

Reduction of NO₂ to nitrous acid on illuminated titanium dioxide aerosol surfaces: implications for photocatalysis and atmospheric chemistry

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Received (in Cambridge, UK) 26th June 2006, Accepted 19th July 2006

First published as an Advance Article on the web 8th August 2006

DOI: 10.1039/b609005b

TiO₂, a component of atmospheric mineral aerosol, catalyses the reduction of NO₂ to nitrous acid (HONO) when present as an aerosol and illuminated with near UV light under conditions pertinent to the troposphere.

Nitrous acid (HONO) plays an important role in atmospheric chemistry, serving as a major source of hydroxyl radicals which play a primary role in the formation of ozone and other secondary atmospheric pollutants.¹ Laboratory studies suggest that in the absence of sunlight HONO is formed heterogeneously on the surfaces of tropospheric aerosol particles according to the disproportionation reaction (1):²



However, daytime HONO concentrations in the troposphere remain poorly explained as significant differences exist between the predictions of theoretical models and observation.³ It has recently been suggested that these discrepancies must imply the presence of a daytime source of nitrous acid.³ George *et al.*⁴ demonstrated enhanced uptake of NO₂ by organic surfaces in the presence of UV light. Very recently, Stemmler *et al.*⁵ have shown that a photo-enhanced reaction of nitrogen dioxide with humic acids is a potential daytime source of tropospheric HONO. Here, based on laboratory measurements of the photoreduction of NO₂ in an aerosol flow tube reactor under conditions of partial pressure, humidity and temperature pertinent to the troposphere, we suggest another possible contribution to daytime HONO production.

Mineral dust aerosol is an important component of the troposphere, comprising fine particles of crustal origin advected from arid regions. However, its possible role in photocatalytic processes has until now not been investigated. Under UV irradiation, titanium dioxide is a very efficient photocatalyst for the degradation of organic molecules to carbon dioxide and water.^{6,7} Thus, although it is a relatively minor component of tropospheric mineral aerosols, it could nevertheless play a significant role in atmospheric chemistry during the daytime. Here we demonstrate that UV-activated TiO₂ photocatalyses the conversion of nitrogen dioxide and water to nitrous acid with high efficiency.

An aerosol of P25 TiO₂ (3 : 1 anatase to rutile ratio, BET surface area $-(50 \pm 5) \text{ m}^2 \text{ g}^{-1}$) was generated from an aqueous (deionised water) suspension using an atomizer (TSI 3076). The

aerosol relative humidity (RH) was controlled using a silica gel drying unit in series with a humidifier. The size distribution was characterised by means of a differential mobility analyser (Hauke EMS VIE 08 DMA). NO₂ (BOC speciality gases, 50 ppm in N₂) was prediluted with nitrogen (BOC, oxygen free) and introduced into the flow tube *via* a sliding injector to give an initial mixing ratio of ~ 100 ppbv. The sliding injector allowed control of the NO₂/aerosol contact time, and NO₂ consumption was measured using a chemiluminescence NO_x analyser (API 200E). HONO concentrations were determined using the method described by Febo *et al.*⁸ The amount of NO_y (defined, in this case, as NO + NO₂ + HONO) was measured by passing the output of the flow tube directly to the analyser as the resultant signal contains a response from any HONO present. The amount of NO_x (NO + NO₂) was also measured by passing the output of the flow tube through a Na₂CO₃ denuder that selectively removes HONO and HNO₃. Any contribution from gas phase HNO₃ may be excluded as no change in signal was observed after passing the reactor output through a NaCl denuder that selectively removed HNO₃.

The TiO₂ aerosols were stable for the time required to obtain measurements. A typical particle size distribution is shown in Fig. 1. This distribution is approximately described by a superposition of two log-normal distributions, extending up to 1 μm as a result of agglomeration of the 30 nm particles in the atomiser suspension. The aerosol surface area exposed to reactant gases was calculated from the measured size distribution by assuming that the particles were spherical. Irradiation was

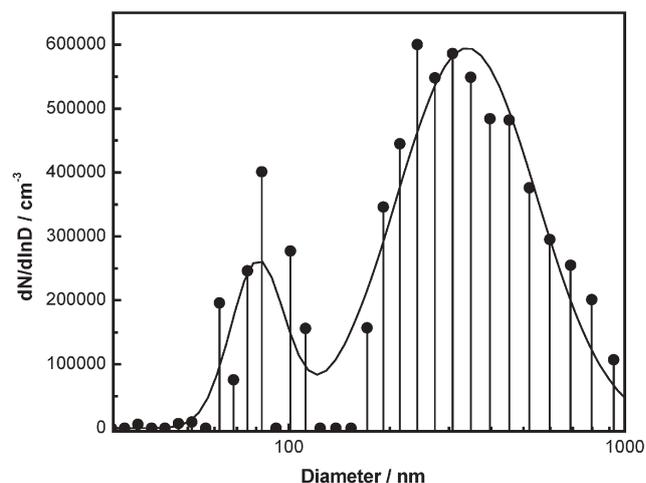


Fig. 1 Typical bimodal aerosol distribution showing an aerosol with a reactive surface area of $0.43 \text{ m}^2 \text{ m}^{-3}$.

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provided by four fluorescent lamps (Phillips TL D18W/08; $\lambda_{\max} = 365$ nm) symmetrically arranged around the flow tube. The light intensity inside the reactor was 1.6 mW cm^{-2} , measured by a calibrated UV-A light meter.

NO_2 consumption rates were measured and HONO production rates calculated by taking the difference in NO_3 and NO_x concentrations (see above) and accounting for HONO loss to the walls of the flow tube. In the absence of light, at all relative humidities HONO production and NO_2 consumption were below the detection limit. This corresponds to a HONO formation rate $< 4 \times 10^{-4} \text{ s}^{-1}$. When the aerosol was exposed to UV light substantial HONO production and NO_2 depletion occurred. Control experiments performed with light but without aerosol showed no measurable NO_2 loss or HONO production, confirming that all the observed photocatalytic activity was due to the TiO_2 aerosol and not the walls of the flow tube. The calculated HONO formation rate constants are shown in Fig. 2.

The data shown in Fig. 2 imply that photocatalytic reactions taking place on the surface of TiO_2 -containing mineral aerosols are a potentially significant source of tropospheric HONO. This view is supported by the NO_2 uptake coefficients (γ) calculated from the rate constants and aerosol surface area according to:

$$\gamma = \frac{\text{no. collisions resulting in loss of molecule from gas phase}}{\text{total no. collisions}} = 4k/vA_s$$

where k is the rate of loss (s^{-1}), v is the mean molecular speed of NO_2 (ms^{-1}) and A_s is the reactive surface area ($\text{m}^2 \text{ m}^{-3}$). Uptake coefficients ranged from 9.6×10^{-4} for 15% RH to 1.2×10^{-4} for 80% RH. These values should be compared with the uptake coefficient of 2×10^{-5} recently reported by Stemmler *et al.*⁵ for the reaction of NO_2 with humic acid surfaces. Clearly, tropospheric mineral dusts containing significant amounts of titanium dioxide or other oxides with appropriate bandgaps (e.g. Fe_2O_3) are plausible candidates for daytime tropospheric HONO production.

Fig. 3 shows the negative correlation between HONO formation rate constant and relative humidity. This behaviour may be understood in terms of increased water adsorption inhibiting NO_2 adsorption and/or electron/hole transfer processes at the TiO_2 /gas interface. Such effects could be amplified by the well

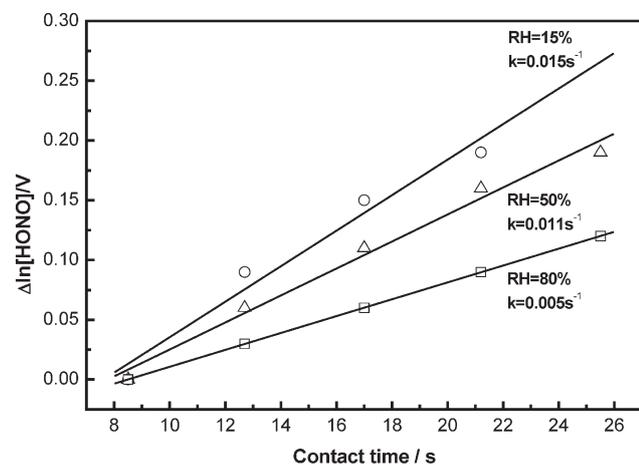


Fig. 2 First-order HONO formation rate plots.

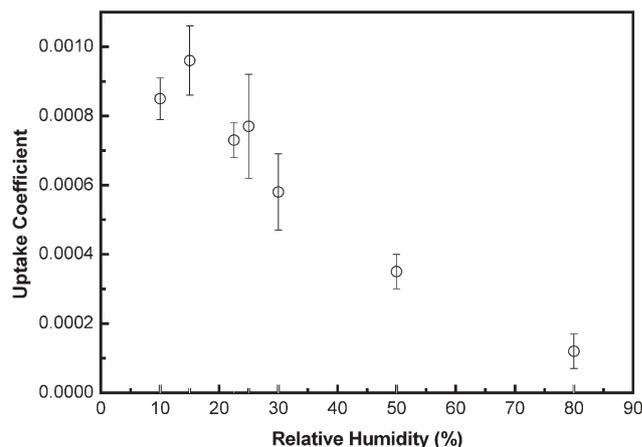


Fig. 3 Dependence of NO_2 uptake coefficient on relative humidity.

known superhydrophilic behaviour of TiO_2 surfaces under UV irradiation.⁹ It appears that at low relative humidities the uptake coefficient begins to fall, most likely as the coverage of water on the surface limits the availability of protons required for the formation of HONO; due to experimental constraints it was not possible to examine this effect further at conditions below 10% R.H.

TiO_2 surfaces irradiated by UV light catalyse both oxidation and reduction reactions.¹⁰ The disproportionation reaction (eqn (1)), occurs in the dark on a variety of surfaces¹¹ to yield gaseous HONO as the reduced species and adsorbed HNO_3 as the oxidised species. The stoichiometry of reaction (1) dictates that the rate of production of HONO must equal half the rate of consumption of NO_2 . As the measured rate of photo-induced HONO production is actually $\sim 75\%$ that of total NO_2 consumption, we may conclude that our observations do not correspond to photo-enhancement of reaction (1): some other mechanism must be at work. The formation of HONO necessarily implies formation of some kind of oxidised species, the identity of which is not clear at present. A plausible candidate is hydrogen peroxide; further experiments are required to clarify this point.

In summary, under conditions pertinent to the daytime troposphere, we have discovered a new source of HONO. The rate of photo-reaction depends very significantly on relative humidity. These results are of significance to an understanding of the NO_x and free radical budgets of the troposphere; they are also relevant to the general field of TiO_2 photocatalysis.

This work was supported under Research Grant NE/B503509/1 awarded by the UK Natural Environment Research Council. R. J. G. and A. O. acknowledge a NERC studentship and a King's College, Cambridge Research Fellowship, respectively. P. T. G. acknowledges the NERC Distributed Institute for Atmospheric Composition (DIAC) for post-doctoral support.

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