

# IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet V.A2.4 MD4

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## NO<sub>2</sub> + mineral oxide (dust) surfaces → products

### Experimental data

<i>Parameter</i>	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: <math>\gamma</math></i>			
$\gamma_{0,PD} = 2 \times 10^{-8}$ ( $\gamma$ -Al <sub>2</sub> O <sub>3</sub> powder, 10 <sup>-5</sup> – 10 <sup>-2</sup> mbar)	298	Underwood, et al., 1999	Kn-MS (a)
	298		
$\gamma_{0,PD} = 7 \times 10^{-7}$ ( $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> powder, 10 <sup>-5</sup> – 10 <sup>-2</sup> mbar)	298		
$\gamma_{0,PD} = 1 \times 10^{-7}$ (TiO <sub>2</sub> powder, 10 <sup>-5</sup> – 10 <sup>-2</sup> mbar)			
$\gamma_{ss,BET} = 1.3 \times 10^{-9}$ ( $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , 5.0x10 <sup>-4</sup> mbar)	299	Börensén et al., 2000	DRIFTS (b)
$\gamma_{ss,BET} = 2.6 \times 10^{-8}$ ( $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , 3.5x10 <sup>-2</sup> mbar)	299		
$\gamma_{0,BET} = 9.1 \times 10^{-6}$ ( $\alpha$ -Al <sub>2</sub> O <sub>3</sub> , 5.3x10 <sup>-6</sup> mbar)	298	Underwood et al., 2001	Kn-MS (c)
$\gamma_{0,BET} = 2.0 \times 10^{-8}$ ( $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , 5.3x10 <sup>-6</sup> mbar)			
$\gamma_{0,BET} = 7.7 \times 10^{-6}$ ( $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> , 5.3x10 <sup>-6</sup> mbar)			
$\gamma_{0,BET} = 4.0 \times 10^{-6}$ ( $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> , 5.3x10 <sup>-6</sup> mbar)			
$\gamma_{0,BET} = 1.3 \times 10^{-7}$ (TiO <sub>2</sub> , 5.3x10 <sup>-6</sup> mbar)			
$\gamma_{0,BET} = 1.2 \times 10^{-5}$ (MgO, 5.3x10 <sup>-6</sup> mbar)			
$\gamma_{0,BET} = 2.2 \times 10^{-5}$ (CaO, 5.3x10 <sup>-6</sup> mbar)			
$\gamma_{0,BET} = 2.1 \times 10^{-6}$ (China loess, 5.3x10 <sup>-6</sup> mbar)			
$\gamma_{0,BET} = 1.2 \times 10^{-6}$ (Saharan sand, 5.3x10 <sup>-6</sup> mbar)			
$\gamma_{0,BET} = (6.2 \pm 3.4) \times 10^{-7}$ (Saharan dust, 4.1x10 <sup>-4</sup> mbar)	298	Ullerstam et al., 2003	Kn-MS/DRIFTS (d)
$\gamma = 9.6 \times 10^{-4}$ (illuminated TiO <sub>2</sub> , 15 % r.h., 1 x 10 <sup>-4</sup> mbar)	298	Gustafsson et al., 2006	AFT-CLD (e)
$\gamma = 1.2 \times 10^{-4}$ (illuminated TiO <sub>2</sub> , 80 % r.h., 1 x 10 <sup>-4</sup> mbar)			
$\gamma_{ss,BET} = (8.1 \pm 0.2) \times 10^{-8}$ (kaolinite, 2.3 x 10 <sup>-4</sup> mbar)	298	Angelini et al., 2007	DRIFTS (f)
$\gamma_{ss,BET} = (2.3 \pm 0.4) \times 10^{-8}$ (kaolinite, 3.6 x 10 <sup>-3</sup> mbar)			
$\gamma_{ss,BET} = (7 \pm 1) \times 10^{-9}$ (pyrophyllite, 1.2 x 10 <sup>-2</sup> mbar)			

$\gamma_{ss,BET} = 1 \times 10^{-9}$ (1% TiO <sub>2</sub> /SiO <sub>2</sub> , SiO <sub>2</sub> , Saharan sand, Arizona Test dust)	295	Ndour et al., 2008	CWFT-CLD/LOPAP (g)
$\gamma_{ss,BET} = 1 \times 10^{-6}$ (illuminated 1% TiO <sub>2</sub> /SiO <sub>2</sub> )			
$\gamma_{ss,BET} = (8.9 \pm 5.2) \times 10^{-9}$ (Saharan sand, 6 x 10 <sup>-8</sup> mbar, 25 % RH)	298	Ndour et al., 2009	CWFT-CLD (h)
$\gamma_{ss,BET} = (1.0 \pm 0.5) \times 10^{-7}$ (illuminated Saharan sand, 6 x 10 <sup>-8</sup> mbar, 25 % RH)			
$\gamma_{0,BET} = (4.3 \pm 1.2) \times 10^{-9}$ (CaCO <sub>3</sub> , 0.28-0.69 mbar, 0 % RH)	296	Li et al., 2010	DRIFTS (i)
$\gamma_{0,BET} = (2.5 \pm 0.1) \times 10^{-9}$ (CaCO <sub>3</sub> , 0.19-0.47 mbar, 60-71 % RH)			

### Comments

- (a) Uptake experiment in a Knudsen flow reactor equipped with residual gas MS detection covering a NO<sub>2</sub> concentration range of 10 ppb to 10 ppm. The powder samples (as is) were thick enough so that the uptake coefficient did not depend on mass. The mineral particle sizes were 18nm, 690nm, 25nm for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> (80% anatase, 20% rutile). The observed uptake coefficient did not depend on the gas phase concentration. The tabulated  $\gamma$  values were corrected using the pore diffusion model. Gaseous NO was observed as product, with a delay after initial exposure to NO<sub>2</sub>. Overall, the ratio of NO<sub>2</sub> to NO was 2:1. FTIR measurements at 5-350mTorr of NO<sub>2</sub> showed nitrite and nitrate species on the surface. It is suggested that a bidentate nitrito species is the first intermediate that disproportionates into a nitrate species and gaseous NO. The suggested mechanism also indicates that saturation will occur, when the product nitrate species reaches monolayer capacity.
- (b) Samples were obtained from ball-milling  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder (100 mesh) and packed into the DRIFTS reactor. Nitrite and nitrate species were observed on the surface. The absorption was calibrated by performing offline analysis with ion chromatography. The suggested mechanism involves disproportionation of physisorbed NO<sub>2</sub> into surface coordinated nitrite and nitrate, followed by release of HONO to the gas phase. The tabulated uptake coefficients were normalized to the BET area of the samples. They increase linearly with increasing NO<sub>2</sub> concentration between 10<sup>-4</sup> and 10<sup>-2</sup> mbar, confirming the second order character of the reaction.
- (c) Bulk dust samples were prepared by spraying an aqueous slurry onto the heated sample holder and kept under vacuum overnight prior to an experiment. Experiments were carried out in the linear mass dependent regime, and the tabulated  $\gamma_0$  values were normalized to the BET surface area of the dust sample and were measured at about 5x10<sup>-6</sup> mbar. A further correction to the uptake coefficient suggested to account for internal roughness of individual particles led to an increase of up to a factor of 2. The uptake coefficient decreased with time, while the surface became saturated (observed at 8x10<sup>-3</sup> Torr). Gaseous NO was observed as a product, with a ratio of NO<sub>2</sub> lost to NO formed of 2:1. Based on earlier work of the same group, this confirmed that an initial surface species, presumably nitrite, reacts with gaseous or adsorbed NO<sub>2</sub> to NO and nitrate.
- (d) Combined Knudsen flow reactor and FTIR diffuse reflectance study in the presence of both SO<sub>2</sub> (5.3x10<sup>12</sup> molecule cm<sup>-3</sup>) and NO<sub>2</sub> ((1.7-10)x10<sup>12</sup> molecule cm<sup>-3</sup>). Mineral dust samples from Cape Verde Islands with a BET area of 50m<sup>2</sup>g<sup>-1</sup> were applied to the heated sample holder as an aqueous suspension. The sample was dried at 333K under vacuum. The listed values are initial uptake coefficients of steady-state uptake experiments in absence of SO<sub>2</sub>. The tabulated uptake coefficients were referred to the BET area of the sample. The sample

masses were kept low to stay within the linear mass regime. Adsorbed nitrite and nitrate species were identified using FTIR. It is suggested that the primary reactive process (in absence of other reactants) is heterogeneous hydrolysis of NO<sub>2</sub> to yield adsorbed HONO and HNO<sub>3</sub>.

- (e) TiO<sub>2</sub> (3:1 anatase to rutile) aerosol was generated by nebulizing an aqueous powder suspension. The surface area in the aerosol flow tube was quantified by an SMPS. NO<sub>2</sub> and HONO were measured using a chemiluminescence detector. The fluorescent lamps had a maximum at 365 nm. The light intensity in the reactor was 1.6 mW cm<sup>-2</sup>. The HONO yield was about 75%. The uptake of NO<sub>2</sub> in the dark was below detection limits.
- (f) Kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) and pyrophyllite ((AlSi<sub>2</sub>O<sub>5</sub>OH)) samples obtained from ball-milling clay powders were packed into a DRIFTS reaction chamber. Nitrate in different conformations was observed as products on kaolinite. The tabulated uptake coefficients are obtained from the rate of nitrate formation during the initial phase of reaction (before nitrate starts to deplete available surface sites) under dry conditions and referred to the BET area of the sample. Formation of HONO was observed over wetted kaolinite samples by UV-VIS spectroscopy in a separate cell.
- (g) Synthetic and authentic dust samples were coated onto the surface of a Duran glass flow tube, irradiated by UV in the wavelength region 300 to 420 nm with an irradiance of 0.069 mWcm<sup>-2</sup>. The light induced uptake coefficient was inversely related to the NO<sub>2</sub> concentration within 10<sup>11</sup> to 10<sup>13</sup> cm<sup>-3</sup>. HONO was observed as product with a yield of 30% from the TiO<sub>2</sub>/SiO<sub>2</sub> mixtures and 80% from Saharan dust.
- (h) Ground Saharan sand samples from Mauritania, Tunisia, Morocco and Algeria were coated onto the surface of a Duran glass atmospheric pressure flow tube, irradiated by UV in the wavelength region 300 to 420 nm with an irradiance of 1.45 mWcm<sup>-2</sup>. Uptake coefficients derived from the observed loss of NO<sub>2</sub> in the gas phase were corrected for gas phase diffusion and referred to the BET surface area. The tabulated values are the average of the values reported for the four individual samples. The variability associated with the different samples was attributed to the variability in mineralogy of the samples assessed through EDX measurements. No pressure dependence was investigated. The uptake coefficient reported for irradiated conditions were upscaled for solar irradiance at 48° zenith angle. As measured they were a factor of 8 to 15 above those measured in the dark.
- (i) CaCO<sub>3</sub> powder was obtained by grinding to particles with 5.6µm diameter, with 0.19m<sup>2</sup>/g external surface area and 4.91 m<sup>2</sup>/g BET surface area. 20mg of the powder were pressed into the DRIFTS sample holder and dried using a desiccator. The tabulated uptake coefficients were obtained from the observed rate of nitrate formation. The nitrate formation rate showed complex behaviour under dry conditions, but apparent first order behaviour with respect to NO<sub>2</sub> under humid conditions (>50 % RH). At low humidity, the humidity dependence indicated competitive adsorption of water and NO<sub>2</sub>; at high humidity, the rate of nitrate formation increased linearly with humidity. Offline analysis with IC and X-ray photoelectron spectroscopy (XPS) confirmed the presence of nitrate under dry conditions, and the presence of nitrite and nitrate under wet conditions.

#### Preferred Values

Parameter	Value	T/K
$\gamma$	$9 \times 10^{-9}$	298

*Comments on preferred values*

Uptake of  $\text{NO}_2$  to mineral oxides is very slow. The available studies agree comparatively well on the reported values for the uptake coefficient, when considering similar materials and reasonably low  $\text{NO}_2$  pressures. Most studies report reactivity at or below the detection limit for silica. For  $\gamma\text{-Al}_2\text{O}_3$  and pyrophyllite uptake coefficients are on the order of  $10^{-8}$ . In this case also the uptake coefficients obtained in a Knudsen cell by Underwood et al. (1999) using thick samples and applying a pore diffusion model agree with those of the later study of the same group using thin samples and normalization to the BET area. In addition, results obtained in the Knudsen cell agree with those derived from the appearance of absorption bands observed in a DRIFTS reactor by Börensén et al. (2000) and Angelini et al. (2007). For the most reactive basic oxides, uptake coefficients can get up to  $10^{-5}$ . For clay minerals and Saharan dust, the uptake coefficient is on the order of  $10^{-6}$  and below at relevant low pressures. The difference between the values observed by Ndour et al. (2010), Ullerstam et al. (2003) and by Underwood et al. (2001) might be due to saturation effects at the higher pressures noted by Ullerstam et al. (2003). The same likely applies to the study by Li et al. (2010) on  $\text{CaCO}_3$  performed at  $\text{NO}_2$  pressures in the range of a few 0.1 mbar. We therefore recommend the value obtained by Ndour et al. (2009) for Saharan dust.

Distinctly different mechanisms are suggested for the different substrates and especially in the presence and absence of water. The reactive process driving uptake is an initial adsorption and reaction of  $\text{NO}_2$  with the surface oxides followed by secondary processes, or heterogeneous hydrolysis of  $\text{NO}_2$  to yield HONO and  $\text{HNO}_3$ . Given that Underwood et al. (1999) observed the predominant appearance of the nitrite species at the lowest pressures used on dry  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ , it is likely that nitrite formation and further oxidation by  $\text{NO}_2$  is important under dry conditions. Similarly, nitrite appeared only initially on dry  $\text{CaCO}_3$  (Li et al., 2010). For more humid conditions and the basic oxide (or carbonate) components of dust, it is likely that the heterogeneous hydrolysis of  $\text{NO}_2$  and displacement reactions of the acids are the processes driving uptake. Given that mineralogy strongly affects the reactivity, we associate a large uncertainty with the uptake coefficient.

All studies indicate that the uptake coefficient is time dependent and decreases strongly after roughly a monolayer equivalent (based on BET area) has been reacted. This is less an issue for carbonates, for which the particle bulk may become accessible through the action of  $\text{HNO}_3$  formed from  $\text{NO}_2$  (Li et al., 2010).

Given the little detailed kinetic information in the atmospherically relevant pressure range, no detailed parameterization of the uptake coefficient is given.

While the reactivity of  $\text{TiO}_2$  is comparable to that of the other materials in the dark, under illumination in the range of 300 to 400 nm, it catalyses the reduction of  $\text{NO}_2$  to HONO or more generally, enhances the uptake of  $\text{NO}_2$  (Gustafsson et al., 2006, Ndour et al., 2008, Ndour et al., 2009). Ndour et al. (2009) use a linear model to extrapolate the measured uptake coefficient to other irradiances:  $\gamma = 1.23 \times 10^{-8} \times I [\text{mW cm}^{-2}]$ .

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