

# IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation

## Data Sheet V.A2.4 MD4

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This data sheet last evaluated: April 2017; last change in preferred values: April 2010.

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

#### Experimental data

Parameter	substrate	$p_{\text{NO}_2}$ /mbar	Temp./ K	RH /%	Reference	Technique/ Comments
<i>Uptake coefficients: <math>\gamma</math></i>						
$\gamma_{0,\text{PD}} = 2 \times 10^{-8}$	$\gamma\text{-Al}_2\text{O}_3$	$10^{-5}\text{-}10^{-2}$	298		Underwood et al., 1999	Kn-MS (a)
$\gamma_{0,\text{PD}} = 7 \times 10^{-7}$	$\alpha\text{-Fe}_2\text{O}_3$	$10^{-5}\text{-}10^{-2}$	298			
$\gamma_{0,\text{PD}} = 1 \times 10^{-7}$	TiO <sub>2</sub>	$10^{-5}\text{-}10^{-2}$	298			
$\gamma_{\text{ss,BET}} = 1.3 \times 10^{-9}$	$\gamma\text{-Al}_2\text{O}_3$	$5.0 \times 10^{-4}$	299		Börensén et al., 2000	DRIFTS (b)
$\gamma_{\text{ss,BET}} = 2.6 \times 10^{-8}$	$\gamma\text{-Al}_2\text{O}_3$	$3.5 \times 10^{-2}$	299			
$\gamma_{0,\text{BET}} = 9.1 \times 10^{-6}$	$\alpha\text{-Al}_2\text{O}_3$	$5.3 \times 10^{-6}$	298		Underwood et al., 2001	Kn-MS (c)
$\gamma_{0,\text{BET}} = 2.0 \times 10^{-8}$	$\gamma\text{-Al}_2\text{O}_3$	$5.3 \times 10^{-6}$				
$\gamma_{0,\text{BET}} = 7.7 \times 10^{-6}$	$\alpha\text{-Fe}_2\text{O}_3$	$5.3 \times 10^{-6}$				
$\gamma_{0,\text{BET}} = 4.0 \times 10^{-6}$	( $\gamma\text{-Fe}_2\text{O}_3$ )	$5.3 \times 10^{-6}$				
$\gamma_{0,\text{BET}} = 1.3 \times 10^{-7}$	TiO <sub>2</sub>	$5.3 \times 10^{-6}$				
$\gamma_{0,\text{BET}} = 1.2 \times 10^{-5}$	MgO	$5.3 \times 10^{-6}$				
$\gamma_{0,\text{BET}} = 2.2 \times 10^{-5}$	CaO	$5.3 \times 10^{-6}$				
$\gamma_{0,\text{BET}} = 2.1 \times 10^{-6}$	China loess	$5.3 \times 10^{-6}$				
$\gamma_{0,\text{BET}} = 1.2 \times 10^{-6}$	Saharan sand	$5.3 \times 10^{-6}$				
$\gamma_{0,\text{BET}} = (6.2 \pm 3.4) \times 10^{-7}$	Saharan dust	$4.1 \times 10^{-4}$	298		Ullerstam et al., 2003	Kn-MS/DRIFTS (d)
$\gamma = 9.6 \times 10^{-4}$ (UV)	TiO <sub>2</sub>	$1 \times 10^{-4}$	298	15	Gustafsson et al., 2006	AFT-CLD (e)
$\gamma = 1.2 \times 10^{-4}$ (UV)	TiO <sub>2</sub>	$1 \times 10^{-4}$		80		
$\gamma_{\text{ss,BET}} = (8.1 \pm 0.2) \times 10^{-8}$	Kaolinite	$2.3 \times 10^{-4}$	298		Angelini et al., 2007	DRIFTS (f)
$\gamma_{\text{ss,BET}} = (2.3 \pm 0.4) \times 10^{-8}$	kaolinite	$3.6 \times 10^{-3}$	298			
$\gamma_{\text{ss,BET}} = (7 \pm 1) \times 10^{-9}$	pyrophyllite	$1.2 \times 10^{-2}$	298			
$\gamma_{\text{ss,BET}} = 1 \times 10^{-9}$	N. Afr. sand		295		Ndour et al., 2008	CWFT-
$\gamma_{\text{ss,BET}} = 1 \times 10^{-6}$ (UV)	1% TiO <sub>2</sub> /SiO <sub>2</sub>					CLD/LOPAP (g)

$\gamma_{ss,BET} = (8.9 \pm 5.2) \times 10^{-9}$	Saharan sand		298	25	Ndour et al., 2009	CWFT-CLD (h)
$\gamma_{ss,BET} = (1.0 \pm 0.5) \times 10^{-7}$ (UV)	Saharan sand	$6 \times 10^{-8}$		25		
$\gamma_{0,BET} = (4.3 \pm 1.2) \times 10^{-9}$	CaCO <sub>3</sub>	0.28-0.69	296	0	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		60-71		
$\gamma_{0,BET} = (6.0 \pm 2.0) \times 10^{-6}$	TiO <sub>2</sub>		300	0	El Zein and Bedjanan, 2012	CWFT-MS (k)
$\gamma_{0,BET} = (1.2 \pm 0.4) \times 10^{-4}$ (UV, $J_{NO_2} = 0.006 \text{ s}^{-1}$ )				0		
$\gamma_{ss,BET} = (5.0 \pm 1.0) \times 10^{-6}$ (UV, $J_{NO_2} = 0.006 \text{ s}^{-1}$ )		$2.3 \times 10^{-5}$	280	0-69		
$\gamma_{ss,BET} = (1.2 \pm 0.2) \times 10^{-6}$ (UV, $J_{NO_2} = 0.006 \text{ s}^{-1}$ )		$5.1 \times 10^{-4}$	280	0-69		
$\gamma_{0,BET} = (2.3 \pm 0.9) \times 10^{-3}$ ( $\exp[(1910 \pm 130)/T]$ ) (UV, $J_{NO_2} = 0.006 \text{ s}^{-1}$ )		$7.7 \times 10^{-5}$	275-320	0-69		
$\gamma_{ss,BET} = (3.3 \pm 0.1) \times 10^{-9}$	CaCO <sub>3</sub>	0.11	298	0	Tan et al., 2016	DRIFTS (j)
$\gamma_{ss,BET} = (2.0 \pm 0.1) \times 10^{-9}$				40		
$\gamma_{ss,BET} = (2.2 \pm 0.2) \times 10^{-9}$				60		
$\gamma_{ss,BET} = (2.3 \pm 0.2) \times 10^{-9}$				85		

### Comments

- (a) NO<sub>2</sub> concentrations ranged from 10 ppb to 10 ppm. The powder samples were thick enough so that the uptake coefficient did not depend on mass. The average 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 NO<sub>2</sub> 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.
- (b) Sieved  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder (100 mesh). Nitrite and nitrate species were observed on the surface. The absorption was calibrated by performing offline analysis with ion chromatography. 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. A further correction to the uptake coefficient 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.
- (d) Combined Knudsen flow reactor and FTIR diffuse reflectance study in the presence of both SO<sub>2</sub> ( $5.3 \times 10^{12}$  molecule cm<sup>-3</sup>) and NO<sub>2</sub> ( $(1.7-10) \times 10^{12}$  molecule cm<sup>-3</sup>). Mineral dust samples from Cape Verde Islands with a BET area of 50 m<sup>2</sup> g<sup>-1</sup> were applied to the heated sample holder as an aqueous suspension. The sample was dried at 333 K under vacuum. The initial uptake coefficients (in absence of SO<sub>2</sub>) were calculated using 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.

- (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) SiO<sub>2</sub>/TiO<sub>2</sub> mixtures and sand samples collected in North Africa 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 mW cm<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 and irradiated by UV (300 to 420 nm, 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. The uptake coefficient reported for irradiated conditions were a factor of 8 to 15 above those measured in the dark.
- (i) CaCO<sub>3</sub> powder (5.6µm diameter particles with 0.19m<sup>2</sup>/g external surface area and 4.91 m<sup>2</sup>/g BET surface area). 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.
- (k) TiO<sub>2</sub> films of Aeroxide P25 (50 ± 15 m<sup>2</sup> g<sup>-1</sup> surface area, ~20 nm particle diameter) generated from a suspension in ethanol, followed by drying and baking at 100-150°C in vacuo. For UV irradiation (315-400, J<sub>NO2</sub> = 0.002 to 0.012) s<sup>-1</sup>). The first order loss rates exhibited significant time dependence and decreased by about an order of magnitude to a steady state value which was insensitive to the presence of water vapor (while the initial loss rates were sensitive to humidity. The linear mass dependent range of the first order loss rate was used to obtain uptake coefficients based on BET surface area, γ<sub>BET</sub>. Steady state uptake coefficients under UV increased by a factor of two when irradiance was varied over a factor of six and showed a negative dependence on O<sub>2</sub> pressure: 3 × 10<sup>-6</sup> / (1+p<sub>O2</sub><sup>0.36</sup>) (p<sub>O2</sub> in Torr).
- (j) CaCO<sub>3</sub> powder with 8.15 m<sup>2</sup>/g BET surface area. The integrated nitrate absorbance was calibrated with post-exposure extraction of the powder and analysis by ion chromatography.

### Preferred Values

Parameter	Value	T/K
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$\gamma$	$9 \times 10^{-9}$	298
<i>Reliability</i>		
$\Delta \log(\gamma)$	1	298

### *Comments on preferred values*

Uptake of NO<sub>2</sub> 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 low NO<sub>2</sub> pressures. Most studies report reactivity at or below the detection limit for silica. For  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and pyrophyllite uptake coefficients are on the order of 10<sup>-8</sup>. 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 Börensen et al. (2000) and Angelini et al. (2007). For the most reactive basic oxides, uptake coefficients can approach 10<sup>-5</sup>. For clay minerals and Saharan dust, the uptake coefficient is on the order of 10<sup>-6</sup> and below at atmospherically relevant NO<sub>2</sub> concentrations. 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 NO<sub>2</sub> concentrations noted by Ullerstam et al. (2003). The same likely applies to the study by Li et al. (2010) on CaCO<sub>3</sub> performed at NO<sub>2</sub> 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 NO<sub>2</sub> with the surface oxides followed by secondary processes, or heterogeneous hydrolysis of NO<sub>2</sub> to yield HONO and HNO<sub>3</sub>. Both Lampimäki et al. (2015) and Underwood et al. (1999) observed the appearance of the predominant nitrite species at the lowest pressures used on dry Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, it is likely that nitrite formation and further oxidation by NO<sub>2</sub> is important under dry conditions. TiO<sub>2</sub> seems to be among the more active substrate for this direct initial redox reaction with NO<sub>2</sub> (El Zein and Bedjanan, 2013), even though no NO<sub>2</sub> uptake on various TiO<sub>2</sub> substrates was detectable by Setyan et al. (2009). Similarly, nitrite appeared only initially on dry CaCO<sub>3</sub> (Li et al., 2010). For more humid conditions and the basic oxide (or carbonate) components of dust, and also at larger NO<sub>2</sub> pressures (Ramis, 1990, Rodriguez et al., 2001, Haubrich et al., 2010), it is likely that secondary oxidation and heterogeneous hydrolysis of NO<sub>2</sub> followed by the displacement reactions of the acids are the processes driving uptake (Lampimäki et al., 2015). 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 HNO<sub>3</sub> formed from NO<sub>2</sub> (Li et al., 2010).

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

While the reactivity of TiO<sub>2</sub> 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 NO<sub>2</sub> to HONO or

more generally, enhances the uptake of NO<sub>2</sub> (Gustafsson et al., 2006, Ndour et al., 2008, Ndour et al., 2009, El Zein and Bedjanan, 2012). N'dour et al. (2009) use a linear model to extrapolate the measured uptake coefficient to other irradiances:  $\gamma = 1.23 \times 10^{-8} \times I$  [mW cm<sup>-2</sup>]. This expression is also consistent with the O<sub>2</sub> pressure dependence measured by El Zein and Bedjanan (2012) for pure TiO<sub>2</sub> when upscaling their low O<sub>2</sub> pressure data to the atmospheric and employing additive mixing for the light induced NO<sub>2</sub> uptake based on TiO<sub>2</sub> content in Saharan dusts (O<sub>2</sub> is a competitive scavenger for electrons). The products of the photocatalytic interaction of NO<sub>2</sub> with TiO<sub>2</sub> are HONO, NO and N<sub>2</sub>O with yields of 65%, 5% and 15%, respectively (Bedjanan and El Zein, 2012), with some differences to other studies (Gustafsson et al., 2006, Ndour et al., 2008) attributed to detailed substrate properties and their preparation. In situ spectroscopy studies also show the presence of both reductive and oxidative processes leading to nitrate and reduced nitrogen species (Lampimäki et al., 2015, Rosseler et al., 2013).

(a) 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) 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.

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