

# Heterogeneous reaction of HO<sub>2</sub> with airborne TiO<sub>2</sub> particles, production of HO<sub>x</sub> by UV-irradiated photocatalytic airborne TiO<sub>2</sub> particles and implications for climate change mitigation strategies

D. R. Moon,<sup>1</sup> T. Ingham,<sup>1,2</sup> G. S. Taverna,<sup>3</sup> C. A. Canto,<sup>1</sup> L.K. Whalley,<sup>1,2</sup> M. T. Baeza-Romero,<sup>4</sup> P.W. Seakins,<sup>1,2</sup> M. P. Chipperfield,<sup>2,3</sup> D. E. Heard,<sup>1,2</sup>

<sup>1</sup> School of Chemistry, University of Leeds. Leeds. UK

<sup>2</sup> National Centre for Atmospheric Science, University of Leeds, Leeds, UK

<sup>3</sup> School of Earth and Environment, University of Leeds, LS2 9JT, UK

<sup>4</sup> Escuela de Ingeniería Industrial, Universidad de Castilla-La Mancha, 45071, Toledo, Spain

\* Corresponding author: chm1drm@leeds.ac.uk

It is suggested that injection of TiO<sub>2</sub> particles into the stratosphere to back-scatter solar radiation maybe an effective measure to mitigate the effects of global warming. TiO<sub>2</sub> particles are well suited to this application because of their high refractive index (Pope et al., 2012). However, the effect of such a measure to stratospheric chemistry is not fully understood. In addition to this, application of TiO<sub>2</sub> coatings to surfaces within the urban environment, such as tunnel walls and building facades, are used to abate ambient levels of NO<sub>2</sub> resulting from traffic emissions and for their self-cleaning properties.

This study investigates the heterogeneous reaction between airborne sub-micron TiO<sub>2</sub> particles and HO<sub>2</sub> radicals using an aerosol flow tube and the FAGE (fluorescence assay by gas expansion) technique. The dependence of the uptake coefficient ( $\gamma_{\text{HO}_2}$ ) to relative humidity (RH) and to intensity of exposure to near-UV light has been determined. Experiments performed in dark conditions at the most stratospherically relevant conditions within this study (RH = 11.1%) determined  $\gamma_{\text{HO}_2} = (2.08 \pm 0.11) \times 10^{-2}$ . A positive dependence of  $\gamma_{\text{HO}_2}$  with RH was observed which showed a correlation between  $\gamma_{\text{HO}_2}$  and the number of monolayers of water adsorbed on the particle surface. These results suggest that solvation of HO<sub>2</sub> by water adsorbed on the TiO<sub>2</sub> surface followed by self-reaction, reaction with its conjugate base or possibly other reactions in the aqueous phase drives the heterogeneous reactions.

Experiments illuminated with near-UV light (365 nm) were performed and showed significant production of OH and HO<sub>2</sub> from the aerosols into the gas phase. The concentrations were dependent on light flux, RH and total particle surface area. While the production of HO<sub>x</sub> in the gas phase has been observed close to TiO<sub>2</sub> surfaces<sup>2,3</sup> it is believed that this phenomena has not been observed from airborne TiO<sub>2</sub> particles and parameterized in this way before.

The stratospheric chemistry model TOMCAT, was used to predict the effect of the injection of TiO<sub>2</sub> particles into the stratosphere on levels of [HO<sub>2</sub>] and [O<sub>3</sub>].

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## References

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