

## Interaction of NO<sub>2</sub> with TiO<sub>2</sub> surface under UV irradiation: uptake and products

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Titanium dioxide, TiO<sub>2</sub>, is a very efficient photocatalyst leading to the degradation of organic species under UV irradiation. In addition, TiO<sub>2</sub> is known to transform nitrogen oxides (NO/NO<sub>2</sub>), via catalytic heterogeneous reactions, to HNO<sub>3</sub>, which remains on the TiO<sub>2</sub> surface. Due to these photocatalytic properties TiO<sub>2</sub> is widely used in a variety of so-called de-polluting building materials aimed to remove the nitrogen oxides from the atmosphere. Titanium dioxide, although being a minor component of mineral dust particles, is believed to be responsible for the photochemical reactivity of atmospheric mineral aerosols. Despite the existence of several experimental studies of the NO<sub>2</sub> reaction with illuminated TiO<sub>2</sub> surface, the quantitative information on its kinetics and products under different atmospheric conditions remains limited, not systematic and sometimes controversial.

In the present work the interaction of NO<sub>2</sub> with TiO<sub>2</sub> 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<sub>2</sub> to TiO<sub>2</sub> reactive uptake coefficient was measured from the kinetics of NO<sub>2</sub> loss on TiO<sub>2</sub> coated Pyrex rods as a function of NO<sub>2</sub> concentration, irradiance intensity ( $J_{\text{NO}_2} = 0.002 - 0.012 \text{ s}^{-1}$ ), relative humidity (RH = 0.06 – 69 %), temperature (T = 275 – 320 K) and partial pressure of oxygen (0.001 – 3 Torr). The initial uptake coefficient of NO<sub>2</sub> on illuminated TiO<sub>2</sub> surface (with 90 ppb of NO<sub>2</sub> and  $J_{\text{NO}_2} = 0.006 \text{ s}^{-1}$ ) 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,  $\gamma$ , 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  $\gamma$  is not linearly dependent on the photon flux and seems to level off under atmospheric conditions. Finally, the following expression for  $\gamma$  was derived,  $\gamma = 2.3 \times 10^{-3} \exp(-1910/T)/(1 + P^{0.36})$  (where P is O<sub>2</sub> pressure in Torr), and recommended for atmospheric applications (for any RH, near 90 ppb of NO<sub>2</sub> and  $J_{\text{NO}_2} = 0.006 \text{ s}^{-1}$ ).

HONO, NO and N<sub>2</sub>O were observed as the products of the NO<sub>2</sub> reactive uptake to illuminated TiO<sub>2</sub> surface with the sum of their yields corresponding to nearly 100% of the nitrogen mass balance. The yield of the products was determined as a function of different parameters such as irradiance intensity, relative humidity, temperature, concentrations of NO<sub>2</sub> and O<sub>2</sub>. The yield of N<sub>2</sub>O was found to be (0.15 ± 0.05) independent of the experimental conditions. The distribution of the products between NO and HONO was found to be independent of temperature in the range T = 280-320 K and was governed by relative humidity: increase in RH led to lower NO and higher HONO yield, with a nearly 65% maximum reached at ~5 % RH. Presence of molecular oxygen was shown to shift the HONO/NO distribution to HONO at low RH (<5%) with no effect at higher RH where HONO yield has its maximum value. The following values for the product yields of the NO<sub>2</sub> interaction with pure TiO<sub>2</sub> under real atmospheric conditions can be recommended from this work: 0.65±0.10, 0.05±0.05 and 0.15±0.05 for HONO, NO and N<sub>2</sub>O, respectively. The mechanism of the photoinitiated heterogeneous reaction and possible atmospheric implications of the obtained results will be discussed.