \text{ cm}^2$ ). Thus, one nominal layer of  $\text{CaCO}_3$  will contain 330 mg of closely

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packed spheres of “effective” grain diameter of  $57\text{ }\mu\text{m}$  knowing full well that the sample in reality is multidisperse and structurally heterogeneous. Therefore, the linear mass-dependent portion of  $\gamma_{ss}$  vs. mass for masses less than 330 mg corresponds to a sample holder that is partially covered with  $57\text{ }\mu\text{m}$  diameter  $\text{CaCO}_3$  particles.

5 The use of the BET surface area and the application of the pore diffusion theory (Keyser et al., 1991) yields  $\gamma_{pd,ss}=(7.4\pm1.7)\times10^{-6}$  for steady state experiments using a grain diameter for  $\text{CaCO}_3$  of  $3.5\text{ }\mu\text{m}$ . This value is lower by a factor of  $10^3$  compared to  $\gamma_{ss}=(2.8\pm0.5)\times10^{-2}$  and  $\gamma_0=0.16\pm0.02$  which were calculated on the basis of the geometrical surface area of the sample as displayed in Table 4. The use of the pore  
10 diffusion theory substantially underestimates the true uptake coefficient so that it may be interpreted as a lower limit for  $\gamma$  whereas  $\gamma_{ss}$  and  $\gamma_0$  based on the geometrical surface area may be regarded as an upper limit, albeit close to the true value of  $\gamma$ . We take the fact that  $\gamma_0$  and  $\gamma_{obs}$  obtained from pulsed valve experiments are identical within experimental uncertainty (Fig. 4) as evidence that  $\text{N}_2\text{O}_5$  only interacts with the  
15 surface layer of the solid sample during a typical pulse decay of 300 ms. We do not rule out that  $\text{N}_2\text{O}_5$  will interact with deeper layers of the sample to some extent under steady state conditions. However, it is unlikely that the true value of  $\gamma$  will drop by more than three orders of magnitude during a steady state uptake experiment typically lasting tens of minutes. We will therefore not further discuss  $\gamma_{pd,ss}$  also in view of the  
20 analysis of field data discussed below that are consistent with  $\gamma_{obs}$  and  $\gamma_0$  values based on the geometric surface area.

## 5. Uptake of $\text{N}_2\text{O}_5$ on mineral dust substrates: results and discussion

Table 5 reports results on experiments performed on 1 g samples of surrogate mineral dust powder at a high initial concentration of  $[\text{N}_2\text{O}_5]_0=(3.8\pm1.0)\times10^{12}\text{ cm}^{-3}$ . The  
25 steady-state uptake coefficients  $\gamma_{ss}$  of  $\text{N}_2\text{O}_5$  range from  $(2.2\pm0.6)\times10^{-3}$  for natural limestone to  $(5.9\pm1.6)\times10^{-2}$  for Saharan Dust using the geometric surface area. At

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a lower initial concentration of  $[\text{N}_2\text{O}_5]_0 = (4.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$  uptake experiments performed on 0.3 g have revealed larger values of  $\gamma_{ss}$  ranging from  $(3.5 \pm 1.1) \times 10^{-2}$  for  $\text{CaCO}_3$  to  $0.2 \pm 0.05$  for Saharan Dust. We also report the observed initial uptake coefficients  $\gamma_0$  for  $\text{N}_2\text{O}_5$  on all the samples of mineral dust at low and high values of  $[\text{N}_2\text{O}_5]$ . For a concentration of  $[\text{N}_2\text{O}_5]_0 = (3.8 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$  the  $\gamma_0$  values range from  $(6.4 \pm 1.9) \times 10^{-3}$  for Arizona test dust to  $(9.0 \pm 2.6) \times 10^{-2}$  for Saharan Dust, whereas at  $[\text{N}_2\text{O}_5]_0 = (4.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$  the  $\gamma_0$  values range from  $0.12 \pm 0.04$  for  $\text{CaCO}_3$  to  $0.43 \pm 0.13$  for natural limestone. For samples such as Saharan Dust,  $\text{CaCO}_3$  and Arizona Test Dust values of  $\gamma_{ss}$  and  $\gamma_0$  decrease between a factor of 3 and 7 from low to high  $[\text{N}_2\text{O}_5]_0$ . As indicated in Table 5, both the values  $\gamma_{ss}$  and  $\gamma_0$  for  $\text{CaCO}_3$  decrease only by a factor 3.5 from low to high  $[\text{N}_2\text{O}_5]$ . On the other hand a particular case is represented by natural limestone which showed a decrease of  $\gamma_{ss}$  and  $\gamma_0$  by a factor of 20 and 40, respectively, when increasing  $[\text{N}_2\text{O}_5]_0$ .  $\text{CaCO}_3$  showed values of  $\gamma_{ss}$  and  $\gamma_0$  higher by a factor of 3 with respect to natural limestone at high  $[\text{N}_2\text{O}_5]_0$ . This difference is reversed by the same amount for low  $[\text{N}_2\text{O}_5]_0$  with  $\gamma$  of natural limestone being highly sensitive to saturation by  $[\text{N}_2\text{O}_5]$ . Natural limestone is a sedimentary rock containing 97%  $\text{CaCO}_3$  by weight and a small percentage of metal oxides (1.9% of  $\text{SiO}_2$ , 0.5% of  $\text{Al}_2\text{O}_3$ , 0.3% of  $\text{Fe}_2\text{O}_3$ , and 0.3% of  $\text{MgO}$ ) that may be responsible for the difference in the kinetic properties of  $\text{CaCO}_3$  and natural limestone. In recent work Krueger et al. (2005) showed that dust containing calcium is very reactive with respect to the uptake of nitric acid. However, because of differences in mineralogy of single dust-particles, not all of the calcium-containing particles react similarly.

It is important to note that for Kaolinite  $\gamma_{ss}$  and  $\gamma_0$  are independent of  $[\text{N}_2\text{O}_5]_0$  over the investigated range. Typical raw data from an uptake experiment of  $\text{N}_2\text{O}_5$  on 1 g of Kaolinite and Saharan Dust are shown in Figs. 6 and 7. In this series of experiments we did not succeed to saturate the samples during the present observation period. Uptake experiments of  $\text{N}_2\text{O}_5$  on 0.2 g of Kaolinite powder were carried out by varying the initial flow of  $\text{N}_2\text{O}_5$  into the reactor (Table 6). Figure 8 displays data for the 8 mm orifice corresponding to a residence time  $\tau_g$  of 1.32 s for a variation of  $[\text{N}_2\text{O}_5]_0$  by a factor

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9.5 that is between  $(4.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$  and  $(3.8 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$ . Figure 8 shows that both  $\gamma_0$  and  $\gamma_{ss}$  remain constant at  $0.19 \pm 0.05$  and  $(2.3 \pm 0.6) \times 10^{-2}$ , respectively, with increasing  $[\text{N}_2\text{O}_5]$  and by changing the gas residence time  $\tau_g$ . From this series of measurements it is evident that  $\gamma_{ss}$  follows a pseudo first order rate law in  $\text{N}_2\text{O}_5$  in contrast to the other substrates which showed a decreasing trend from low to high  $[\text{N}_2\text{O}_5]$  (see Fig. 3 and Table 5).

In recent work the uptake of  $\text{N}_2\text{O}_5$  on Saharan Dust was found to be independent of  $[\text{N}_2\text{O}_5]$  (Seisel et al., 2005). An initial uptake  $\gamma_0 = (8.0 \pm 0.3) \times 10^{-2}$  was found, whereas the steady state value  $\gamma_{ss} = (1.3 \pm 0.3) \times 10^{-2}$  was lower by a factor of five with respect to the present results at  $[\text{N}_2\text{O}_5]_0 = (3.8 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$ .

We have observed delayed production of  $\text{HNO}_3$  upon uptake of  $\text{N}_2\text{O}_5$  for every sample investigated. Gas phase  $\text{HNO}_3$  formation may be due to the heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$  according to Reaction (9). In order to understand the gas phase production of  $\text{HNO}_3$  we want to stress that all the investigated samples have a non negligible amount of adsorbed water available on the substrate surface. The quantities of  $\text{H}_2\text{O}_{(\text{ads})}$  that still remain on the different mineral dust substrates at our experimental conditions as reported in Table 5 and were measured by gravimetric measurements. The hygroscopic properties of mineral aerosol samples have been examined in recent work (Gustafsson et al., 2005) which showed significant water adsorption on Arizona Test Dust compared to  $\text{CaCO}_3$ . In Table 5 we also report the percentage of gas phase  $\text{HNO}_3$  produced with respect to  $\text{N}_2\text{O}_5$  taken up during a reaction time of 200 s. At  $[\text{N}_2\text{O}_5] = (3.8 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$ , Arizona Test Dust and Kaolinite turned out to be the samples to produce the largest amount of gas phase  $\text{HNO}_3$ , that is 72% and 30%, respectively, with respect to  $\text{N}_2\text{O}_5$  taken up. On the other hand, Saharan Dust and  $\text{CaCO}_3$  have been the samples with a lower yield of absolute  $\text{HNO}_3$  produced, namely 5% and 6%, respectively. At  $[\text{N}_2\text{O}_5] = (4.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$  we obtained lower yields of gas phase  $\text{HNO}_3$  compared to  $[\text{N}_2\text{O}_5]$  ten times higher. In this case we may correlate the low yield of  $\text{HNO}_3$  to the large rate of uptake of  $\text{N}_2\text{O}_5$  and of  $\text{HNO}_3$  on mineral dust.

Adsorbed  $\text{HNO}_3$  may then form salts such as  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$  and surface nitrates as shown in other experimental studies (Börensén et al., 2000; Goodman et al., 2001; Vogt and Finlayson-Pitts, 1994). A recent study on the reactivity of gaseous  $\text{HNO}_3$  on atmospheric mineral dust samples reported values for the uptake of  $\text{HNO}_3$  on  $\text{CaCO}_3$ , Saharan Dust and Arizona Test Dust (Hanisch and Crowley, 2001a). In that work, a value of  $\gamma_0=0.11$  was determined for Saharan Dust at  $[\text{HNO}_3]=(5.6\pm0.4)\times10^{11}\text{ cm}^{-3}$ , 0.14 for  $\text{CaCO}_3$  and  $6.6\times10^{-2}$  for Arizona Test Dust. These results are consistent with the trend of the present yields of  $\text{HNO}_3$  measured for nominally the same mineral dust samples. Whenever the uptake coefficient of  $\text{HNO}_3$  on the mineral substrates was low such as for Arizona Test Dust and Kaolinite, we find increased amounts of  $\text{HNO}_3$  in the gas phase. Conversely, the reverse is true for samples that rapidly take up  $\text{HNO}_3$  as for  $\text{CaCO}_3$  and Saharan Dust (Börensén et al., 2000).

## 6. Conclusions and atmospheric implications

We have shown in this work that  $\text{N}_2\text{O}_5$  undergoes a heterogeneous reaction with surrogate substrates of mineral dust aerosol at  $T=298\pm2\text{ K}$ . The measured uptake coefficient showed different values for high and low  $\text{N}_2\text{O}_5$  concentrations with the least differences for Saharan Dust. These  $\gamma$  values are generally larger than the ones used in a recent global modeling simulation of heterogeneous chemistry on mineral dust aerosol at dry conditions (Bauer et al., 2004) where  $\gamma=3.0\times10^{-3}$  for  $\text{N}_2\text{O}_5$  has been used. The  $\gamma$  values resulting from the present measurements are larger by at least a factor of 10. Therefore, the uptake of  $\text{N}_2\text{O}_5$  on mineral dust aerosols may potentially have a greater influence on the reduction of the global ozone concentration compared to the estimated value of 0.7% (Bauer et al., 2004).

The measured uptake coefficient  $\gamma$  of  $\text{N}_2\text{O}_5$  on sulfuric acid aerosols was reported to lie within the range 0.06–0.12 at a temperature between 230 and 300 K (Hanson and Lovejoy, 1994). Other measurements reported  $\gamma$  values of 0.05 on aqueous surfaces over a temperature range from 282 to 294 K (van Doren et al., 1990). To our knowledge

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no reaction probabilities of  $\text{N}_2\text{O}_5$  on mineral aerosol have been determined to date. In a recent numerical modeling study the interaction of  $\text{N}_2\text{O}_5$  ( $\gamma=0.1$ ),  $\text{O}_3$  and  $\text{HO}_2$  radicals with dust resulted in a decrease of tropospheric ozone of up to 10% near the dust source areas (Dentener et al., 1996).

5 The photolytic rate of  $\text{NO}_3$  ( $J(\text{NO}_3)=0.2\text{ s}^{-1}$ ) is too fast to allow its recombination with  $\text{NO}_2$  to  $\text{N}_2\text{O}_5$  during daylight. Therefore, the heterogeneous chemistry of  $\text{N}_2\text{O}_5$  is important only at night-time. The heterogeneous reaction of  $\text{N}_2\text{O}_5$  is most effective during the night when  $RH$  is at a maximum in the boundary layer. Thus, under these conditions, dust particles are likely to contain significant quantities of adsorbed water and the assumed high values of  $\gamma$  seem justified (Dentener and Crutzen, 1993). In a recent global modeling study  $\gamma=0.02$  ( $RH=70\%$ ) and  $\gamma=3.0\times 10^{-3}$  ( $RH=30\%$ ) for humid and dry conditions have been used as upper and lower limits, respectively (Bauer et al., 2004). The modeling results show that when applying the high value for the uptake coefficient 0.8% of the global ozone mass is removed by uptake of  $\text{N}_2\text{O}_5$  on aerosols. The observed reaction products of the heterogeneous reaction of  $\text{N}_2\text{O}_5$  with mineral dust, mainly  $\text{HNO}_3$ , may also have an influence on the oxidizing potential of the atmosphere as well as on the atmospheric ozone balance. Previous laboratory work (Goodman et al., 2000; Hanisch and Crowley, 2001a; Seisel et al., 2004) has shown the importance of the reactivity of  $\text{HNO}_3$  on mineral dust substrates. In addition, modeling studies have quantitatively shown decreases in ozone concentration close to the area of  $\text{HNO}_3$  destruction (Bauer et al., 2004).

25 The Saharan dust sample, from Cape Verde (SDCV), that we have used is mineralogically representative of atmospheric dust aerosol. Its composition has been described in the literature (Coudé-gaussen et al., 1994) and closely simulates atmospheric particles of crustal origin (Desboeufs et al., 1999). The clay fraction ( $<2\text{ }\mu\text{m}$ ) of dust from Cape Verde shows a kaolinite-illite-chlorite assemblage which is typical for central Saharan Dust. In the free troposphere mineral dust aerosol of a size less than  $2\text{ }\mu\text{m}$  have a settling velocity of approximately  $50\text{ cm h}^{-1}$  (Seinfeld and Pandis, 1998). Therefore it can remain in the atmosphere for several days, travel long distances and

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undergo heterogeneous reactions with trace gases.

The loss rate constant ( $k_{\text{het}}^M$ ) due to heterogeneous uptake of a gas species  $M$  onto small aerosol particles is given by  $k_{\text{het}}^M = \frac{\gamma A \bar{c}}{4}$  if the rate is not limited by diffusion, where  $\gamma$  is the uptake coefficient of  $M$  and is a function of the mineral dust aerosol composition,  $A$  is the surface area density of the dust aerosol and  $\bar{c}$  is the mean molecular speed of  $M$ . Assuming a surface area density for Saharan Dust of about  $1.5 \times 10^{-6} \text{ cm}^2 \text{ cm}^{-3}$  (de Reus et al., 2000), we estimate  $k_{\text{het}}^{\text{N}_2\text{O}_5} = 1.76 \times 10^{-3} \text{ s}^{-1}$  ( $\tau_{\text{het}}^{\text{N}_2\text{O}_5} = 9.5 \text{ min}$ ) for  $\text{N}_2\text{O}_5$  based on  $\gamma = 0.2$  for Saharan dust at  $[\text{N}_2\text{O}_5] < (4.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$  (16 ppb). From the difference between the  $\text{N}_2\text{O}_5$  formation and loss in the presence of the equilibrium with  $\text{NO}_3$  we obtain the expression for the  $\text{N}_2\text{O}_5$  steady state lifetime given in Eq. (11) (Brown et al., 2003):

$$\tau_{ss}^{\text{N}_2\text{O}_5} = \left( k_{\text{het}}^{\text{N}_2\text{O}_5} + \frac{k_{\text{het}}^{\text{NO}_3} k_1(T)}{k_{-1} [\text{NO}_2]} \right)^{-1} \quad (11)$$

$k_1(T)$  and  $k_{-1}$  are the rate constant for thermal decomposition of  $\text{N}_2\text{O}_5$  and its inverse at atmospheric pressure according to equilibrium (11), respectively. From recent work on the  $\text{NO}_3$  heterogeneous reaction on mineral dust we have obtained  $\gamma = 0.2$  which leads to  $k_{\text{het}}^{\text{NO}_3} = 2.4 \times 10^{-3} \text{ s}^{-1}$  ( $\tau_{\text{het}}^{\text{NO}_3} = 7 \text{ min}$ ) for  $\text{NO}_3$  (Karagulian and Rossi, 2005).

At  $T = 273 \text{ K}$   $k_1(273 \text{ K}) = 3.1 \times 10^{-3} \text{ s}^{-1}$  ( $\tau = 5 \text{ min}$ ) (Atkinson et al., 1997) and equilibrium (1) is shifted to the left. For  $[\text{NO}_2]$  a typical value is 10 ppb in polluted air so that the pseudo first-order recombination rate constant  $k_{-1} [\text{NO}_2]$  is  $0.48 \text{ s}^{-1}$  and is thus much larger than the rate constant for heterogeneous loss  $k_{\text{het}}^{\text{NO}_3} = 2.4 \times 10^{-3} \text{ s}^{-1}$ . Therefore, the second term of expression (11) will be negligible and the steady state lifetime  $\tau_{ss}^{\text{N}_2\text{O}_5}$  of  $\text{N}_2\text{O}_5$  will be determined by its heterogeneous loss rate constant  $k_{\text{het}}^{\text{N}_2\text{O}_5}$ .

At  $T = 293 \text{ K}$  equilibrium (1) is shifted to the right with  $k_1(293 \text{ K}) = 4.6 \times 10^{-2} \text{ s}^{-1}$  ( $\tau = 20 \text{ s}$ ) which is an order of magnitude larger than at  $T = 273 \text{ K}$ . Therefore, both terms

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in Eq. (11) will be of comparable magnitude which will decrease the steady state lifetime of  $\text{N}_2\text{O}_5$  with respect to 273 K somewhat.

The calculated overall steady state lifetime for  $\text{N}_2\text{O}_5$  at 293 K ( $\tau_{ss}^{\text{N}_2\text{O}_5}=8.5$  min) is significantly larger than the thermal dissociation lifetime ( $\tau=20$  s) of  $\text{N}_2\text{O}_5$ . At the same  
5 surface area concentration for dust aerosol of  $1.5 \times 10^{-6} \text{ cm}^2 \text{ cm}^{-3}$ , the heterogeneous loss rate  $k_{\text{het}}^{\text{hydr}}$  due to hydrolysis (Reaction (2)) is  $2.25 \times 10^{-4} \text{ s}^{-1}$  corresponding to a lifetime of 74 min. This means that some  $\text{N}_2\text{O}_5$  may be irreversibly converted to  $\text{HNO}_3$  during the night by hydrolysis. During January 2004, Wood et al. (2005) performed in situ measurement of  $\text{N}_2\text{O}_5$  in Contra Costa Country, California, and derived a steady  
10 state lifetime for  $\text{N}_2\text{O}_5$  that ranged from 5 to 30 min at  $[\text{N}_2\text{O}_5]=200$  ppt ( $5.0 \times 10^9 \text{ cm}^{-3}$ ) in the temperature range 275–285 K which is comparable to  $\tau_{ss}^{\text{N}_2\text{O}_5}$  calculated above. The measured lifetime for  $\text{N}_2\text{O}_5$  from the field thus supports the heterogeneous loss rates of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  measured in the present work.

15 *Acknowledgements.* We gratefully acknowledge OFES for funding this work in the context of the EU subproject MINATROC which is part of the EU Environment and Climate Program.

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**Table 1.** Characteristic parameters and relevant kinetic expressions.

Definition	Value
Reactor volume, $V$	2000 cm <sup>3</sup>
Reactor surface area, $A_r$	1500 cm <sup>3</sup>
Sample surface area, $A_s$	19.5 cm <sup>2</sup> (TEFLON holder), 4.5 cm <sup>2</sup> (DELRIN holder)
Collision frequency $\omega$ for N <sub>2</sub> O <sub>5</sub> with $A_s$ ( $M=108$ )	$\omega=1.81(T/M)^{1/2}A_s$
Orifice diameters (nominal)	1, 4, 8 and 14 mm
Rate constant of effusion	$k_{\text{esc}} \text{ (s}^{-1}\text{)}$
$k_{\text{esc}}$ (Experimentally determined values	0.02( $T/M$ ) <sup>1/2</sup> s <sup>-1</sup> for 1 mm orifice
for orifice diameters of nominal diameter)	0.25( $T/M$ ) <sup>1/2</sup> s <sup>-1</sup> for 4 mm orifice
	0.8( $T/M$ ) <sup>1/2</sup> s <sup>-1</sup> for 8 mm orifice
	1.9( $T/M$ ) <sup>1/2</sup> s <sup>-1</sup> for 14 mm orifice
Observed rate constant for heterogeneous reaction from steady state experiments,	$k_{\text{obs}}=(S_i/S_f-1)k_{\text{esc}}$
$S_i$ = initial <i>MS</i> -signal; $S_f$ = final <i>MS</i> -signal	
Measured uptake coefficient	$\gamma_{\text{obs}}=k_{\text{obs}}/\omega$

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**Table 2.** Uptake experiments with N<sub>2</sub>O<sub>5</sub> on CaCO<sub>3</sub> as a function of sample mass at [N<sub>2</sub>O<sub>5</sub>]<sub>0</sub>=(4.0±1.0)×10<sup>11</sup> cm<sup>-3</sup>.

CaCO <sub>3</sub> Mass in g	γ <sub>0</sub>	γ <sub>ss</sub>	Yield of HNO <sub>3</sub> <sup>c</sup>	Yield of CO <sub>2</sub> <sup>c</sup>
0.33 <sup>a</sup>	0.16±0.03	(2.0±0.6)×10 <sup>-2</sup>	5.2%	47.8%
0.51 <sup>a,b</sup>	0.2±0.05	(2.2±0.5)×10 <sup>-2</sup>	5.4%	42.4%
0.58 <sup>a</sup>	0.18±0.05	(2.3±0.5)×10 <sup>-2</sup>	—	—
0.73 <sup>a</sup>	0.22±0.04	(2.4±0.4)×10 <sup>-2</sup>	5.4%	50%
2 <sup>a</sup>	0.18±0.025	(1.6±1.6)×10 <sup>-2</sup>	5.4%	50%

<sup>a</sup> Uptake measurements performed with a surface sample area A<sub>s</sub>=19.6 cm<sup>2</sup>.<sup>b</sup> Uptake experiment displayed in Fig. 1.<sup>c</sup> The yield is given as a percentage with respect to the total number of molecules of N<sub>2</sub>O<sub>5</sub> taken up during a reaction time of 550 s.

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**Table 3.** Relationship between  $\gamma_0$  and  $\gamma_{ss}$  at different residence times  $\tau_g$  (s<sup>-1</sup>) of N<sub>2</sub>O<sub>5</sub> interacting with 580 mg of CaCO<sub>3</sub> powder for data plotted in Fig. 2, surface sample area  $A_s=19.6$  cm<sup>2</sup>;  $F_0^{N_2O_5}=2.3\times 10^{15}$  molecule s<sup>-1</sup>.

Orifice (mm)	$\gamma_0$	$\gamma_{ss}$	$\tau_g$ (s)
14	$(1.6\pm 0.13)\times 10^{-1}$	$(6.0\pm 1.2)\times 10^{-2}$	0.34
8	$(8.5\pm 0.8)\times 10^{-2}$	$(3.0\pm 0.7)\times 10^{-2}$	0.81
4	$(3.4\pm 1.0)\times 10^{-2}$	$(1.8\pm 1.1)\times 10^{-2}$	2.72
1	$(1.1\pm 1.0)\times 10^{-2}$	$(1.0\pm 1.0)\times 10^{-2}$	30

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**Table 4.** Summary of uptake experiments with N<sub>2</sub>O<sub>5</sub> on CaCO<sub>3</sub> as a function of sample mass ([N<sub>2</sub>O<sub>5</sub>]=(4.0±1.0)×10<sup>11</sup> cm<sup>-3</sup>, orifice diameter = 14 mm, A<sub>s</sub>=19.6 cm<sup>2</sup>).

Mass (g)	$\gamma_{ss}$	$\gamma_0$	$\gamma_{0(\text{pulsed valve})}$	<sup>a</sup> Number of formal layers	<sup>b</sup> Number of nominal layers
0.11	(8.0±5.0)×10 <sup>-3</sup>	(5.5±2.0)×10 <sup>-2</sup>	(4.7±1.5)×10 <sup>-2</sup>	5	0.3
0.15	(1.5±0.5)×10 <sup>-2</sup>	(6.4±3.0)×10 <sup>-2</sup>		7	0.5
0.33	(2.0±0.6)×10 <sup>-2</sup>	0.16±0.03	0.13±0.018	16	1
0.51	(2.2±0.5)×10 <sup>-2</sup>	0.2±0.02		25	1.5
0.58	(2.3±0.5)×10 <sup>-2</sup>	0.18±0.02		30	1.8
0.73	(2.4±0.5)×10 <sup>-2</sup>	0.22±0.02	0.21±0.016	36	2.2
1.0	(2.7±0.4)×10 <sup>-2</sup>	0.15±0.025		50	3
1.3	(2.8±0.5)×10 <sup>-2</sup>	0.16±0.024		64	4
1.6	(2.8±0.5)×10 <sup>-2</sup>	0.15±0.024	0.15±0.015	80	5
1.8	(2.8±0.5)×10 <sup>-2</sup>	0.17±0.03		90	5.5

Effective diameter of <sup>a</sup> 3.5 μm and <sup>b</sup> 57 μm.

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**Table 5.** Summary of uptake experiments of N<sub>2</sub>O<sub>5</sub> on mineral dust samples: initial ( $\gamma_0$ ) and steady state ( $\gamma_{ss}$ ) uptake coefficients.

Mineral dust sample	$^a\gamma_0$	$^a\gamma_{ss}$	$^a\text{HNO}_3$	H <sub>2</sub> O <sub>(ads)</sub> [mg g <sup>-1</sup> ]
Kaolinite	0.14±0.04	(2.2±0.6)×10 <sup>-2</sup>	30%	23
Natural Limestone	(1.1±0.3)×10 <sup>-2</sup>	(2.2±0.6)×10 <sup>-3</sup>	18%	7
Arizona Test Dust	(6.4±1.9)×10 <sup>-2</sup>	(1.6±0.4)×10 <sup>-2</sup>	72%	22
CaCO <sub>3</sub>	(3.3±1.0)×10 <sup>-2</sup>	(6.2±1.8)×10 <sup>-3</sup>	5%	4
Saharan Dust	(9.0±2.6)×10 <sup>-2</sup>	(5.9±1.6)×10 <sup>-2</sup>	6%	20
	$^b\gamma_0$	$^b\gamma_{ss}$	$^b\text{HNO}_3$	
Kaolinite	(0.16±0.04)	(2.1±0.6)×10 <sup>-2</sup>	17%	
Natural Limestone	(0.43±0.13)	(4.3±1.3)×10 <sup>-2</sup>	12%	
Arizona Test Dust	(0.2±0.06)	(0.11±0.03)	20%	
CaCO <sub>3</sub>	(0.12±0.04)	(2.1±0.6)×10 <sup>-2</sup>	5%	
Saharan Dust	(0.3±0.08)	0.2±0.05	4%	

Uptake experiments were performed at <sup>a</sup> [N<sub>2</sub>O<sub>5</sub>]<sub>0</sub>=(3.8±0.5)×10<sup>12</sup> cm<sup>-3</sup> using 1 g of sample powder for A<sub>s</sub>=19.6 cm<sup>2</sup>; <sup>b</sup> [N<sub>2</sub>O<sub>5</sub>]<sub>0</sub>=(4.0±1.0)×10<sup>11</sup> cm<sup>-3</sup> using 300 mg of sample powder for A<sub>s</sub>=4.9 cm<sup>2</sup>. The yield of HNO<sub>3</sub> is given as a percentage with respect to the total molecules of N<sub>2</sub>O<sub>5</sub> taken up after a given reaction time of 200 s at orifice diameter of 8 mm.



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**Table 6.** Summary of uptake experiments of N<sub>2</sub>O<sub>5</sub> on 200 mg Kaolinite for data plotted in Fig. 8: initial ( $\gamma_0$ ) and steady state ( $\gamma_{ss}$ ) uptake coefficients ( $A_s=4.9\text{ cm}^2$ ).

[N <sub>2</sub> O <sub>5</sub> ] molecules cm <sup>-3</sup>	$\gamma_0$	$\gamma_{ss}$
<sup>a</sup> (4.0±1.0)×10 <sup>11</sup>	0.16±0.04	(2.1±0.6)×10 <sup>-2</sup>
<sup>b</sup> (6.2±1.5)×10 <sup>11</sup>	0.23±0.06	(2.6±0.5)×10 <sup>-2</sup>
<sup>a</sup> (9.0±0.5)×10 <sup>11</sup>	0.22±0.06	(2.2±0.5)×10 <sup>-2</sup>
<sup>b</sup> (2.1±0.5)×10 <sup>12</sup>	0.18±0.05	(2.4±0.7)×10 <sup>-2</sup>
<sup>a</sup> (3.8±0.5)×10 <sup>12</sup>	0.16±0.04	(2.2±0.6)×10 <sup>-2</sup>

<sup>a</sup> Orifice diameter = 8 mm; <sup>b</sup> Orifice diameter = 4 mm.

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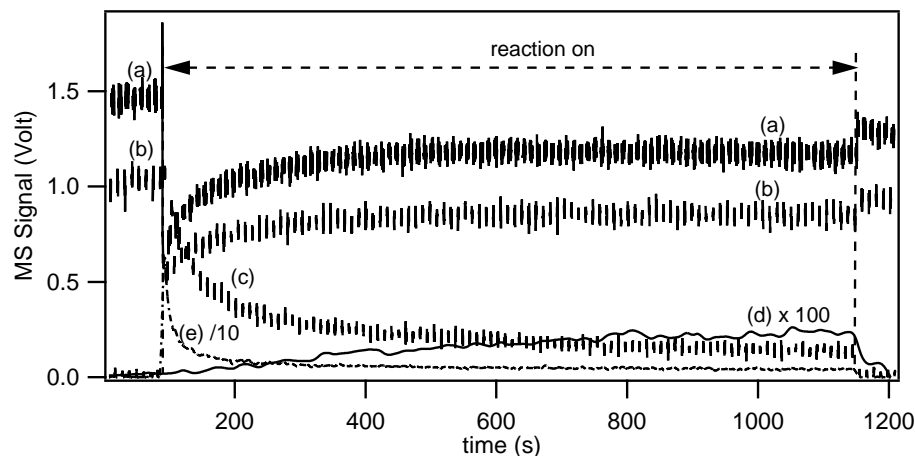
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**Fig. 1.** Typical  $\text{N}_2\text{O}_5$  uptake experiment on a sample of 510 mg of  $\text{CaCO}_3$ . Curves (a), (b), (c), (d) and (e) correspond to the raw MS signals monitored at m/e 46, m/e 30, m/e 44, m/e 63 and m/e 18, respectively, using an orifice diameter of 14 mm,  $A_s=19.6\text{ cm}^2$  and  $[\text{N}_2\text{O}_5]_0=(4.0\pm1.0)\times10^{11}\text{ cm}^{-3}$ .

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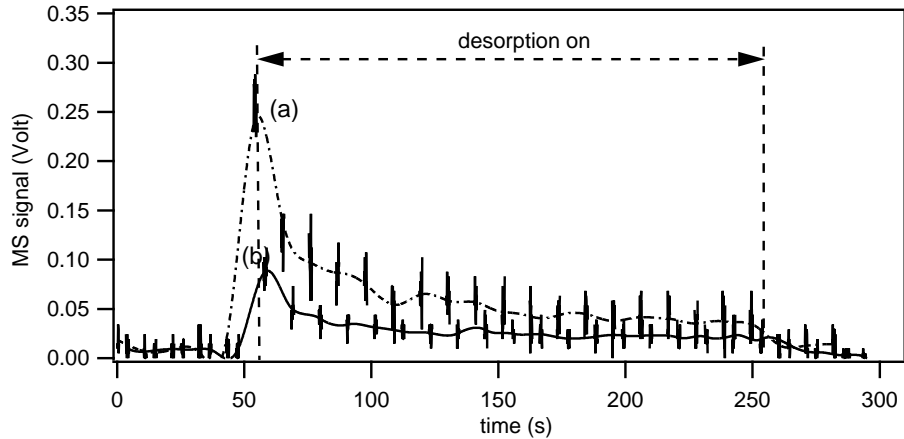
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**Fig. 2.** Desorption of  $\text{CO}_2$  and  $\text{NO}$  after  $\text{N}_2\text{O}_5$  uptake on a sample of 510 mg  $\text{CaCO}_3$  displayed in Fig. 1. Curves (a) and (b) correspond to the raw MS signals monitored at  $m/e$  44 and  $m/e$  30, respectively, at an orifice diameter of 14 mm and  $A_s=19.6\text{ cm}^2$ .

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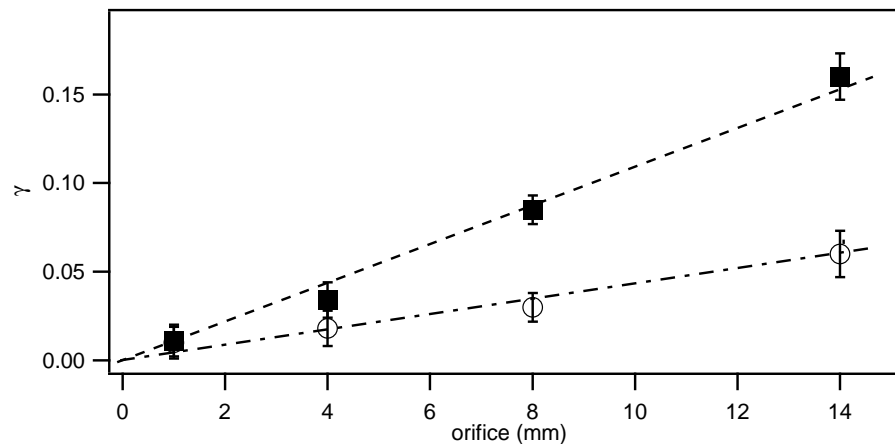
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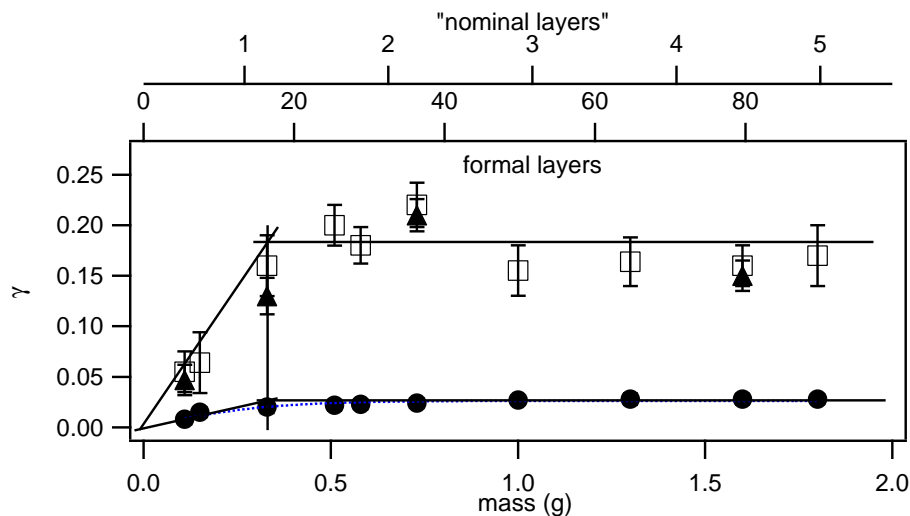
**Fig. 3.** Dependence of  $\gamma_0$  (full squares) and  $\gamma_{ss}$  (open circles) for the uptake of  $\text{N}_2\text{O}_5$  on 580 mg  $\text{CaCO}_3$  powder on orifice size:  $A_s$  is  $4.9\text{ cm}^2$ ,  $F_0^{\text{N}_2\text{O}_5} = 2.3 \times 10^{15}\text{ molecule s}^{-1}$ .

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**Fig. 4.** Dependence of the uptake coefficient  $\gamma_0$  (open squares) and  $\gamma_{ss}$  (full circles) on sample mass at  $[\text{N}_2\text{O}_5]_0 = (4.0 \pm 1.0) \times 10^{11} \text{ cm}^{-3}$  at an orifice diameter of 14 mm for the uptake of  $\text{N}_2\text{O}_5$  on  $\text{CaCO}_3$  powder ( $A_s = 19.6 \text{ cm}^2$ ). Full triangles represent pulsed valve experiments carried out at the same experimental conditions.

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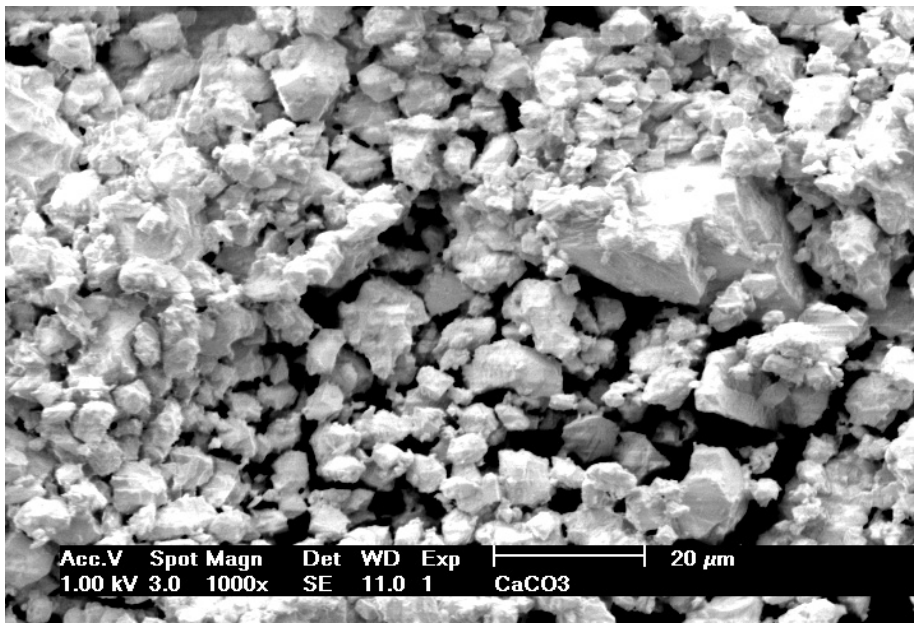
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**Fig. 5.** SEM-image of  $CaCO_3$  powder sample used in this work.

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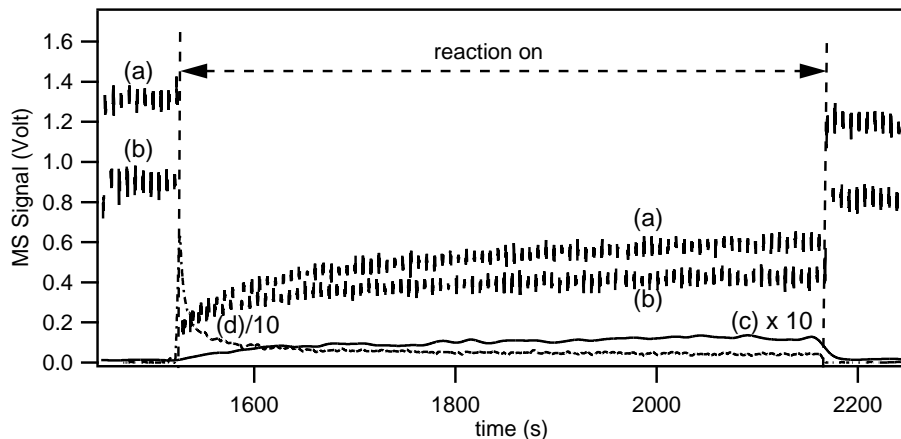
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**Fig. 6.** Typical  $\text{N}_2\text{O}_5$  uptake experiment on a sample of 1 g of Kaolinite. Curves (a), (b), (c) and (d) correspond to the raw *MS* signals monitored at  $m/e$  46,  $m/e$  30,  $m/e$  18 and  $m/e$  63, respectively, using an orifice diameter of 8 mm and  $[\text{N}_2\text{O}_5]_0 = (3.8 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$ .

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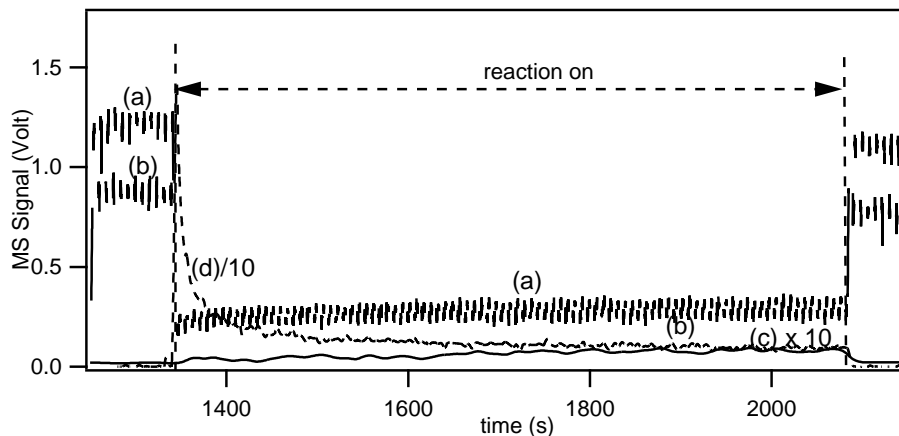
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**Fig. 7.** Typical  $\text{N}_2\text{O}_5$  uptake experiment on a sample of 1 g of Saharan Dust. Curves **(a)**, **(b)**, **(c)** and **(d)** correspond to the raw *MS* signals monitored at  $m/e$  46,  $m/e$  30,  $m/e$  18 and  $m/e$  63, respectively, using an orifice diameter of 8 mm and  $[\text{N}_2\text{O}_5]_0 = (3.8 \pm 0.5) \times 10^{12} \text{ cm}^{-3}$ .

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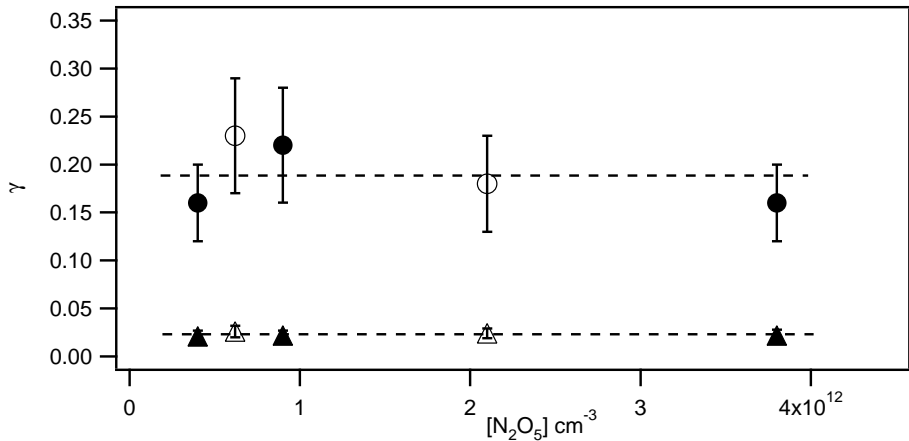
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**Fig. 8.**  $\text{N}_2\text{O}_5$  on 200 mg Kaolinite: uptake coefficient  $\gamma$  of  $\text{NO}_3$  as a function of  $[\text{N}_2\text{O}_5]$ : initial ( $\gamma_0$ , open circles) and steady state ( $\gamma_{ss}$ , full triangles) uptake coefficients for  $A_s=4.9\text{ cm}^2$ . Full and empty symbols are referred to uptake experiments carried out with an orifice diameter of 4 and 8 mm orifice diameter, respectively.

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