Interaction of NO2 with TiO2 surface under UV irradiation: measurements of the uptake coefficient

A. El Zein, Y Bedjanian

Atmos. Chem. Phys., 12, 1013–1020, 2012
www.atmos-chem-phys.net/12/1013/2012/
doi:10.5194/acp-12-1013-2012

Atmospheric Chemistry and Physics

Interaction of NO_2 with TiO_2 surface under UV irradiation: measurements of the uptake coefficient

A. El Zein and Y. Bedjanian

Institut de Combustion, Aérothermique, Réactivité et Environnement (ICARE), CNRS-INSU, OSUC (UMS3116), 45071 Orléans Cedex 2, France

Correspondence to: Y. Bedjanian (yuri.bedjanian@cnrs-orleans.fr)

Received: 27 September 2011 – Published in Atmos. Chem. Phys. Discuss.: 12 October 2011
Revised: 17 January 2012 – Accepted: 17 January 2012 – Published: 20 January 2012

Abstract. The interaction of NO_2 with TiO_2 solid films was studied under UV irradiation using a low pressure flow reactor (1–10 Torr) combined with a modulated molecular beam mass spectrometer for monitoring of the gaseous species involved. The NO_2 to TiO_2 reactive uptake coefficient was measured from the kinetics of NO_2 loss on TiO_2 coated Pyrex rods as a function of NO_2 concentration, irradiance intensity (J_{NO_2} = 0.002–0.012 s^{-1}), relative humidity (RH = 0.06–69 %), temperature (T = 275–320 K) and partial pressure of oxygen (0.001–3 Torr). TiO_2 surface deactivation upon exposure to NO_2 was observed. The initial uptake coefficient of NO_2 on illuminated TiO_2 surface (with 90 ppb of NO_2 and $J_{NO_2} \cong 0.006\ s^{-1}$) was found to be $\gamma_0 = (1.2 \pm 0.4) \times 10^{-4}$(calculated using BET surface area) under dry conditions at T = 300 K. The steady state uptake, γ, was several tens of times lower than the initial one, independent of relative humidity, and was found to decrease in the presence of molecular oxygen. In addition, it was shown that γ is not linearly dependent on the photon flux and seems to level off under atmospheric conditions. Finally, the following expression for γ was derived, $\gamma = 2.3 \times 10^{-3}$ exp(-1910/T)/(1 + $P^{0.36}$) (where P is O_2 pressure in Torr), and recommended for atmospheric applications (for any RH, near 90 ppb of NO_2 and $J_{NO_2} = 0.006\ s^{-1}$).

1 Introduction

Titanium dioxide (TiO_2) is a very efficient photocatalyst leading to the degradation of organic species under UV irradiation (e.g. Henderson, 2011). In addition, TiO_2 is known to transform nitrogen oxides (NO/NO_2), via catalytic heterogeneous reactions, to HNO_3, which remains on the TiO_2 surface (Ibusuki and Takeuchi, 1994; Dalton et al., 2002; Devahasdin et al., 2003; Negishi et al., 1998; Ohko et al., 2008). Due to these photocatalytic properties TiO_2 is widely used in a variety of so-called de-polluting building materials aimed to remove the nitrogen oxides from the atmosphere.

However, the antipolluting nature of the TiO_2-containing materials was recently questioned (Langridge et al., 2009; Monge et al., 2010; Ndour et al., 2009a). Ndour et al. (2009a) have shown that nitrate ions adsorbed onto mixed TiO_2/SiO_2 and pure TiO_2 can be converted into gaseous NO and NO_2 under UV irradiation. Moreover, it was shown that the interaction of NO_2 with TiO_2 (Monge et al., 2010) and commercial self-cleaning TiO_2-containing window glass (Langridge et al., 2009) results in the formation of nitrous acid (HONO) in the gas phase, that may have a negative environmental impact (Monge et al., 2010). In contrast, Laufs et al. (2010) working with TiO_2 doped commercial paints observed an efficient decomposition of HONO on the photolytic samples and concluded that the paint surfaces do not represent a source of HONO. So the question seems to remain open, pending further studies.

Titanium dioxide, although being a minor component of mineral dust particles (Karagulian et al., 2006), was shown recently to be responsible for the photochemical reactivity of atmospheric mineral aerosols (Ndour et al., 2008). Thus the information on the photoinitiated uptake of atmospheric trace gases to TiO_2 surface is of great importance for the modelling of the day time chemistry of the atmosphere. Only a few studies are known, in which the uptake coefficient of NO_2 to irradiated pure TiO_2 or TiO_2-doped surfaces was measured (Gustafsson et al., 2006; Monge et al., 2010; Ndour et al.,

2008, 2009b). The information available for the uptake coefficient of NO_2 to the illuminated TiO_2 surface remains limited and will be discussed below in association with the data from the present study.

On the basis of the above information, it is clear that complementary studies are needed in order to better determine both the rate and products of the NO_2 interaction with illuminated pure TiO_2, real mineral aerosols, as well as with different de-polluting building materials containing TiO_2. This paper reports results of measurements of the uptake coefficient of NO_2 to the TiO_2 surface as a function of different parameters such as NO_2 concentration, irradiance intensity, relative humidity, temperature and partial pressure of oxygen. A detailed study of the reaction products is the subject of our ongoing research.

2 Experimental

2.1 Preparation of TiO_2 films

Solid TiO_2 films were deposited on the outer surface of a Pyrex tube (0.9 cm i.d.) using a TiO_2 (Sigma Aldrich, Aeroxide P25, $(50\pm15)\,m^2g^{-1}$ surface area, $\sim$20 nm particle diameter) suspension in ethanol. Prior to film deposition, the Pyrex tube was treated with hydrofluoric acid and washed with distilled water and ethanol. Then the tube was immersed into the suspension, withdrawn and dried with a fan heater. As a result rather homogeneous (to the eye) films of TiO_2 were formed at the Pyrex surface. In order to eliminate possible residual traces of ethanol, prior to uptake experiments, the freshly prepared TiO_2 samples were heated at (100–150) °C during (20–30) min under pumping. In order to measure the mass of the sample on the Pyrex tube the deposited TiO_2 film was mechanically removed at the end of the kinetic experiments.

2.2 Flow reactor

Interaction of NO_2 with solid TiO_2 films was studied at 1–10 Torr total pressure (He being used as the carrier gas with 0.07–0.35 SLM flow rate) using the flow tube technique with mass spectrometric detection of the gaseous species involved. A modulated molecular beam mass spectrometer (BALZERS QMG 420) was used. The molecular beam, resulting from a differential pumping system, was modulated in the first vacuum chamber, allowing for a synchronous detection via a lock-in amplifier. In the second vacuum chamber containing the quadrupole mass spectrometer, the electron impact ion source (operating at 25–30 eV energy) was surrounded by a copper device cooled by liquid nitrogen, which allowed to significantly reduce the background spectrum. This chamber was pumped by means of a turbomolecular pump. The ions were detected via an electron multiplier. All the species were detected at their parent peaks. A typical detection limit for NO_2 was nearly 2×10^{10} molecules cm^{-3}.

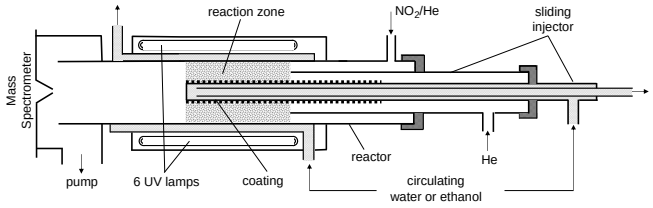

Fig. 1. Diagram of the flow photoreactor used.

The absolute concentration of NO_2 in the reactor was calculated from its flow rate obtained from the measurements of the pressure drop of a NO_2/He mixture in a calibrated volume flask. H_2O was introduced into the reactor by flowing He through a bubbler containing thermostated water. The H_2O flow rate was calculated from the H_2O vapor pressure and total (H_2O + He) pressure and the measured flow rate of He through the bubbler.

The main reactor (Fig. 1) consisted of a Pyrex tube (40 cm length and 2.4 cm i.d.) with a jacket for the thermostated liquid circulation. Experiments were carried out using a coaxial configuration of the flow reactor with movable triple central injector: the Pyrex tube with deposited sample was introduced into the main reactor along its axis. This tube could be moved relative to the outer tube of the injector. This allowed the variation of the sample length exposed to NO_2. The third (inner) tube of the movable injector was used for circulation of the thermostated liquid inside the tube covered with TiO_2 sample. This allowed maintaining the same temperature in the main reactor and on the sample surface in the measurements of the temperature dependence. In addition, the sample could be heated up to a few hundreds °C by means of a coaxial cylindrical heater which could be introduced inside the tube with the sample.

The reactor was surrounded by 6 lamps (Sylvania BL350, 8 W, 315–400 nm with peak at 352 nm). The actinic flux inside the reactor was not measured in the present study, however, in order to characterize the irradiance intensity in the reactor we have directly measured the NO_2 photolysis frequency as a function of the number of lamps switched on. In these experiments NO_2 was introduced into the photoreactor through the central tube of the movable injector (shadowed to prevent NO_2 photolysis inside it) and the concentration of NO_2 was monitored by the mass spectrometer as a function of the NO_2 residence time (up to 13 s) in the irradiated part of the reactor. Experiments were carried out with rather high NO_2 concentrations ($\sim10^{14}$ molecule cm^{-3}). Under such experimental conditions, the loss of NO_2 is due to two processes: NO_2 photolysis $NO_2 + h\nu \rightarrow NO + O$ and a secondary reaction with oxygen atoms

$$NO_2 + O \rightarrow NO + O_2$$

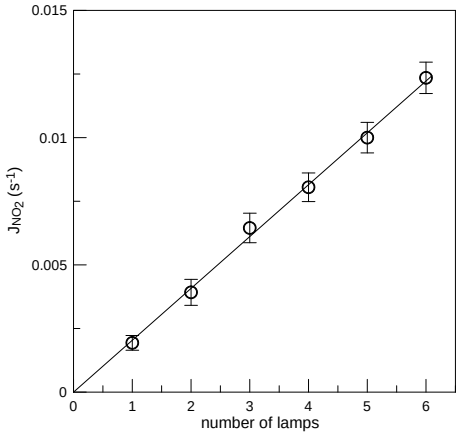

Fig. 2. Photolysis frequency of NO_2 (J_{NO_2}) as a function of the number of UV lamps switched on.

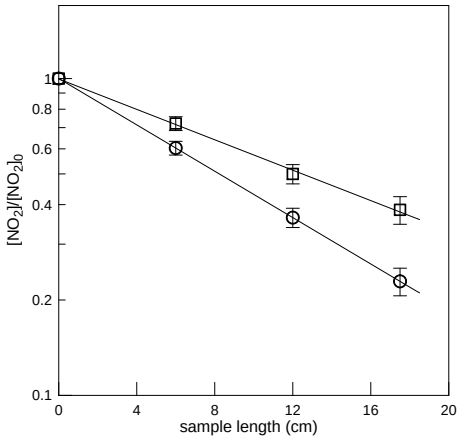

Fig. 3. Examples of kinetics of NO_2 consumption on TiO_2 surface: $T = 300$ K, sample mass = 0.3 mg cm^{-1}, $J_{NO_2} \cong 0.006\,s^{-1}$. Circles: initial uptake, $P = 1$ Torr, $[NO_2] = 3.3\times10^{12}$ molecule cm^{-3}, flow velocity = 420 cm s^{-1}; squares: $P = 9$ Torr, exposure time = 150 min, $[NO_2] = 1.5\times10^{12}$ molecule cm^{-3}, flow velocity = 42 cm s^{-1}.

This latter being much faster than NO_2 photolysis, the rate of NO_2 loss is:

$$d[NO_2]/dt = -2\ J_{NO_2}[NO_2]$$

The values of J_{NO_2} determined from the exponential decays of NO_2 for different numbers of lamps switched on are shown in Fig. 2. One can note that the resulting values of J_{NO_2} in our system (from 0.002 to 0.012 s^{-1}) are close to the corresponding values in the atmosphere.

2.3 Data analysis

The purpose of this study was to measure the uptake coefficient of NO_2 (γ) determined as the probability of reactive NO_2 loss per collision with the TiO_2 surface:

$$\gamma = \frac{4k'}{\omega}\frac{V}{S}$$

where k' (s^{-1}) is the first-order rate constant of NO_2 loss, ω the average molecular speed (355.9–383.9 m s^{-1} for T = 275–320 K), V the volume of the reaction zone, and S the surface area of the TiO_2 sample. To calculate the uptake coefficient, two parameters should be determined experimentally: the rate constant k' and the TiO_2 film surface area accessible to NO_2.

Figure 3 displays examples of NO_2 loss kinetics in the heterogeneous reaction with the TiO_2 surface. These data were obtained by varying the length of the TiO_2 film in contact with NO_2, which is equivalent to varying the reaction time. The NO_2 decays were found to be exponential and were treated with the first-order kinetics formalism, the rate constant being determined as:

$$k' = -\frac{d\ln([NO_2])}{dt}$$

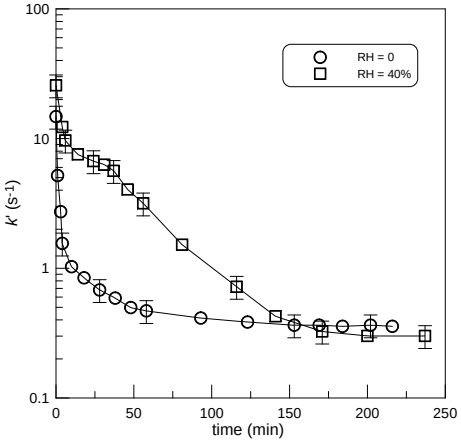

Fig. 4. Dependence of the first order rate constant of NO_2 loss on TiO_2 surface upon exposure time: $T = 280$ K, P = 1–9 Torr, $J_{NO_2} \cong 0.006\,s^{-1}$, sample mass $\approx$0.4 mg cm^{-1}, $[NO_2] \cong 10^{13}$ molecule cm^{-3}.

where t is the reaction time defined by the ratio sample length/flow velocity. The values of the first-order rate constants, k', determined from the decays of NO_2 were corrected for the diffusion limitation in the NO_2 radial transport from the volume to the reactive surface of the reactor (Bedjanian et al., 2005 and refs therein). Corrections applied to k' did not exceed 10 %.

The data presented in Fig. 3 show a decrease of the NO_2 loss rate with exposure time indicating TiO_2 sample deactivation during the heterogeneous reaction: the value of k' for initial uptake is much higher than that observed after 150 min of exposure to NO_2 (note, that the flow velocities corresponding

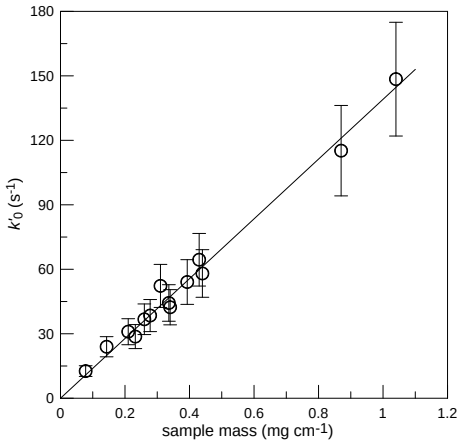

Fig. 5. Dependence of the initial rate of NO_2 loss on the mass of TiO_2 sample (per 1 cm length of the support tube): $P = 1$ Torr, $T = 300$ K, $J_{NO_2} \cong 0.006\,s^{-1}$, $[NO_2] \sim 10^{12}$ molecule cm^{-3}.

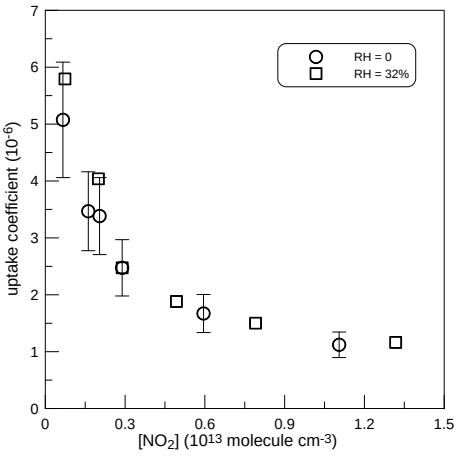

Fig. 6. Uptake coefficient as function of the initial concentration of NO_2: $T = 280$ K, $P = 9$ Torr, $J_{NO_2} \cong 0.006\,s^{-1}$, sample mass = 0.32 mg cm^{-1}. Error bars represent estimated 20 % uncertainty on the measurements of γ.

to the two curves in Fig. 3 differ by a factor of 10). Dependence of k' upon the exposure time of the TiO_2 film to NO_2 is shown in Fig. 4. One can note that the rate of NO_2 loss is decreasing with time approaching a steady state value after approximately 2 h of exposure. This value, under the conditions of these experiments, is by a factor near 50 lower than the rate of initial NO_2 uptake, k'_0, corresponding to the first seconds of the TiO_2 sample exposure to NO_2. The data presented in Fig. 4 show that the steady state values of k' are very similar for dry conditions and 40% RH, although the TiO_2 sample deactivation is faster under dry conditions.

Specific experiments have been carried out in order to determine the TiO_2 surface area involved in interaction with NO_2 under experimental conditions used. For that, the NO_2 loss rate k' was measured as a function of the thickness of TiO_2 coating. The results observed for the initial (corresponding to the first 10–30 s of exposure) uptake of NO_2 on TiO_2 are shown in Fig. 5 as a dependence of the rate constant of NO_2 loss on the mass of TiO_2 deposited per unity length of the support tube (equivalent to the thickness of the coating which was assumed to be homogeneous and evenly dense). The observed linear dependence of the reaction rate on the thickness of the TiO_2 film indicates that the entire surface area of the TiO_2 samples (at least, for samples with masses up to 1 mg cm^{-1}) is involved in the interaction with NO_2 and, consequently, the BET surface area should be used for calculations of the uptake coefficient. The data presented in Fig. 5 provide the following value for the initial uptake coefficient of NO_2 on the illuminated TiO_2 surface ($J_{NO_2} \cong 0.006\,s^{-1}$) under dry conditions at $T = 300$ K:

$$\gamma_0 = (1.2 \pm 0.4) \times 10^{-4}$$

where the uncertainty includes the statistical one and those on the BET surface area and on the measurements of k'_0. It should be noted that the value obtained for γ_0, being calculated with the BET surface area (50 $m^2 g^{-1}$), should be considered as a lower limit. On the other hand, the upper limit of γ_0 can also be estimated. Thus, applying the geometric (projected) surface area to the data observed with the smallest mass of TiO_2 used in these experiments (Fig. 5, $m = 0.08$ mg cm^{-1}, $k'_0 = 12.7\,s^{-1}$) one gets the value of 1.9×10^{-3} for the uptake coefficient which is an upper limit of γ_0.

Similar experiments carried out under dark conditions allowed to determine the initial uptake coefficient of NO_2 on TiO_2 in the absence of irradiation (calculated with BET surface area):

$$\gamma_0(\text{dark}) = (6.0 \pm 2.0) \times 10^{-6}$$

under dry conditions at $T = 300$ K.

3 Results

The present study was focused on the determination of the steady state value of γ as a function of different parameters; even though the initial uptake was measured under certain experimental conditions (see above). The experimental data presented below for the uptake coefficient,γ, correspond to its steady state value. Experiments were carried out with TiO_2 masses near 0.3 mg cm^{-1} at total pressure of 9 -10 Torr of Helium in the reactor and mostly at $T = 280$ K. This relatively low temperature was chosen as the standard temperature of this study in order to be able to ensure a reasonable level of relative humidity at the rather low total pressure in the reactor.

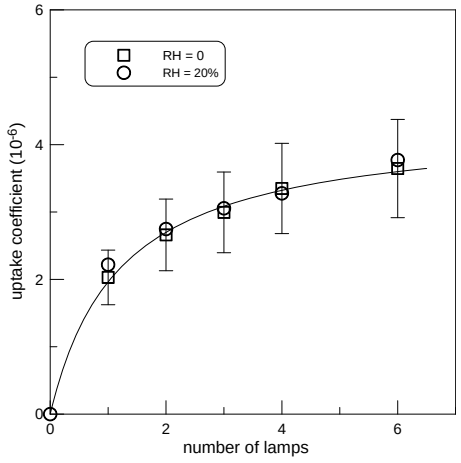

Fig. 7. Uptake coefficient as a function of the irradiation intensity (number of lamps switched on): $T = 280$ K, $P = 9$ Torr, sample mass = 0.47 mg cm^{-1}, [NO_2] $\approx 2\times10^{12}$ molecule cm^{-3}. The line is drawn to guide the eye.

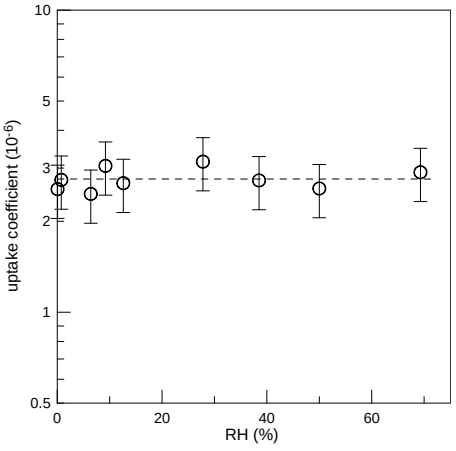

Fig. 8. Uptake coefficient as a function of relative humidity: $T =$ 280 K, $P = 9$ Torr, $J_{NO_2} \cong 0.006$ s^{-1}, sample mass = 0.38 mg cm^{-1}, [NO_2] $\approx 2\times10^{12}$ molecule cm^{-3}, RH = (0.06–69) %.

3.1 Dependence on NO_2 concentration

The dependence of γ on the gas phase concentration of NO_2 measured under dry conditions and RH = 32% with $[NO_2]_0$ varied in the range (0.06–1.32) $\times10^{13}$ molecule cm^{-3} is shown in Fig. 6. One can note that the uptake coefficient decreases upon increase of the initial NO_2 concentration. The negative dependence on [NO_2] may be due to the surface saturation by the adsorbed precursor and/or depletion of photo-produced intermediates. With the purpose of comparison, the measurements of the uptake coefficient under different experimental conditions presented below were carried out with the initial concentration of NO_2 fixed at nearly 2×10^{12} molecule cm^{-3}. This value is the result of a compromise between the need to work at lower concentrations and the NO_2 detection sensitivity.

3.2 Dependence on irradiation intensity

Dependence of the uptake coefficient on the illumination intensity was studied by switching on the different number of lamps in the reactor, from 1 to 6. As shown above, this corresponds to the variation of the NO_2 photolysis frequency from 0.002 to 0.012 s^{-1}. The results obtained under dry conditions and at RH = 20 % are shown in Fig. 7. One can note that less than two-fold increase of γ is observed whereas the irradiation intensity is changed by a factor of 6. This observation seems to be of great importance as it shows that the γ-values measured at low irradiation intensities could not be extrapolated in a linear way to those relevant to the atmosphere. The three series of experiments presented below were carried out using 3 lamps switched on ($J_{NO_2} \cong 0.006$ s^{-1}).

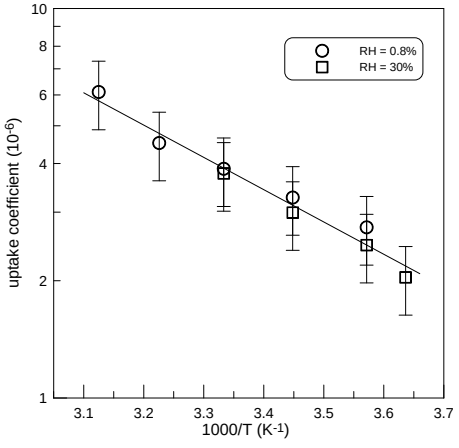

Fig. 9. Temperature dependence of the uptake coefficient measured at $T = 275$–320 K under 0.8 and 30% relative humidity: $P = 9$ Torr, $J_{NO_2} \cong 0.006$ s^{-1}, sample mass = 0.34 mg cm^{-1}, [NO_2] $\approx 2\times10^{12}$ molecule cm^{-3}.

3.3 Dependence on relative humidity

The data presented in Figs. 4, 6 and 7 observed under different relative humidity in the reactor show that the steady state uptake coefficient is not sensitive to this parameter. Figure 8 displays the results of the measurements of γ in the extended range of RH, from 0.06 to 69 %. The presented data clearly show that the uptake coefficient is independent of RH in this range. The dashed line in Fig. 8 corresponds to the mean value of $\gamma = 2.8\times10^{-6}$.

3.4 Dependence on temperature

The temperature dependence of the uptake coefficient measured in the temperature range (275–320) K is shown in

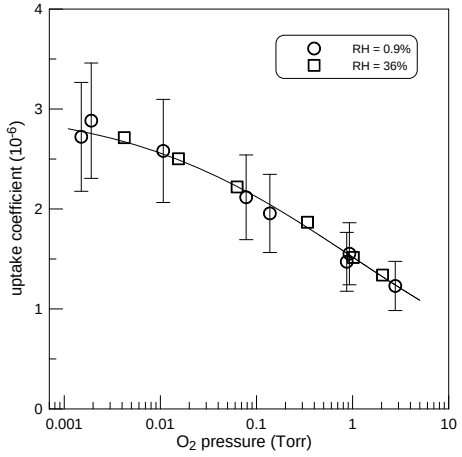

Fig. 10. Uptake coefficient as a function of partial pressure of oxygen: $T = 280$ K, $P = 9$ Torr, $J_{NO_2} \cong 0.006\,s^{-1}$, sample mass = 0.38 mg cm^{-1}, [NO_2]$\approx 2\times10^{12}$ molecule cm^{-3}.

Fig. 9. The uptake coefficient is found to increase with increasing temperature. The data observed with two different RH at $T = 280$, 290 and 300 K are similar in the range of experimental uncertainty indicating insignificant RH dependence of γ at these temperatures. The solid line in Fig. 9 represents an exponential fit to the experimental data and provides the following Arrhenius expression for γ:

$$\gamma = (2.3\pm0.9)\times10^{-3}\exp[(-1910\pm130)/T]$$

at $T = 275$–320 K (uncertainties are 1σ statistical ones).

3.5 Dependence on O_2 concentration

In this series of experiments the uptake coefficient of NO_2 was measured in the presence of O_2 in the reactor. The partial pressure of oxygen was varied between 0.002 and 3 Torr, the total pressure (O_2 + He) in the reactor being near 10 Torr. The results of these experiments are shown in Fig. 10. A slight inverse dependence of the uptake coefficient on O_2 pressure is observed: an increase of the oxygen pressure by three orders of magnitude leads to a decrease of γ by a factor of 3. Similarity of the data observed with different RH (0.9 and 36 %) indicates that the uptake coefficient remains independent of the relative humidity in the whole range of oxygen concentrations used. The solid line in Fig. 10 represents a fit to the experimental data and corresponds to the following expression:

$$\gamma = 3\times10^{-6}/(1+P^{0.36})$$

where P is the partial pressure of O_2 (in Torr).

4 Discussion

The results of the present study can be compared with available data from previous studies. The dark reaction of NO_2 with TiO_2 surface was investigated in three studies using a Knudsen cell reactor coupled to a quadrupole mass spectrometer (Underwood et al., 1999, 2001; Setyan et al., 2009). The following values were determined by Underwood et al. (1999, 2001) for the initial uptake coefficient ([NO_2] being varied from 3×10^{11} to 3×10^{14} molecule cm^{-3}): γ_0(dark) = 4×10^{-4} using geometric surface area and $\sim10^{-7}$ for the uptake coefficient, corrected for the effect of bulk diffusion. The value of γ_0 (dark) = 6×10^{-6} determined in the present study using BET surface area, lies between the above two values. On the contrary, Setyan et al. (2009) have not observed any NO_2 uptake on the TiO_2 surface. Although these authors did not give any estimation of the upper limit of the uptake coefficient, simple calculations show that the value of γ_0 from the present study would lead to an initial drop of NO_2 signal at least by a factor of 1.5 under their experimental conditions. The reason for the lower NO_2 uptake to TiO_2 surface in the study of Setyan et al. (2009) compared with the present one, could be the mode of preparation of solid samples. Note that in the present work TiO_2 samples were heated under pumping prior to uptake measurements.

A deactivating behaviour of TiO_2 in the reaction with NO_2 under UV irradiation observed in the present study supports the previous observations of Ohko et al. (2008). These authors have observed that the photocatalytic activity was decreased with accumulation of HNO_3 on the TiO_2 surface and concluded that the produced HNO_3 inhibited the photocatalytic heterogeneous reaction as a physical barrier. They reported that, when the steady state was reached, the photocatalytic activity remained at nearly 8% of the initial one. This value is in a fair agreement with a few percent steady state photocatalytic activity observed in the present study. In contrast to these two studies, time independent uptake of NO_2 on TiO_2 films was observed by Ndour et al. (2008): no surface deactivation has been observed on the synthetic TiO_2/SiO_2 samples exposed over hours to NO_2 concentrations up to 300 ppb. In several previous studies (e.g. Lin et al., 2006; Ohko et al., 2008) it was observed that the photocatalytic activity of the TiO_2 film can be fully regenerated after rinsing with water. In the present work, we have observed similar behaviour: the deactivated TiO_2 sample was regenerated after being immersed in water.

Gustafsson et al. (2006) studied the uptake of NO_2 on illuminated P25 TiO_2 aerosols using initial NO_2 concentrations similar to those of the present study ($\cong 2\times10^{12}$ molecule cm^{-3}). The measured uptake coefficient was found to negatively correlate with relative humidity and to range from 9.6×10^{-4} for 15% RH to 1.2×10^{-4} for 80% RH. Considering the method used by Gustafsson et al. (2006) (continuous flow of the aerosol/NO_2 mixture, i.e. rather short aerosol to NO_2 exposure times) these values should

be considered as corresponding to initial uptake and can be compared with $\gamma_0 = 1.2\times10^{-4}$ determined in the present study under dry conditions. Agreement between the results from the two studies seems to be reasonable, especially if one considers that the uptake coefficients measured by Gustafsson et al. (2006) seem to represent an upper limit of γ_0 because the aerosol surface area available for the reaction was calculated from the measured aerosol size distribution by assuming that the particles have the same surface areas as spheres of the same electrical mobility. Gustafsson et al. (2006) observed a negative correlation between the HONO formation rate in the reaction of NO_2 with TiO_2 and relative humidity. This behaviour was interpreted as a result of increased water adsorption inhibiting NO_2 adsorption and/or electron/hole transfer processes at the TiO_2/gas interface. In the present study the impact of RH on the initial uptake of NO_2 has not been studied, however we have not observed any influence of RH on the uptake coefficient of NO_2 under steady state conditions.

The only value for the steady state uptake coefficient of NO_2 on an irradiated pure TiO_2 surface was reported by Monge et al. (2010). These authors measured $\gamma = 1.5\times10^{-6}$ at $T = 298$ K, 30 % relative humidity under atmospheric pressure of N_2 and $[NO_2] = 3.8\times10^{12}$ molecule cm^{-3}. This value is in a good agreement with that measured in the present study at $T = 298$ K: $\gamma \cong 3.8\times10^{-6}$ (see Fig. 9). However, it should be noted that when comparing the above two numbers one should consider that the results were determined under different irradiance conditions, the NO_2 photolysis rate being 6×10^{-3} and 4.75×10^{-4} s^{-1} in the present study and in Monge et al. (2010), respectively.

It is also interesting to compare the data on NO_2 uptake to pure TiO_2 from the present study with those measured on mineral dust originating from different locations of the Sahara desert (Ndour et al., 2009b). The reported uptake coefficients of NO_2 (25 ppb) on four different Sahara sand samples were between 0.35 and 1.46×10^{-7} at $T = 298$ K, 25% relative humidity, in an atmosphere of N_2. The value of γ measured in the present study on pure TiO_2 under these conditions is near 8×10^{-6} (from Fig. 6 and temperature dependence of γ), i.e. by a factor of 50–200 higher. Considering that TiO_2 content in the sand samples used by Ndour et al. (2009b) was between 0.2 and 1 wt% and assuming that their photoreactivity was mainly due to TiO_2, the agreement between the results observed on pure TiO_2 (present study) and real dust samples with low TiO_2 content (Ndour et al., 2009b) seems to be very satisfactory.

So far, the effect of oxygen on the rate of NO_2 loss on irradiated TiO_2 surface has been considered only in one study (Monge et al., 2010). These authors have observed that the uptake coefficient of NO_2 on pure TiO_2 was highly influenced by the presence of O_2, and reported a value of γ one order of magnitude higher in 1 atm of N_2 compared with that in N_2:O_2 (85 %:15%) mixture. Interestingly, the application of the expression for the dependence of γ on the pressure of O_2 from the present study, $\gamma \sim (1 + P^{0.36})^{-1}$, to the experimental conditions used by Monge et al. (2010), gives a factor of 6.5 for the expected difference between the values of γ in presence and absence of oxygen. This seems to indicate that the analytic expression for the dependence of γ on O_2 pressure derived in the present study at rather low pressures of oxygen is applicable under atmospheric conditions. The effect of oxygen was suggested to be due to competition between O_2 and NO_2 for scavenging the electrons at the surface of the photocatalyst (Monge et al., 2010).

The extended data set obtained in the present study for the uptake coefficient of NO_2 to the TiO_2 surface seems to allow calculating γ values for atmospheric conditions. Dependencies of γ on temperature and pressure of oxygen can be combined, giving the following final expression for γ:

$$\gamma = \frac{2.3\times10^{-3}\exp(-1910/T)}{1+P^{0.36}}$$

where T is the temperature (K) and P is the oxygen pressure (Torr). This expression is applicable for any atmospheric relative humidity and for $J_{NO_2} = 0.006$ s^{-1}. Let's note that the dependence on the photon flux is not significant, at least, in the range of J_{NO_2} values between 0.002 and 0.012 s^{-1} considered in the present study. An important parameter in the calculation of γ is the concentration of NO_2. The above expression was derived from the experiments carried out with $[NO_2] \approx 2\times10^{12}$ molecule cm^{-3} (nearly 90 ppb for $P = 1$ atm). As shown in Fig. 6, at lower NO_2 concentrations the value of γ will be higher.

The atmospheric and environmental impact of the interaction of NO_2 with irradiated TiO_2-containing mineral aerosols and depolluting materials is strongly dependent on the gaseous and surface bound products of this process. In previous studies, HONO (Gustafsson et al., 2006; Ndour et al., 2008; Monge et al., 2010; Beaumont et al., 2009) and NO (Ohko et al., 2008; Monge et al., 2010) in the gas phase as well as nitric acid/nitrate anion on the surface (e.g. Dalton et al., 2002; Devahasdin et al., 2003; Lin et al., 2006; Ndour et al., 2008; Negishi et al., 1998; Ohko et al., 2008) were observed as the NO_2 + TiO_2 reaction products. In the present study we have observed HONO, NO and, in addition, N_2O to be released into the gas phase as a result of the heterogeneous reaction of NO_2 with TiO_2 surface. The formation of NO_3^- on the surface of the TiO_2 sample was also observed by means of ion chromatography. The individual yields of the gas phase products were found to be strongly dependent on the experimental conditions such as relative humidity, temperature and concentration of oxygen in the reactive system. A detailed product study of the heterogeneous NO_2 + TiO_2 reaction is a subject of our current work and will be published in a separate paper.

Acknowledgements. This study was supported by LEFE – CHAT programme of CNRS (Photona project) and the ANR Photodust project. A. E. Z. is very grateful to région Centre for financing his PhD grant.

Edited by: M. Ammann

The publication of this article is financed by CNRS-INSU.

References

Beaumont, S. K., Gustafsson, R. J., and Lambert, R. M.: Heterogeneous Photochemistry Relevant to the Troposphere: H_2O_2 Production during the Photochemical Reduction of NO_2 to HONO on UV-Illuminated TiO_2 Surfaces, Chem. Phys. Chem., 10, 331–333, 2009.

Bedjanian, Y., Lelièvre, S., and Le Bras, G.: Experimental study of the interaction of HO_2 radicals with soot surface, Phys. Chem. Chem. Phys., 7, 334–341, 2005.

Dalton, J. S., Janes, P. A., Jones, N. G., Nicholson, J. A., Hallam, K. R., and Allen, G. C.: Photocatalytic oxidation of NO_x gases using TiO_2: a surface spectroscopic approach, Environ. Pollut., 120, 415–422, 2002.

Devahasdin, S., Fan Jr, C., Li, K., and Chen, D. H.: TiO_2 photocatalytic oxidation of nitric oxide: transient behavior and reaction kinetics, J. Photoch. Photobio. A, 156, 161–170, 2003.

Gustafsson, R. J., Orlov, A., Griffiths, P. T., Cox, R. A., and Lambert, R. M.: Reduction of NO_2 to nitrous acid on illuminated titanium dioxide aerosol surfaces: implications for photocatalysis and atmospheric chemistry, Chem. Commun., 3936–3938, 2006.

Henderson, M. A.: A surface science perspective on photocatalysis, Surf. Sci. Rep., 66, 185–297, 2011.

Ibusuki, T. and Takeuchi, K.: Removal of low concentration nitrogen oxides through photoassisted heterogeneous catalysis, J. Mol. Catal., 88, 93–102, 1994.

Karagulian, F., Santschi, C., and Rossi, M. J.: The heterogeneous chemical kinetics of N_2O_5 on $CaCO_3$ and other atmospheric mineral dust surrogates, Atmos. Chem. Phys., 6, 1373–1388, doi:10.5194/acp-6-1373-2006, 2006.

Langridge, J. M., Gustafsson, R. J., Griffiths, P. T., Cox, R. A., Lambert, R. M., and Jones, R. L.: Solar driven nitrous acid formation on building material surfaces containing titanium dioxide: A concern for air quality in urban areas?, Atmos. Environ., 43, 5128–5131, 2009.

Laufs, S., Burgeth, G., Duttlinger, W., Kurtenbach, R., Maban, M., Thomas, C., Wiesen, P., and Kleffmann, J.: Conversion of nitrogen oxides on commercial photocatalytic dispersion paints, Atmos. Environ., 44, 2341–2349, 2010.

Lin, Y.-M., Tseng, Y.-H., Huang, J.-H., Chao, C. C., Chen, C.-C., and Wang, I.: Photocatalytic Activity for Degradation of Nitrogen Oxides over Visible Light Responsive Titania-Based Photocatalysts, Environ. Sci. Technol., 40, 1616–1621, 2006.

Monge, M. E., D'Anna, B., and George, C.: Nitrogen dioxide removal and nitrous acid formation on titanium oxide surfaces-an air quality remediation process?, Phys. Chem. Chem. Phys., 12, 8991–8998, 2010.

Ndour, M., D'Anna, B., George, C., Ka, O., Balkanski, Y., Kleffmann, J., Stemmler, K., and Ammann, M.: Photoenhanced uptake of NO_2 on mineral dust: Laboratory experiments and model simulations, Geophys. Res. Lett., 35, L05812, doi:10.1029/2007GL032006, 2008.

Ndour, M., Conchon, P., D'Anna, B., Ka, O., and George, C.: Photochemistry of mineral dust surface as a potential atmospheric renoxification process, Geophys. Res. Lett., 36, L05816, doi:10.1029/2008GL036662, 2009a.

Ndour, M., Nicolas, M., D'Anna, B., Ka, O., and George, C.: Photoreactivity of NO_2 on mineral dusts originating from different locations of the Sahara desert, Phys. Chem. Chem. Phys., 11, 1312–1319, 2009b.

Negishi, N., Takeuchi, K., and Ibusuki, T.: Surface structure of the TiO_2 thin film photocatalyst, J. Mater. Sci., 33, 5789–5794, 1998.

Ohko, Y., Nakamura, Y., Fukuda, A., Matsuzawa, S., and Takeuchi, K.: Photocatalytic Oxidation of Nitrogen Dioxide with TiO_2 Thin Films under Continuous UV-Light Illumination, J. Phys. Chem. C, 112, 10502–10508, 2008.

Setyan, A., Sauvain, J. J., and Rossi, M. J.: The use of heterogeneous chemistry for the characterization of functional groups at the gas/particle interface of soot and TiO_2 nanoparticles, Phys. Chem. Chem. Phys., 11, 6205–6217, 2009.

Underwood, G. M., Miller, T. M., and Grassian, V. H.: Transmission FT-IR and Knudsen Cell Study of the Heterogeneous Reactivity of Gaseous Nitrogen Dioxide on Mineral Oxide Particles, J. Phys. Chem. A, 103, 6184–6190, 1999.

Underwood, G. M., Song, C. H., Phadnis, M., Carmichael, G. R., and Grassian, V. H.: Heterogeneous reactions of NO_2 and HNO_3 on oxides and mineral dust: A combined laboratory and modeling study, J. Geophys. Res., 106, 18055–18066, 2001.