

We thank the two anonymous referees and D. Visioni for their helpful comments.

We have replied to each point in turn below, the comments are given in italics first, with our response then given in normal type. Where appropriate, the text for the revised manuscript then follows in red type within speech marks.

Anonymous Referee #1

Clearly you are a Shakespearean scholar! Thanks for the adapted quotation from “A midsummer night’s dream”.

Comment 1: P2 L41 "showing sulphate aerosols to be unsuitable for solar radiation management" - this line is too strong. There are arguments why sulphate, or indeed any aerosol, should not be used. But if aerosol injection is to be considered, then sulphate is a significant contender by virtue of being nature’s choice. i.e. in its favour is that there are natural experiments (volcanoes) with which to evaluate its performance and there are unlikely to be any surprises. The same cannot be said of titania.

Response 1: We entirely agree. We have softened the language. We discuss the eruption of Mt Pinatubo and the subsequent effects of the increased sulphate aerosol on observed stratospheric ozone concentrations. The revised text is stated as follows:

“showing that sulphate aerosols could be unsuitable for solar radiation management”

Comment 2: P4 L96 - be more precise about the temperature that the experiment was conducted at, provide mean and standard deviation, rather than ~293 K.

Response 2: All experiments were conducted at room temperature. However, due to the time it takes to conduct an experiment not all experiments could be conducted on the same day. The average temperature across all experiments was 293 K. The standard deviation of the temperatures was 3 K. This has been stated in the new manuscript as follows:

“A schematic diagram of the experiment is shown in Figure 1, and all experiments were undertaken at room temperature (293 ± 3 K) and under normal laboratory levels of illumination.”

Comment 3: P4 L98 - what is the flow tube material? What wavelengths of light are omitted when the flow tube is shrouded?

Response 3: The aerosol flow tube was made of borosilicate glass. The experiments were conducted within a laser laboratory where there is no natural light present. Any light that could enter the flow tube would originate from the standard fluorescence strip lights in the laboratory. Therefore the wavelengths of light omitted when the flow tube is shrouded would be within the visible wavelength region.

“In this investigation a borosilicate glass aerosol flow tube coupled with a sensitive HO₂ detector based on chemical conversion followed by laser-induced fluorescence detection of

OH (George et al., 2013) has been used to study the kinetics of the heterogeneous reaction of HO₂ with airborne TiO₂ nanoparticles at different RH.”

Comment 4: P5 L117 - what form of titania was used (rutile, anatase etc.)? N.b. the surface characteristics of different forms of titania might have different surface reactivity.

Response 4: We specify that the titania used is a blend known as Degussa (P5 L117), which consists of 80% anatase and 20% rutile. This particular blend is often used within laboratory experiments and is readily available.

“A solution of TiO₂ (Aldrich Chemistry 718467, 99.5% Degussa i.e. a blend of TiO₂ polymorphs 80% anatase and 20% rutile, 5 g in 500 ml of Milli-Q water) was placed in a commercial atomizer (TSI 3076) in order to produce a 1 L min⁻¹ flow entrained with TiO₂ particles, referred to as the aerosol flow.”

Comment 5: P5 L136 - why do the particle diameters vary under different RH conditions? Titania is not significantly hygroscopic (as shown later in the paper with only monolayers of water being present at RH < 70%) so what is causing the size changes? Is it size dependent particle losses?

Response 5: We are unsure ourselves to the precise reason for this, however, we agree that the cause may be associated with differences in aerosol transmission through the experimental setup at different RH before aerosols reach the flow tube. However, by placing the SMPS before and after the aerosol flow tube we have shown that there is not significant losses of aerosol in the flow tube. Another possible reason could be that aerosol generation could change slightly from day to day due, for example, to a blockage in some parts of the delivery set up (the measurements of the size distribution at the two RH were not done in the same day).

Comment 6: P11 L265 - define V_{bridge}

Response 6: V_{bridge} is defined as an oxygen vacancy within the main body of the text on P12 L272. We have defined it at first usage here in the caption.

“Figure 6. Simplified diagram of the important steps of HO₂ reactive uptake onto the surface of TiO₂. Grey circles = Ti, blue circles = O, orange circles = H, green circles = oxygen vacancy (V_{bridge}), solid black lines = chemical bond and dashed lines = hydrogen bond.”

Comment 7: P14 L349 - only one SEM image is shown, presumably other images showed similar sphericity to the particle shown in Fig.7?

Response 7: Many other images were taken which do indeed show that all particles are spherical, however, due to the method of sample preparation for the SEM it was difficult to find a particle in isolation as most were agglomerated together.

Comment 8: P366 L366 - note that a gamma of 1 implies every collision is reactive. This result maybe implies the laboratory work was not required?

If the measured HO₂ uptake coefficient at room temperature is used, then the model shows that this reaction has negligible effect on stratospheric O₃ or HO₂. However, as outlined in the paper, the uptake coefficient is likely to be much higher at the very low temperatures found in the stratosphere. It is not possible to measure the uptake coefficient at these temperatures, and so a value of 1 (the highest possible) was assumed. The impact on O₃ and HO₂ is still small, but there is an effect. However, although the experimental values are not used in the model, the experiments are still very valuable, as they enable the mechanism for uptake of HO₂ on TiO₂ to be explored. In addition, TiO₂ provides a good model for mineral dusts and hence these experiments aid to help the interpretation of uptake of trace gases onto mineral dusts. The use of TiO₂ as an environmental catalyst is also not confined to the stratosphere and the dataset may be relevant for tropospheric applications of TiO₂ aerosols, for example in its use for the surface oxidation of pollutants such as VOCs and NO₂.

Comment 9: P15 L388 - insert "to" in "...in order (to) follow..."

Response 9: This has been amended.

"N₂O₅ is decreased by up to 0.5% in the region of TiO₂ particles, which is assumed to follow the distribution of sulphate particles after the Mt. Pinatubo eruption, in order to follow the approach of previous modelling studies."

Comment 10: P16 L395 - the deviation between the consequences of N₂O₅ uptake between this study and the study of Tang et al. is interesting. A plausible explanation is provided but the authors are encouraged to discuss this discrepancy with the Tang et al. modellers (if they have not already).

Response 10: Prior to submission we had a brief verbal discussion with Dr James Keeble (University of Cambridge) who performed the modelling work in Tang et al (2014). Based on that discussion we suggested possible deviations in the modelling approaches which may be responsible for the differences in the N₂O₅ response. Following this review comment we have been in further contact with Dr Keeble. This has not led to any definitive conclusions, as that would require significant extra work. However, along the lines suggested by the reviewer we have agreed to keep in contact and investigate these differences in future work. We have mentioned the need for further work in the text.

"Production of OH and HO₂ from irradiated TiO₂ surfaces should be evaluated in future studies together with studies of uptake at lower temperature to fully understand the consequences of injection of TiO₂ particles into the stratosphere".

Anonymous Referee #2

Comment 1: *The experiments were conducted very carefully but I question the authors' choice to study this reaction at room temperature when the relevant temperatures for solar geoengineering aerosol would be much lower. They did a careful study of the impact of adsorbed water on the reaction but this is irrelevant for stratospheric conditions. This dataset*

is valuable, even for our understanding of mineral dust chemistry in the troposphere, but the relevance for the stratosphere is in question.

Response 1: We acknowledge in the manuscript that the experiments were not conducted at stratospherically relevant temperatures, and state the experimental difficulties which prevent us from performing experiments at such temperatures (P3 L86, P14 L365). However, this represents the first measurements of HO₂ onto TiO₂ aerosols, and stratospheric TiO₂ injection has been suggested as a mitigation strategy. Both previous studies of N₂O₅ and ClONO₂ onto TiO₂ aerosols by Tang et al. were also conducted only at room temperature for the same reason. Although the application is framed within the context of stratospheric injection of aerosols for solar radiation management schemes, we agree that the dataset is also valuable for our understanding of mineral dust chemistry in the troposphere and evaluating the feasibility of other environmental catalytic applications of TiO₂ within the troposphere such as removal of VOCs and NO₂.

Comment 2: In the comparison to existing datasets, instead of comparing the reactive uptake coefficient for HO₂ on TiO₂ to other species on TiO₂, which is like comparing to apples to oranges, you can perhaps look at trends (ClONO₂ on H₂SO₄ vs. TiO₂ and HO₂ on H₂SO₄ vs. TiO₂, etc).

Response 2: We accept this point although it is still useful to compare the behaviour of HO₂ towards TiO₂ aerosols with the very few other studies of uptake of trace gases onto TiO₂ aerosols, as it gives the opportunity to compare and contrast the likely mechanisms for uptake of trace gases onto TiO₂ aerosols. There have been very limited studies of HO₂ uptake onto solid surfaces which have been coated with H₂SO₄ aerosol material (Gershenson et al., Faraday Discussions, 1995, 100, 83-100) and we have included a comparison of these experiments with uptake onto TiO₂. The modified text is as follows:

“Measurements of $\gamma(\text{HO}_2)$ have been made onto sulphuric acid aerosols and thin films. These values are not consistent and range from > 0.1 to < 0.01 (Cooper and Abbatt, 1996; Thornton and Abbatt, 2005; Hanson et al., 1992; Gershenson et al., 1995). The most recent measurement of $\gamma(\text{HO}_2)$ on aqueous phase sulphuric acid aerosols was conducted at 35% RH (Thornton and Abbatt, 2005). That study estimated a value of $\gamma(\text{HO}_2) = 0.006 \pm 0.004$, lower than onto TiO₂ aerosols. Whilst the aerosols in that study are unlike sulphuric acid aerosols in the stratosphere, formed via condensation of sulphuric acid vapour onto existing solid aerosols, the relatively low value of $\gamma(\text{HO}_2)$ measured is consistent with the likely low partitioning of HO₂ to its more reactive conjugate base, O₂⁻, and a lower solubility of HO₂ in aerosols with a low pH. The study concludes that heterogeneous uptake of HO₂ onto sulphuric acid aerosols would show a strong negative temperature dependence driven by the temperature dependence of the Henry’s Law coefficient. It is likely that at temperatures typical of the lower stratosphere (205 – 215 K) $\gamma(\text{HO}_2)$ onto sulphuric acid particles approach 1 (Gershenson et al., 1995).”

References:

Cooper, P. L., and Abbatt, J. P. D.: Heterogeneous interactions of OH and HO₂ radicals with surfaces characteristic of atmospheric particulate matter, *Journal of Physical Chemistry*, 100, 2249-2254, 1996.

Thornton, J., and Abbatt, J. P. D.: Measurements of HO₂ uptake to aqueous aerosol: Mass accommodation coefficients and net reactive loss, *J. Geophys. Res.-Atmos.*, 110, 10.1029/2004jd005402, 2005.

Hanson, D. R., Burkholder, J. B., Howard, C. J., and Ravishankara, A. R.: Measurement of hydroxyl and hydroperoxy radical uptake coefficients on water and sulfuric acid surfaces, *The Journal of Physical Chemistry*, 96, 4979-4985, 10.1021/j100191a046, 1992.

Gershenson, Y. M., Grigorieva, V. M., Ivanov, A. V., and Remorov, R. G.: O₃ and OH sensitivity to heterogeneous sinks of HO_x and CH₃O₂ on aerosol particles, *Faraday Discussions*, 100, 83-100, 1995.

Comment from Daniele Visoni

Comment 1: I find this paper very interesting, and laboratory work on the topic of solar radiation management very promising. However, I have a comment regarding the discussion on sulfate geoengineering (SG) in the Introduction. In particular, while on line 34- 35 effects on ozone depletion by SG are mentioned, in the following lines only old papers discussing ozone measurements after the Pinatubo eruption are mentioned, and from that comes the conclusion that those result are "showing sulphate aerosols to be unsuitable for solar radiation management". However, in recent years many papers regarding possible SG consequences on ozone depletion have been published. Discussion paper if this would not change the scope of the paper itself, since it focuses on TiO₂ particles, I would suggest adding some updated citations on the matter just to represent in an objective way the ongoing discussion of solar radiation management methods. I include some possible papers to be cited regarding SG

Response 1: This comment is helpful, thank you, and the introduction have be amended accordingly to include citation of the 2017 Review on sulfate geoengineering. The following text has been added:

"The impact of sulphate geoengineering to stratospheric ozone concentrations is projected to decrease in time as concentrations of Br and Cl containing atmospheric species are expected to fall, so much so that beyond 2050 the additional available surface area provided by sulphate geoengineering is predicted to enhance conversion of NO_x (NO_x = NO + NO₂) to HNO₃ resulting in an increase of stratospheric ozone (Visoni et al., 2017)."

Reference:

Visoni, D., Pitari, G., and Aquila, V.: Sulfate geoengineering: a review of the factors controlling the needed injection of sulfur dioxide, *Atmos. Chem. Phys.*, 17, 3879-3889, 10.5194/acp-17-3879-2017, 2017.

Heterogeneous reaction of HO₂ with airborne TiO₂ particles and its implication for climate change mitigation strategies

Daniel R. Moon¹, Giorgio S. Taverna², Clara Anduix-Canto¹, Trevor Ingham^{1,3}, Martyn P. Chipperfield^{2,3}, Paul W. Seakins^{1,3}, Maria-Teresa Baeza-Romero⁴, Dwayne E. Heard^{1,3}*

¹ School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK

² School of Earth and Environment, University of Leeds, LS2 9JT, UK

³ National Centre for Atmospheric Science, School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK

⁴ Escuela de Ingeniería Industrial, Universidad de Castilla-La Mancha, 45071, Toledo, Spain

* Corresponding author. Email: d.e.heard@leeds.ac.uk

Abstract.

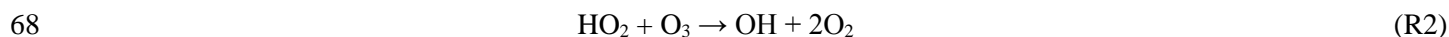
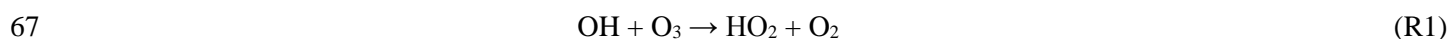
One geoengineering mitigation strategy for global temperature rises resulting from the increased concentrations of greenhouse gases is to inject particles into the stratosphere to scatter solar radiation back to space, with TiO₂ particles emerging as a possible candidate. Uptake coefficients of HO₂, $\gamma(\text{HO}_2)$, onto sub-micrometre TiO₂ particles were measured at room temperature and different relative humidities (RH) using an atmospheric pressure aerosol flow tube coupled to a sensitive HO₂ detector. Values of $\gamma(\text{HO}_2)$ increased from 0.021 ± 0.001 to 0.036 ± 0.007 as the RH was increased from 11% to 66%, and the increase in $\gamma(\text{HO}_2)$ correlated with the number of monolayers of water surrounding the TiO₂ particles. The impact of the uptake of HO₂ onto TiO₂ particles on stratospheric concentrations of HO₂ and O₃ was simulated using the TOMCAT three-dimensional chemical transport model. The model showed that by injecting the amount of TiO₂ required to achieve the same cooling effect as the Mt. Pinatubo eruption, heterogeneous reactions between HO₂ and TiO₂ would have a negligible effect on stratospheric concentrations of HO₂ and O₃.

27 1. Introduction

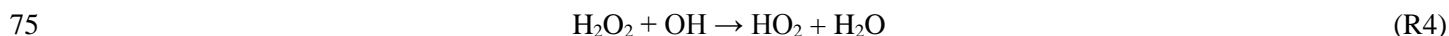
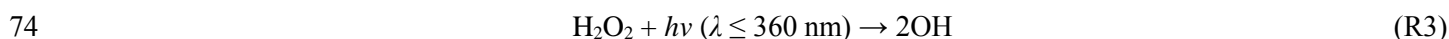
28 It has been suggested that injection of aerosols into the stratosphere in order to scatter solar radiation back to space
29 could be a possible solar radiation management scheme (Shepherd and Working Group on Geoengineering the
30 Climate, 2009). Such a scheme would have the effect of cooling the Earth's surface and serve as a measure to
31 mitigate enhanced global warming. A possible candidate for stratospheric injection is sulphuric acid aerosols as these
32 aerosols occur naturally in the stratosphere. These aerosols are formed by transport of precursors, e.g. SO₂ and
33 carbonyl sulphide (OCS), from the troposphere to the stratosphere (Holloway and Wayne, 2010), which form
34 sulphuric acid vapour that condenses onto particles. However, injection of these particles could have important
35 negative effects on the stratosphere through enhanced ozone depletion. Concentrations of sulphate aerosols can
36 increase dramatically as the result of volcanic eruptions. Following the eruption of Mt. Pinatubo in 1991, it was
37 estimated that around 30 Tg of H₂SO₄ was injected in the stratosphere, dramatically increasing stratospheric aerosol
38 loading and hence the available surface area for heterogeneous chemistry to occur. Following this volcanic event,
39 the average global lower tropospheric temperature decreased by 0.5 K (Dutton and Christy, 1992), however,
40 stratospheric ozone concentrations reached a record low in northern mid-latitudes (Dutton and Christy,
41 1992;McCormick et al., 1995) showing that sulphate aerosols could be unsuitable for solar radiation management.
42 The impact of sulphate geoengineering to stratospheric ozone concentrations is projected to decrease in time as
43 concentrations of Br and Cl containing atmospheric species are expected fall, so much so that beyond 2050 the
44 additional available surface area provided by sulphate geoengineering is predicted to enhance conversion of NO_x
45 (NO_x = NO + NO₂) to HNO₃ resulting in an increase of stratospheric ozone (Visioni et al., 2017). Other candidates
46 for particle types, such as TiO₂, have been put forward due to their large refractive indices (Pope et al., 2012), meaning
47 that less stratospheric aerosol loading would be necessary to achieve the same level of cooling. The refractive index
48 of TiO₂ at 550 nm is 2.5 compared to a value of 1.5 for naturally occurring sulphate aerosols (Tang et al., 2014).
49 Assuming that the size of TiO₂ particles can be optimised, it has been reported that to achieve the same cooling effect
50 that sulphate aerosols had during the Mt. Pinatubo event, approximately three times less in mass, and seven times
51 less in volume of TiO₂ would be required compared with sulphuric acid (Pope et al., 2012). However, the impacts
52 of the presence of TiO₂ particles on stratospheric chemistry have to be determined before this kind of geoengineering
53 solution can be considered. Mineral dust particles are commonly found in the troposphere and contribute the largest
54 fraction to tropospheric aerosol loading in terms of mass (Textor et al., 2006;Huneus et al., 2011). Typically TiO₂
55 (which is classified as a mineral) constitutes from 0.1% to 10% of overall atmospheric mineral dust loading depending
56 on the location of sources (Usher et al., 2003;Karagulian et al., 2006).

57 The heterogeneous chemistry of sulphate aerosols in the stratosphere is fairly well understood (Ammann et al., 2013);
58 for example the conversion of NO_x to nitric acid in the aerosol via N₂O₅ adsorption and reaction, and also the
59 activation of chlorine via the reaction of ClONO₂ with HCl to form Cl₂ and nitric acid within cold aerosols. However,
60 the heterogeneous reactivity of mineral particles, in particular TiO₂, is not as well understood. Removal and
61 production of trace gases in the stratosphere may significantly perturb concentrations of O₃, therefore it is important
62 when assessing the potential impact of such a solar radiation management scheme to evaluate the kinetics of likely
63 heterogeneous chemistry.

64 The hydroperoxyl radical, HO₂, is an important species within the stratosphere, being present at about 5 parts per
65 trillion per unit volume (pptv) around the tropopause, and is involved in a HO_x catalytic cycle responsible for about
66 40% of O₃ depletion in the lower stratosphere via to the following reactions (Wennberg, 1994):



70 Moreover, HO₂ can also react with stratospheric ClO and BrO to produce HOCl and HOBr respectively, which can
71 be photolysed to produce further OH and atomic halogen species that can contribute to O₃ loss. HO₂ can undergo
72 self-reaction upon surfaces of mineral dust, which is thought to result in the generation of H₂O₂ (Matthews et al.,
73 2014), whose two predominant removal pathways are photolysis and reaction with OH (Versick et al., 2012):



76 Although the kinetics of the uptake of HO₂ onto Arizona Test Dust (ATD), a proxy of mineral dust, has been
77 previously investigated (Matthews et al., 2014; Bedjanian et al., 2013) the heterogeneous reaction of HO₂ with TiO₂
78 has not been studied. However, the kinetics of N₂O₅ uptake (Tang et al., 2014) and ClONO₂ (Tang et al., 2016) onto
79 TiO₂ have been studied. The heterogeneous reaction of N₂O₅ results in the conversion to reactive nitrogen oxides
80 (NO and NO₂) involved in a catalytic cycle that leads to significant O₃ depletion and non-reactive HNO₃. The reactive
81 uptake coefficient, γ , which is the probability that a species will collide with an aerosol and be removed by reaction,
82 was measured to be more than an order of magnitude larger for HO₂ onto ATD than for N₂O₅ and ClONO₂ onto TiO₂
83 sub-micron particles, and contrasting dependences of γ with relative humidities (RH) were observed. Therefore, by
84 analogy it is expected that HO₂ uptake onto TiO₂ may be faster than N₂O₅ uptake. ClONO₂ uptake by TiO₂ particles
85 resulted in similar values of γ , however, no dependency of γ with RH between 7 – 33% was observed.

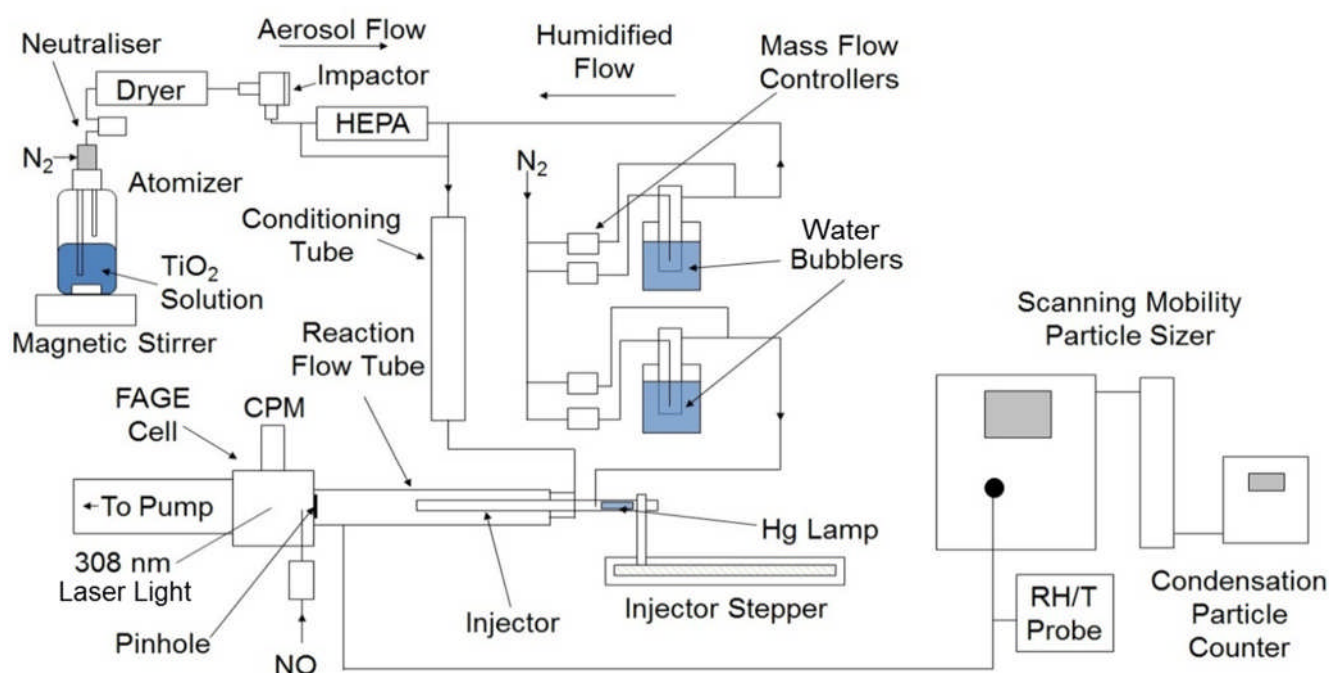
86 In this investigation a borosilicate glass aerosol flow tube coupled with a sensitive HO₂ detector based on chemical
87 conversion followed by laser-induced fluorescence detection of OH (George et al., 2013) has been used to study the
88 kinetics of the heterogeneous reaction of HO₂ with airborne TiO₂ nanoparticles at different RH. While it has been
89 possible here to study such kinetics over a range of RH representative to those typically found in the lower
90 stratosphere (< 40%) (Wennberg, 1994), experimental limitations meant that experiments were only conducted at
91 room temperature (~293 K). The TOMCAT off-line three-dimensional (3D) chemical transport model (Chipperfield;
92 1999) has also been used to predict the likely impact of HO₂ uptake by TiO₂ particles on the stratospheric
93 concentrations of HO₂ and O₃.

94

95 **2. Methods.**

96 **2.1. Overview of experimental apparatus**

97 The experimental setup deployed for this investigation is similar to other investigations of HO₂ uptake by aerosols
98 undertaken at the University of Leeds (George et al., 2013; Matthews et al., 2014; Lakey et al., 2016) therefore a
99 detailed description of the components of the experiment is not given. A schematic diagram of the experiment is
100 shown in Figure 1, and all experiments were undertaken at room temperature (-293 ± 3 K) and under normal
101 laboratory levels of illumination. For some experiments the flow tube was covered with a black shield to eliminate
102 light and no differences in the results were observed.



103
104 **Figure 1.** Schematic diagram of the aerosol flow tube experiment. CPM: Channel Photomultiplier, HEPA: high-
105 efficiency particulate air filter, FAGE: fluorescence assay by gas expansion, RH/T: Relative Humidity/Temperature.

106
107 Compressed nitrogen, which had been passed through a gas purification system (TSI 3074B) consisting of particle
108 filters, a dryer and a carbon filter, was used as the carrier gas for the experiments. A humidified flow of TiO₂ particles
109 was introduced through two inlets located at the rear of the aerosol flow tube and the flow of HO₂ radicals enters the
110 flow tube via the movable injector. The total flow through the flow tube (107 cm length, 5.9 cm I.D.) was 5.4 L
111 min⁻¹ which resulted in a Reynolds number of 130, and therefore is considered laminar as confirmed by radial
112 concentration gradient measurements of gases exiting the injector (George et al., 2013). Experiments consisted of
113 moving the injector using a linear drive (BSL Engineering 15 KR4610A) to different fixed positions along the flow
114 tube (30-70 cm from injector tip to HO₂ detector inlet in steps of 5 cm) corresponding to reaction times between ~ 8
115 and 20 s from the injector, with detection of HO₂ at the end of the flow tube. All gas flows within the experiment
116 were controlled using mass flow controllers (Brookes and MKS). The RH of the flow was measured using a probe

117 (Rotronics) in the exhaust of the flow tube, which itself was calibrated against a dew point hygrometer (Buck
118 Research Instruments CR-4).

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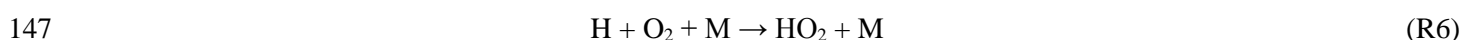
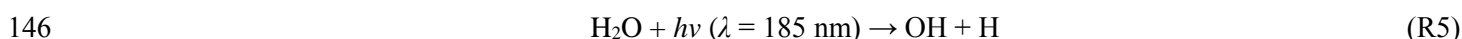
120 2.2. Aerosol Generation and Detection

121 A solution of TiO₂ (Aldrich Chemistry 718467, 99.5% Degussa i.e. a blend of TiO₂ polymorphs 80% anastase and
122 20% rutile, 5 g in 500 ml of Milli-Q water) was placed in a commercial atomizer (TSI 3076) in order to produce a 1
123 L min⁻¹ flow entrained with TiO₂ particles, referred to as the aerosol flow. The aerosol flow was then passed through
124 a neutraliser (Grimm 5522) to reduce static wall losses, a diffusion drier (TSI 3062) and an impactor (TSI 1035900)
125 to ensure larger aerosols, beyond the detection range of the SMPS (~ 750 nm diameter), do not enter the aerosol flow
126 tube. A high-efficiency particulate air (HEPA, PALL Life Sciences) filter situated within a by-pass loop was used
127 to control the number concentration of particles entering the aerosol flow tube. The aerosol flow was then mixed
128 with a humidified flow of nitrogen (3 L min⁻¹) to control the RH within the system. The RH of the humidified flow
129 was altered by changing the ratio of dry nitrogen and nitrogen passed through a water bubbler. This flow was then
130 passed through a conditioning tube (residence time ~ 6 s) before entering the aerosol flow tube to allow time for
131 water adsorption onto the surface of the TiO₂ particles to equilibrate at the given RH.

132 The total surface area of TiO₂ particles available for heterogeneous reaction with HO₂ was measured with a SMPS
133 instrument from the flow exiting the aerosol flow tube. Previous experiments showed that there is a negligible loss
134 of aerosols during the transit of the flow tube (George et al., 2013). The SMPS consisted of a Differential Mobility
135 Analyzer (DMA, TSI 3080, 3081) that creates a monodisperse flow of aerosols based on their electrical mobility
136 which is related to their size. A condensation particle counter (CPC, TSI 3775) connected in parallel to the DMA
137 quantified particle number concentrations. These two instruments connected in parallel can be used to create an
138 aerosol size distribution from which the total surface area and average radius of particles can be calculated by making
139 the assumption that particles are spherical (as demonstrated experimentally in section 3.2 below). The average
140 diameter of the particles is 136 nm and 173 nm at RH = 11% and 37%, respectively.

141 2.3 HO₂ Generation and Detection

142 HO₂ radicals were produced within the movable injector (110 cm length, 1.9 cm O.D., 1.6 cm I.D.) by passing a 1.3
143 L min⁻¹ humidified flow of nitrogen (consisting of a mixture of 0.9 L min⁻¹ of dry N₂ and 0.4 L min⁻¹ N₂ passed
144 through a water bubbler) containing trace amounts of oxygen over a mercury lamp (L.O.T.-Oriol 6035) via the
145 following reactions:



148 OH is also created by the photolysis of water vapour in R5, but no OH was observed exiting the injector, presumably
149 owing to rapid losses at the walls of the injector. HO₂ was sampled by a 0.7 mm diameter pinhole at the end of the
150 flow tube, and after chemical conversion to OH by addition of excess NO (50 sccm, BOC, 99.5 %) just inside the

151 pinhole, laser induced fluorescence (LIF) at low-pressure (the fluorescence assay by gas expansion (FAGE) technique
152 (Heard and Pilling, 2003)) was used to measure OH. The relative LIF signal from converted HO₂ was calibrated
153 using an established method (Winiberg et al., 2015) developed for field measurements of OH and HO₂ radicals.
154 Hence the experiment is able to measure the absolute concentration of HO₂ during passage from the injector to the
155 sampling inlet. The Q₁(2) line of the OH ($A^2\Sigma^+ v' = 0 - X^2\Pi_{1-} v'' = 0$) transition at ~ 308 nm was used to detect OH.
156 A Nd:YAG pumped dye laser (JDSU Q201-HD Q-series, Sirah Cobra Stretch) was used to produce the required 308
157 nm radiation (line width ~ 0.1 cm⁻¹) at a pulse repetition rate of 5 kHz. As the flows through the movable injector
158 (1.3 L min⁻¹) and mercury lamp current (20 mA) were kept constant, it is assumed that the initial HO₂ concentration,
159 [HO₂]₀ (defined in this investigation as [HO₂] at the first injector position, i.e. 30 cm downstream of the injector),
160 determined by calibration to be 1.6 × 10⁹ molecule cm⁻³, was the same for all experiments. These HO₂ concentrations
161 are ~ 50 times higher than typical levels in the sunlit stratosphere (Wennberg et al., 1994). A reference fluorescence
162 cell, in which a large concentration of OH was generated and detected by LIF, was used to facilitate the identification
163 of OH lines and tune the laser wavelength. The FAGE cell was continuously evacuated using a combination of a
164 rotary pump (Edwards, model E1M80) and a roots blower (EH1200), and was kept at 0.8–0.9 Torr, which was
165 monitored using a capacitance monitor (Tylan General, CDC 11).

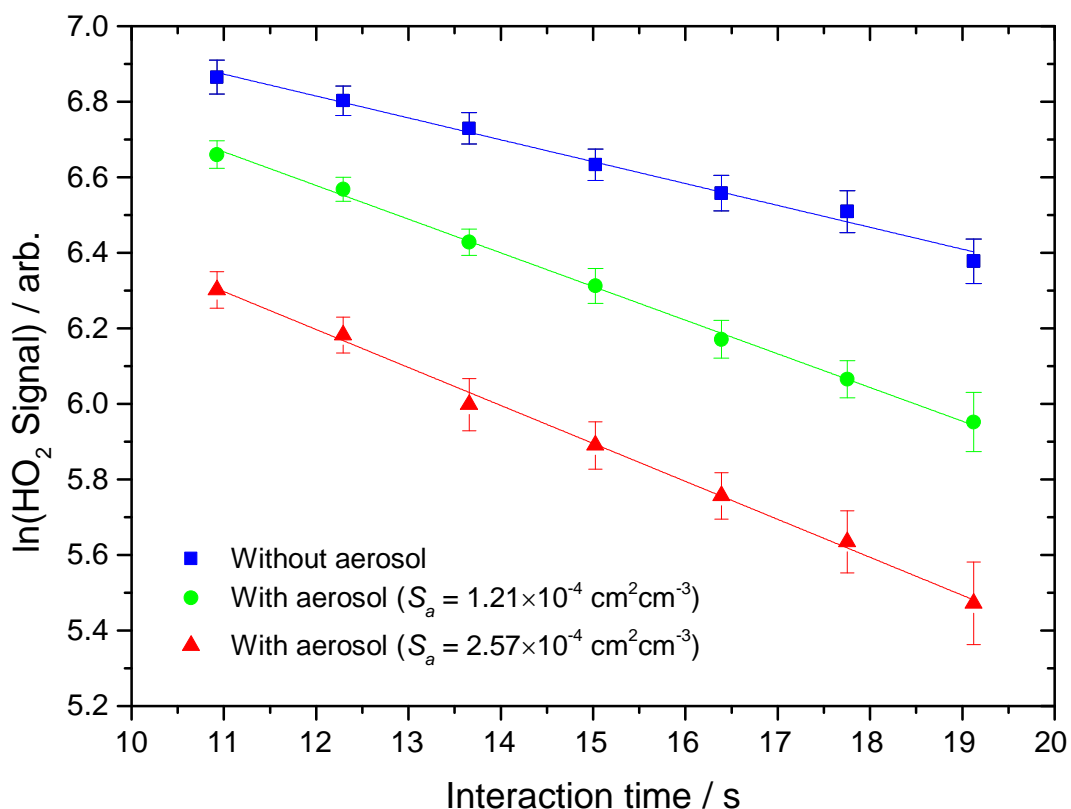
166 2.4. Experimental Procedure and Data Analysis

167 The HO₂ signal was measured at 8 positions as the moveable injector was drawn back from 30 to 70 cm using the
168 linear stepper drive and again as the moveable injector was pushed forwards back to its initial position. The HO₂
169 signal was averaged over 20 s (average of twenty 1 s measurement points, each corresponding to 5000 laser shots) at
170 each injector position with a 22 s delay between measurements at each injector position in order to allow time for
171 mechanical vibrations to subside, and to ensure a full flush of the aerosol flow tube so that the LIF signal corresponds
172 to HO₂ emitted from the injector position being measured. The laser power was recorded for each injector position
173 and used to normalise the HO₂ signal to correct for any fluctuations in laser power (< 5%). The HO₂ signals with the
174 injector moving forwards and backwards were then averaged, and this procedure repeated six times with varying
175 concentrations of aerosols present in the aerosol flow tube. The wall loss rate of HO₂ (k_{wall}) was determined by
176 recording the HO₂ decay in the absence of aerosols, but at the same RH, and was repeated four times for each
177 experiment.

178 The HO₂ concentration as a function of time along the flow tube can be expressed as:

$$179 \quad \ln[\text{HO}_2]_t = \ln[\text{HO}_2]_0 - k_{\text{obs}} t \quad (\text{Eqn. 1})$$

180 where [HO₂]_t and [HO₂]₀ are concentrations of HO₂ at time t and $t = 0$ respectively, and k_{obs} is the observed pseudo-
181 first-order rate coefficient for HO₂ uptake. As the HO₂ signal is directly proportional to the concentration of HO₂,
182 the gradient of a plot of ln(HO₂ Signal) against time (calculated from the injector position and measured flow rate)
183 yields k_{obs} , as shown in Figure 2.



184

185 **Figure 2.** Measured HO₂ signal at different interaction times, in the presence of TiO₂ particles (surface area density
 186 $1.21 \times 10^{-4} \text{ cm}^2 \text{ cm}^{-3}$ and $2.57 \times 10^{-4} \text{ cm}^2 \text{ cm}^{-3}$, green circles and red triangles respectively) and in their absence (blue
 187 squares). The RH in the aerosol flow tube was 11%, the lowest used in this study. The lines represent linear-least
 188 squares fits to the data yielding $k_{\text{obs}} = 0.079 \pm 0.005 \text{ s}^{-1}$ and $k_{\text{obs}} = 0.093 \pm 0.003 \text{ s}^{-1}$ (aerosols present, green circles
 189 and red triangles respectively) and $0.049 \pm 0.003 \text{ s}^{-1}$ (no aerosols, k_{wall}).

190 The flow tube was coated with halocarbon wax (Halocarbon Products Corporation, Halocarbon Wax Series 600) to
 191 reduce HO₂ wall loss rate (k_{wall}) and an average of k_{wall} from several determinations in the absence of aerosols was
 192 subtracted from k_{obs} . A correction (typically about 30%) to account for non-plug flow conditions in the aerosol flow
 193 tube using the procedure outlined by Brown (Brown, 1978) was applied to yield, k' , the pseudo-first-order loss of
 194 HO₂ by heterogeneous reaction with TiO₂ particles. The relationship between k' and total surface area of TiO₂
 195 particles (S_a) can be expressed as (George et al., 2013):

$$196 \quad k' = \frac{w_{\text{HO}_2} \gamma_{\text{obs}} S_a}{4} \quad (\text{Eqn. 2})$$

197 where w_{HO_2} is the mean velocity of HO₂ ($\sim 435 \text{ ms}^{-1}$ at 293 K) and γ_{obs} is the observed reactive uptake coefficient,
 198 obtained from a plot of k' versus S_a , an example of which is given in Figure 3. γ_{obs} was in turn corrected (typically
 199 $\sim 1\%$) to account for the gas diffusion limitation (Fuchs and Sutugin, 1970), to yield $\gamma(\text{HO}_2)$.

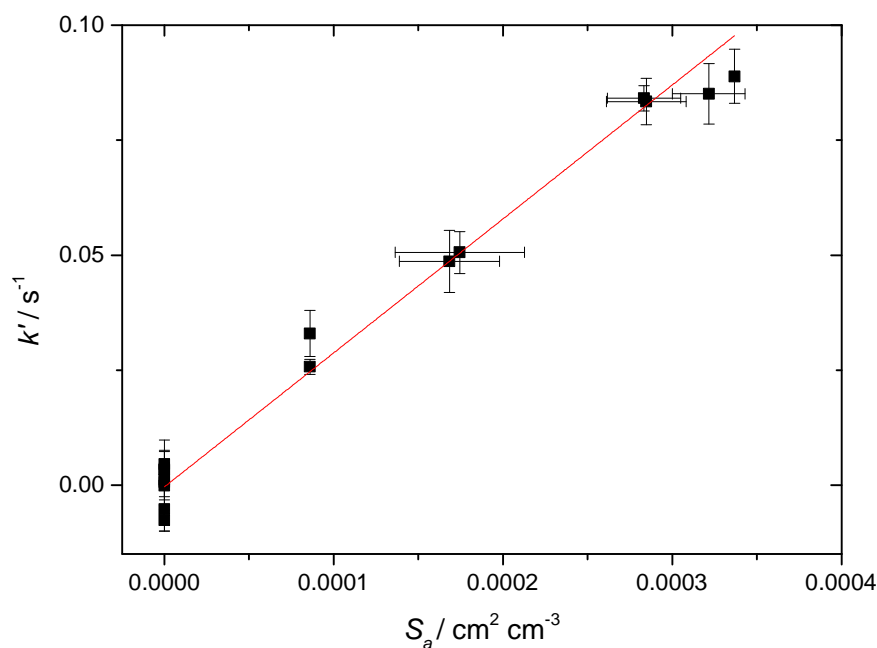


Figure 3. First order rate coefficient for loss of HO₂ due to heterogeneous reaction with TiO₂ particles at different total surface areas for T = 296 K and RH = 37%. The gradient yielded a value of $\gamma(\text{HO}_2) = (2.68 \pm 0.01) \times 10^{-2}$, with the uncertainty representing 2 σ random errors from the fit (95% confidence limits).

2.5. TOMCAT Model Description

The TOMCAT off-line three-dimensional (3D) chemical transport model (CTM) (Chipperfield, 1999, 2006) has been used to predict the impact of the heterogeneous reaction of TiO₂ with HO₂ to stratospheric concentrations of O₃ and HO₂. The model has been widely used in previous studies of stratospheric chemistry and performs well in reproducing stratospheric ozone and the trace species which control its distribution (Chipperfield et al., 2015). The model includes a detailed treatment of stratospheric chemistry of O_x, HO_x, NO_y, Cl_y and Br_y species along with the main source gases. The model has a comprehensive gas-phase chemistry scheme and includes a number of heterogeneous reactions on stratospheric sulphate aerosols and polar stratospheric clouds (Chipperfield, 1999).

The loss rate of HO₂ due to heterogeneous reaction with TiO₂ was included in the model as:

$$k = 0.25 S_a w_{\text{HO}_2} \gamma(\text{HO}_2) \quad (\text{Eqn. 3})$$

where S_a is the surface area density of TiO₂, and w_{HO_2} and $\gamma(\text{HO}_2)$ are defined above. Three TOMCAT simulations were performed at a horizontal resolution of $5.6^\circ \times 5.6^\circ$ and 32 levels from the surface to ~ 60 km. The model was forced with wind and temperature fields from the European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-Interim reanalyses and integrated for 2 years from January 2007 until December 2008, initialised with the output from a standard TOMCAT run which had spun-up from 1977. More information on the model experiments is given in Section 3.3.

222 **3. Results and Discussion**

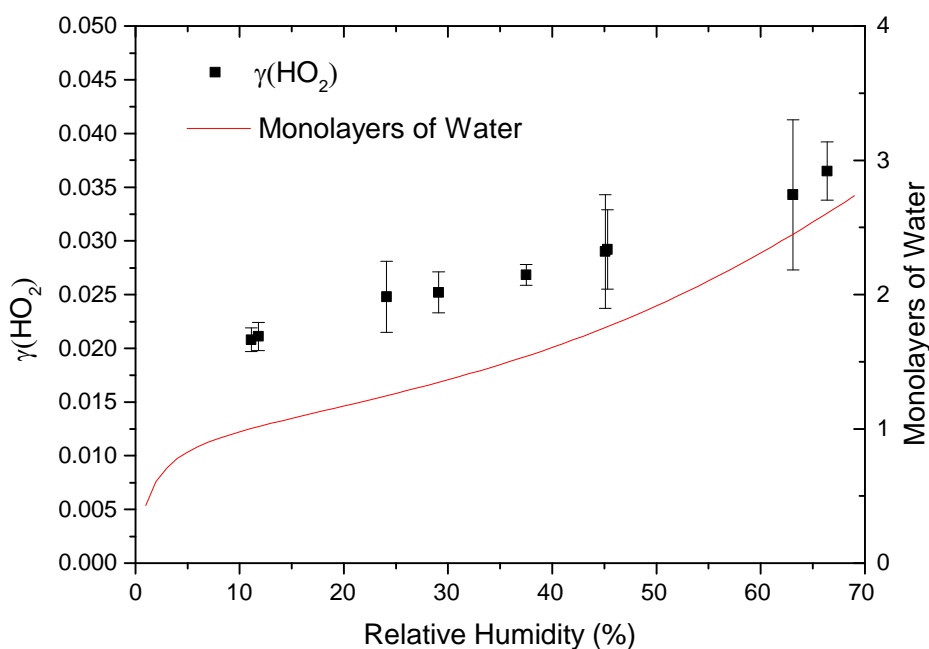
223 **3.1. The reactive uptake coefficient dependence with relative humidity**

224 The reactive uptake coefficient for HO₂ radicals, $\gamma(\text{HO}_2)$, onto TiO₂ particles was determined at eight different RH
 225 (11 - 66%), as shown in Figure 4 and summarised in Table 1. The number of monolayers of water adsorbed onto the
 226 surface of TiO₂ particles has been previously determined experimentally by transmission FTIR spectroscopy
 227 (Goodman et al., 2001), and is also shown as a function of RH in Figure 4.

228 **Table 1.** Reactive HO₂ uptake coefficients, $\gamma(\text{HO}_2)$, for TiO₂ particles at different RH.

RH (%) \pm 1.0	$\gamma(\text{HO}_2) \times 10^{-2}$
11.1	2.08 \pm 0.11
11.8	2.11 \pm 0.13
24.9	2.48 \pm 0.33
29.1	2.54 \pm 0.18
37.5	2.68 \pm 0.09
45.1	2.90 \pm 0.53
45.3	2.92 \pm 0.37
63.1	3.43 \pm 0.27
66.4	3.65 \pm 0.70

229



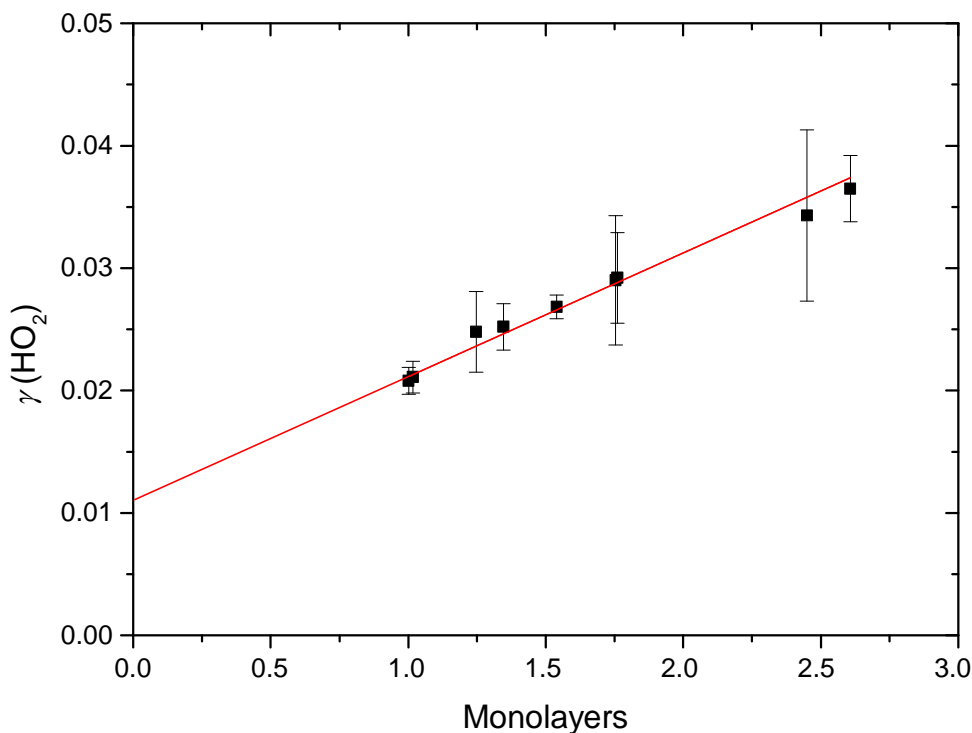
230

231 **Figure 4.** Reactive uptake coefficients of HO₂, $\gamma(\text{HO}_2)$, onto airborne TiO₂ particles (black squares, left y axis) at
 232 different RH for $T = 295 \pm 2$ K. The number of monolayers of the adsorbed water on TiO₂ particles (red curve, right
 233 y axis) at 296 K is also plotted as a function of RH, determined using FTIR spectroscopy (Goodman et al., 2001).

234 The results clearly show a positive dependence of $\gamma(\text{HO}_2)$ across the range of RH investigated, and as shown in Figure
 235 5, $\gamma(\text{HO}_2)$ correlates well with the number of monolayers of water adsorbed onto the TiO_2 particles, V/V_m , determined
 236 by Goodman *et al.* (2001), and which was parameterised by Eqn. 4:

$$237 \quad \frac{V}{V_m} = \left[\frac{c\left(\frac{P}{P_0}\right)}{1-\left(\frac{P}{P_0}\right)} \right] \left[\frac{1-(n+1)\left(\frac{P}{P_0}\right)^n + n\left(\frac{P}{P_0}\right)^{n+1}}{1+(c-1)\left(\frac{P}{P_0}\right) - c\left(\frac{P}{P_0}\right)^{n+1}} \right] \quad (\text{Eqn. 4})$$

238 where V is the volume of gas (water vapour) adsorbed at equilibrium pressure P , V_m is volume of gas necessary to
 239 cover the surface of the adsorbent TiO_2 particles with a complete monolayer, P is the equilibrium pressure of the
 240 adsorbing gas, P_0 is the saturation vapour pressure of the adsorbing gas at that temperature, c is a temperature-
 241 dependent constant related to the enthalpies of adsorption of the first and higher layers and n is the asymptotic limit
 242 of monolayers (~ 8).

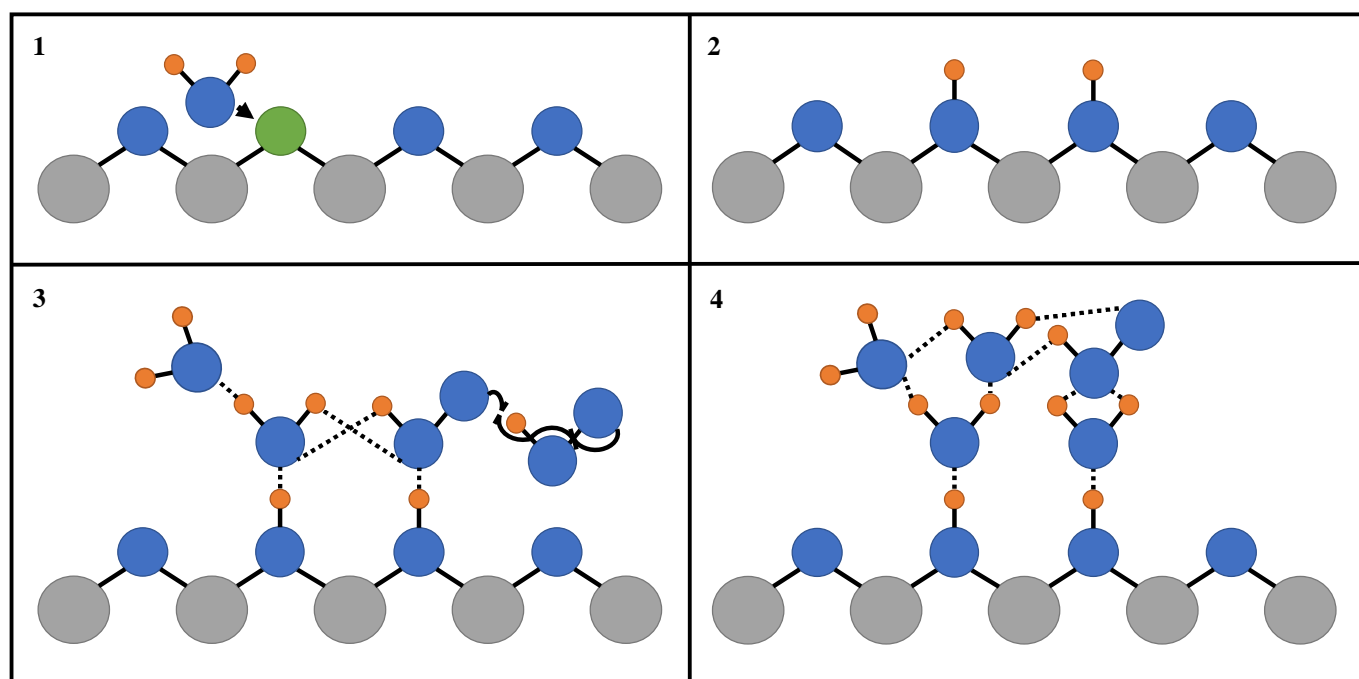


243
 244 **Figure 5.** Variation of the reactive uptake coefficient, $\gamma(\text{HO}_2)$, with the number of monolayers of water surrounding
 245 TiO_2 particles (as determined by Goodman *et al.*, 2001) for $T = 295 \pm 2$ K. The red line represents a linear least-
 246 squares fit to the data ($r^2 = 0.987$).

247
 248 Wall losses of HO_2 also increase as RH is increased within the aerosol flow tube, and so in the absence of aerosols,
 249 the $[\text{HO}_2]$ for a given distance from the injector will decrease with RH. Previous work in this laboratory has shown
 250 that $\gamma(\text{HO}_2)$ for uptake on ATD aerosols increases as the $[\text{HO}_2]$ is lowered (Matthews *et al.*, 2014), and hence some
 251 of the positive dependence of $\gamma(\text{HO}_2)$ with RH shown in Figure 4 might be expected simply owing to the $[\text{HO}_2]$
 252 impinging on the aerosol for a given injector position decreasing with RH. To investigate this further, uptake onto

253 TiO₂ at RH = 11% was measured as a function of [HO₂]₀ exiting the injector, and $\gamma(\text{HO}_2)$ increased from 2.08×10^{-2}
 254 to 2.72×10^{-2} as [HO₂]₀ was decreased from 1.6×10^9 molecule cm⁻³ to 8.9×10^8 molecule cm⁻³. However, the wall
 255 loss rate for HO₂ only increased from 0.049 to 0.079 s⁻¹ across the entire range of RH (11% to 66%) resulting in only
 256 a small change in [HO₂], decreases of $\sim 2.6 \times 10^8$ molecule cm⁻³ and $\sim 2.7 \times 10^8$ molecule cm⁻³ at the first and last
 257 injector position, respectively. In previous studies of HO₂ uptake onto ATD (Matthews et al., 2014) it was shown
 258 that the increase of $\gamma(\text{HO}_2)$ with decreasing [HO₂] is linear. Therefore, assuming the same behaviour for uptake onto
 259 TiO₂ particles, the expected change in $\gamma(\text{HO}_2)$ as a result of RH increasing from 11-66% due only to a change in
 260 initial HO₂ concentration is only $\Delta\gamma(\text{HO}_2)=0.0023$ (or $\sim 6\%$ of the averaged measured $\gamma(\text{HO}_2)$ across this range).
 261 Hence the $\uparrow 75\%$ increase in $\gamma(\text{HO}_2)$ observed in Figure 4 across this range of RH is due to another reason.

262 Figure 5 shows that, for the range of RH studied, $\gamma(\text{HO}_2)$ is a linear function of the number of monolayers of water
 263 surrounding a TiO₂ particle, suggesting that water plays a role in the reactive HO₂ uptake process on TiO₂ particles.
 264 Studies using ambient pressure photoelectron spectroscopy (APPEs) (Yamamoto et al., 2008) have shown that water
 265 adsorption on rutile, a polymorph of TiO₂ (110), occurs in distinct steps, as illustrated in Figure 6.



267 **Figure 6.** Simplified diagram of the important steps of HO₂ reactive uptake onto the surface of TiO₂. Grey circles
 268 = Ti, blue circles = O, orange circles = H, green circles = oxygen vacancy (V_{bridge}), solid black lines = chemical
 269 bond and dashed lines = hydrogen bond. Panel 1 shows the diffusion of water molecule towards a bridging O
 270 vacancy. Panel 2 shows the resultant formation of two neighbouring bridging OH groups at the original site of the
 271 O vacancy. Panel 3 shows the bridging OH groups acting as anchoring sites for water and HO₂ adsorption via
 272 hydrogen bonding leading to multilayer water adsorption and HO₂ self-reaction via an Eley-Rideal type
 273 mechanism. Panel 4 shows the build-up of a more extensive hydrogen bonded network as more water molecules
 274 adsorb onto the particle, which stabilises HO₂ increasing its desorption lifetime and hence probability that it will
 275 react.

276 First, water molecules dissociate at O-vacancies (V_{bridge}) in bridge sites, producing a stoichiometric amount of
277 adjacent bridging OH groups ($\text{OH}_{\text{bridge}}$) equal to twice the initial vacancy concentration upon initial exposure of rutile
278 to water vapour:



280 This step takes place even at very low RH, with these bridging OH groups acting as nucleation sites for subsequent
281 water adsorption by anchoring water molecules to form strongly bound $\text{OH-H}_2\text{O}$ complexes. The $\text{OH-H}_2\text{O}$
282 complexes continue to act as nucleation centres for further water adsorption. The wetting properties of TiO_2 (110)
283 are thus driven by moderate amounts of strongly attractive OH sites that nucleate water molecules. These $\text{OH-H}_2\text{O}$
284 complexes have a relatively high enthalpy of adsorption for water of -72 kJ mol^{-1} (Ketteler et al., 2007), whereas
285 additional adsorption of water beyond a monolayer of water coverage is more characterised by enthalpies associated
286 with the bulk enthalpy of water condensation (-45 kJ mol^{-1}) (Chen et al., 2012), explaining the variation of the number
287 of monolayers of water with RH shown in Figure 4. Computational studies (Aloisio and Francisco, 1998) showed
288 that in the gas-phase HO_2 can also readily form complexes with water through hydrogen bonding with a binding
289 energy of 28.9 kJ mol^{-1} . The observed correlation of $\gamma(\text{HO}_2)$ with the number of monolayers of water surrounding
290 TiO_2 particles could be explained by two effects. An increase in the network of hydrogen bonding would increase
291 the stability of a molecular system, $\sim 20.9 \text{ kJ mol}^{-1}$ for each hydrogen bond (Joshi and Ghanty, 2013), or that simply
292 more HO_2 can adsorb onto the particle surface as the number of available sites for hydrogen bonding increases. An
293 increase in the adsorption lifetime of HO_2 owing to the more extended H-bonding network (Joshi and Ghanty, 2013)
294 will result in an increased probability of HO_2 reacting with another HO_2 , increasing the value of $\gamma(\text{HO}_2)$:



296 For up to ~ 2 monolayers of H_2O , an Eley-Rideal (ER) mechanism of a gas phase HO_2 molecule reacting an adsorbed
297 HO_2 is more likely than for two adsorbed HO_2 molecules diffusing together to react via a Langmuir-Hinshelwood
298 (LH) mechanism. The coverage of V_{bridge} across the surface of TiO_2 (110) is 0.125 monolayers (i.e. one vacancy for
299 every eight unit cells) (Ketteler et al., 2007) meaning water will initially adsorb onto the surface of the particle in
300 clusters. As the binding energy of the HO_2 water complex is fairly high, the rate of HO_2 diffusion across the surface
301 after the initial adsorption at a bridging site will be slow, making a LH type mechanism seem unlikely. Above ~ 2
302 monolayers, the adsorbed water clusters will begin to interact with each other via an extended H-bonded network
303 more characteristic of bulk liquid water, allowing HO_2 to diffuse around the thin surface film of water with
304 thermodynamic properties similar to liquid water (Ketteler et al., 2007).

305 The superoxide ion, O_2^- , which is the conjugate base of HO_2 , reacts with HO_2 over a hundred times quicker than with
306 HO_2 via:



308 It is unlikely that O_2^- will form readily on the surface of the particle at low coverages of water. O_2^- can form on
309 surfaces via direct surface-oxygen electron transfer, photo-induced electron transfer, surface intermolecular electron

310 transfer or decomposition of hydrogen peroxide (H_2O_2) (Anpo et al., 1999). The dissociation of HO_2 to O_2^- occurs in
311 bulk liquid ($pK_a = 4.7$, (Thornton and Abbatt, 2005)), however, water surrounding the particles only begins to acquire
312 liquid like properties once the coverage of water is greater than ~ 2 monolayers. If significant formation of O_2^- does
313 occur above ~ 2 monolayers of H_2O , then owing to its much higher reactivity, some deviation from linearity of $\gamma(\text{HO}_2)$
314 versus monolayers of water (Figure 5) might be expected. However, this was not observed, although the number of
315 data points is very limited.

317 3.2. Comparison of $\gamma(\text{HO}_2)$ with literature values

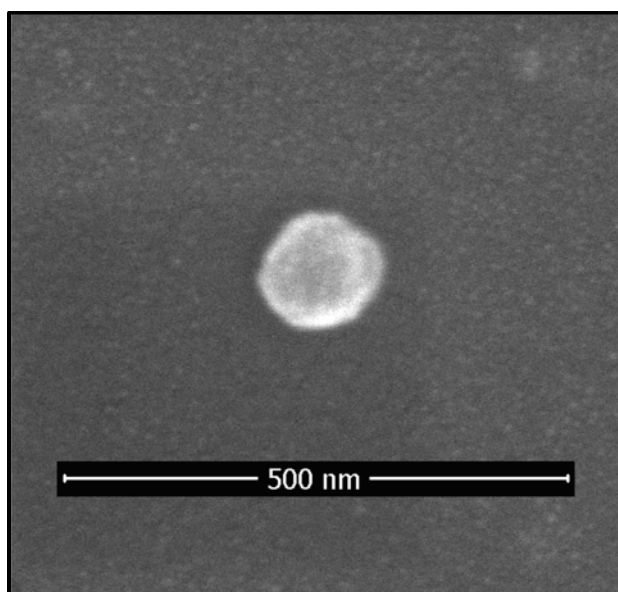
318 There are previous studies of HO_2 uptake onto ATD (Matthews et al., 2014), a proxy for mineral dust, and both N_2O_5
319 (Tang et al., 2014) and ClONO_2 (Tang et al., 2016) uptake onto TiO_2 particles. Values of $\gamma(\text{HO}_2)$ measured for ATD
320 are comparable to those measured onto TiO_2 particles at similar concentrations of HO_2 in the aerosol flow tube
321 ($\gamma(\text{HO}_2)_{\text{ATD}} \sim 0.008 - 0.030$). For ATD, $\gamma(\text{HO}_2)$ was only determined at 4 values of RH, but a general increase with
322 RH was observed (although there was a dip around RH = 50% before a further increase), consistent with HO_2 uptake
323 being driven by the number of defects in the crystal lattice of mineral dust surfaces which provides bridging OH
324 groups upon exposure to water and subsequently by the number of monolayers of water adsorbed onto the surface of
325 such aerosols. The number of monolayers of water on the ATD surface at different RH has been determined
326 (Gustafsson et al., 2005), and also showed a general increase with RH but with a shoulder around RH = 50% where
327 the observed $\gamma(\text{HO}_2)$ also contained a small dip.

328 Values of $\gamma(\text{N}_2\text{O}_5)$ (Tang et al., 2014) and $\gamma(\text{ClONO}_2)$ (Tang et al., 2016) onto TiO_2 particles were an order of
329 magnitude lower than $\gamma(\text{HO}_2)$ and may be associated with the lower polarity of these molecules compared to HO_2 . It
330 is likely that, as with uptake of HO_2 , both N_2O_5 and ClONO_2 react with TiO_2 via complexing with bridging OH
331 groups and adsorbed H_2O , therefore less polar molecules will be less bound to the surface and more likely to desorb
332 back into the gas phase, leading to a smaller γ . The dependence of $\gamma(\text{N}_2\text{O}_5)$ for TiO_2 with RH is also different to that
333 for HO_2 observed here, with a small decrease of $\gamma(\text{N}_2\text{O}_5)$ observed as the RH is increased from $\sim 5 - 23\%$ where a
334 minimum is reached, then beyond 23% $\gamma(\text{N}_2\text{O}_5)$ increases as RH is increased. (Tang et al., 2014). Competition
335 between water and N_2O_5 for surface active OH groups was suggested for the initial observed decrease in $\gamma(\text{N}_2\text{O}_5)$
336 with RH, whereas for RH $> \sim 23\%$ heterogeneous hydrolysis of N_2O_5 to form HNO_3 starts to drive reactive uptake
337 resulting in an increase of $\gamma(\text{N}_2\text{O}_5)$ (Tang et al., 2014). Measurements of $\gamma(\text{ClONO}_2)$ onto TiO_2 particles were only
338 made at two values of RH, insufficient to determine any systematic dependence, although Tang *et al.* (2016) expected
339 $\gamma(\text{ClONO}_2)$ to increase as more water adsorbs onto the surface of TiO_2 particles.

340 Measurements of $\gamma(\text{HO}_2)$ have been made onto sulphuric acid aerosols and thin films. These values are not consistent
341 and range from > 0.1 to < 0.01 (Cooper and Abbatt, 1996; Thornton and Abbatt, 2005; Hanson et al., 1992; Gershenson
342 et al., 1995). The most recent measurement of $\gamma(\text{HO}_2)$ on aqueous phase sulphuric acid aerosols was conducted at
343 35% RH (Thornton and Abbatt, 2005). The study estimated a value of $\gamma(\text{HO}_2) = 0.006 \pm 0.004$, lower than onto
344 TiO_2 aerosols. Whilst these aerosols in that study are unlike sulphuric acid aerosols in the stratosphere, formed via
345 condensation of sulphuric acid vapour onto existing solid aerosols, the relatively low value of $\gamma(\text{HO}_2)$ measured is

346 consistent with the likely low partitioning of HO₂ to its more reactive conjugate base, O₂⁻, and a lower solubility of
347 HO₂ in aerosols with a low pH. The study concludes that heterogeneous uptake of HO₂ onto sulphuric acid aerosols
348 would show a strong negative temperature dependence driven by the temperature dependence of the Henry's Law
349 coefficient. It is likely that at temperatures typical of the lower stratosphere (205 – 215 K) $\gamma(\text{HO}_2)$ onto sulphuric
350 acid particles \approx ~~1~~ approach 1 (Gershenson et al., 1995).

351 George et al. (2013) previously measured $\gamma(\text{HO}_2)$ onto dry salt aerosols. Values of $\gamma(\text{HO}_2)$ for NaCl and (NH₄)₂SO₄
352 at RH values (33 – 54%) below their deliquescence point were below the limit of detection ($\gamma(\text{HO}_2) < 0.004$). Values
353 of $\gamma(\text{HO}_2)$ for TiO₂ reported here (Figure 4 and Table 1) are more than an order of magnitude greater than that of
354 solid salts, even for RH = 11%. A possible explanation for the difference in $\gamma(\text{HO}_2)$ values could be that even though
355 the sizes of the aerosols determined by the SMPS are similar, dry salt aerosols are more spherical in shape than TiO₂
356 particles which may be more fractal in nature. As the SMPS indirectly measures the surface area of aerosols by
357 measuring their mobility through an electric field, an assumption that the aerosol is spherical has to be made. If this
358 is not the case, this may lead to a significant under-prediction of the surface area of non-spherical aerosols and
359 therefore an over-prediction of $\gamma(\text{HO}_2)$. In order to measure the geometry of the TiO₂ particles, a scanning electron
360 microscope (SEM, FEI Nova NanoSEM 450) operating at 3 kV was used to image the TiO₂ nanoparticles used within
361 these experiments. Samples for the SEM were prepared by dispersing the nanoparticles in ethanol and allowing a
362 drop of this solution to dry on a silicon wafer. The wafer with nanoparticles was then mounted on SEM stubs using
363 conductive carbon tapes and coated with 2 nm of Ir, using a Cressington 208HR high resolution sputter coater. Figure
364 7 shows an example of an SEM image providing evidence that the TiO₂ particles are spherical and therefore any error
365 associated with SMPS measurements of surface area is minimal. A more likely explanation for the higher $\gamma(\text{HO}_2)$
366 for TiO₂ particles is that dry salt aerosols do not adsorb a significant amount of water onto their surface until the
367 deliquescence point reached, whereas at RH = 11% Figure 4 shows that the TiO₂ particles already have a monolayer
368 coverage which can form relatively strongly bound complexes with HO₂. Measurements of $\gamma(\text{HO}_2)$ onto aqueous salt
369 aerosols show that $\gamma(\text{HO}_2)$ significantly increases above the deliquescence point (George et al., 2013) and is
370 comparable to $\gamma(\text{HO}_2)$ measured for TiO₂ ($\gamma(\text{HO}_2) \sim 0.01$).



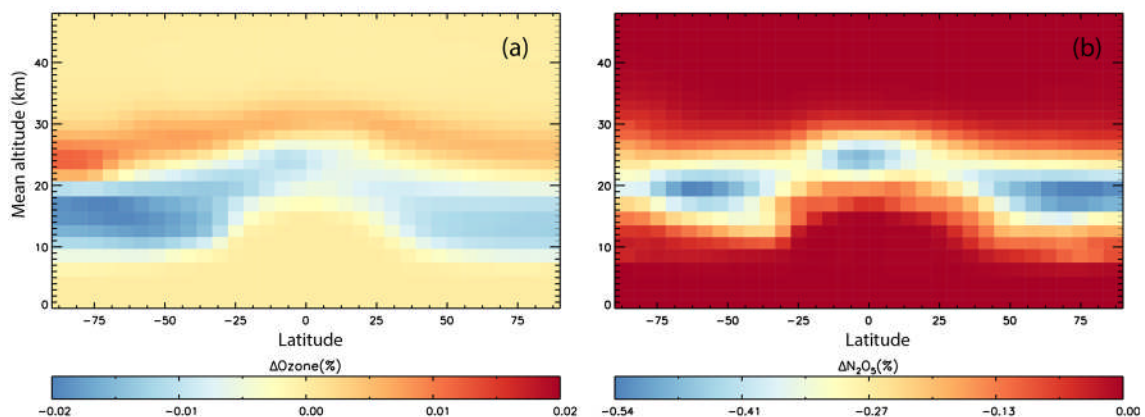
372 **Figure7.** SEM image of a single TiO₂ particle magnified 80,000× used within this study.

373 **3.3 Implications of HO₂ uptake by TiO₂ for stratospheric chemistry**

374 The effect of HO₂ uptake onto TiO₂ particles upon the stratospheric concentrations of HO₂ and O₃ was assessed using
375 the TOMCAT model (Chipperfield, 1999, 2006). At RH relevant to the lower stratosphere (< 40%) the measurements
376 showed that $\gamma(\text{HO}_2)$ is in the range 0.020 - 0.028 at 295 K. An inverse temperature dependence of $\gamma(\text{HO}_2)$ onto dry
377 sea-salt aerosols has previously been observed (Remorov et al., 2002), and although there have been no systematic
378 experimental studies of the temperature dependence of $\gamma(\text{HO}_2)$, parameterisations have developed (Thornton et al.,
379 2008;Macintyre and Evans, 2011). At stratospherically relevant temperatures ($T = 200 - 220$ K), $\gamma(\text{HO}_2)$ is likely to
380 be considerably larger than observed at 295 K, however it is not possible to cool the aerosol flow tube/SMPS system
381 to verify this experimentally. Therefore $\gamma(\text{HO}_2) = 1$ was used in the model simulations representing an upper limit,
382 with three TOMCAT simulations performed as follows. A control simulation, similar to that presented in
383 Chipperfield et al. (2015) did not include TiO₂ particles. A specified latitude-height distribution of TiO₂ particles was
384 then included in two simulations with an effective aerosol surface area density equal to that of sulphate aerosols in
385 1992 the year after the eruption of Mt. Pinatubo. This is an assumption which allows for the fact that less TiO₂ mass
386 is needed in order to produce the same radiative impact as sulphate aerosol from Mt. Pinatubo, but the TiO₂ particle
387 size is smaller. Hence these effects largely cancel (Tang et al., 2014). Stratospheric injection via a geo-engineering
388 solution will result initially in a different distribution of TiO₂ particles compared with after the Mt. Pinatubo eruption,
389 but it is assumed that following mixing and transport the distributions would resemble one another and not lead to
390 any significant difference in model behaviour and the conclusions drawn. Support from this assumption comes from
391 a model run in which a globally uniform distribution of TiO₂ was assumed initially and which yielded very similar
392 results.

393 The first of these simulations included only the loss of N₂O₅ on TiO₂ particles with $\gamma(\text{N}_2\text{O}_5) = 0.005$, the upper limit
394 used in the modelling of Tang et al. (2014), which allows us to compare our results with their study. The second TiO₂
395 simulation also included the loss of HO₂ on TiO₂ particles with a $\gamma(\text{HO}_2) = 1$, as discussed above. Figure 8 shows
396 the impact of including heterogeneous loss of N₂O₅ on TiO₂ particles in the model.

397



398

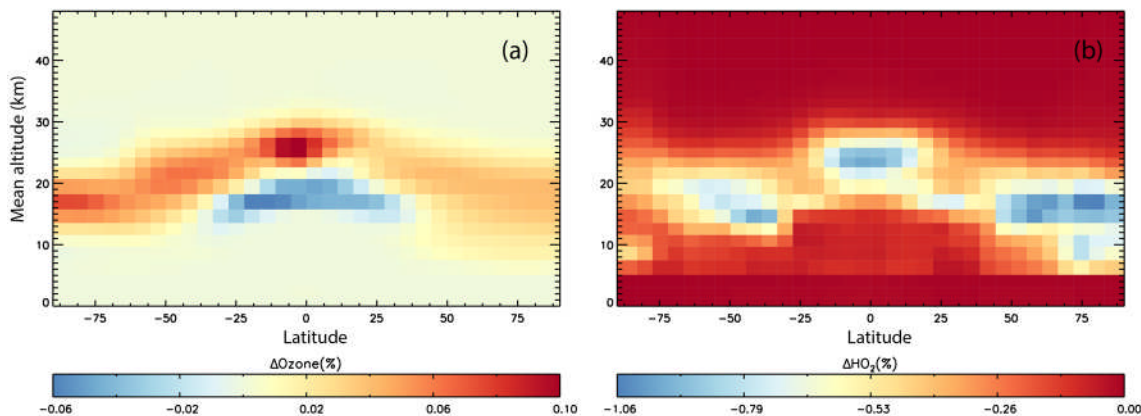
399 **Figure 8.** Annual mean change (%) in atmospheric O₃ (a) and N₂O₅ (b) calculated using the TOMCAT 3-D model
400 from inclusion of heterogeneous loss of N₂O₅ on TiO₂ particles for 2008 and using $\gamma(\text{N}_2\text{O}_5) = 0.005$.

401

402 N₂O₅ is decreased by up to 0.5% in the region of TiO₂ particles, which is assumed to follow the distribution of
403 sulphate particles after the Mt. Pinatubo eruption, in order to follow the approach of previous modelling studies.
404 Assuming a globally uniform distribution initially yielded results that were very similar. Inclusion of uptake is only
405 a minor effect and considerably smaller than the impact of around -20% modelled by Tang et al. (2004) for the same
406 assumed $\gamma(\text{N}_2\text{O}_5) = 0.005$. The reasons for this are not clear, although it is noted that the effect modelled in our off-
407 line chemical transport model, with specified meteorology, is clearly confined to regions of high aerosol loading.
408 The impacts modelled in the nudged chemistry-climate model study of Tang et al. (2004) are not confined to the
409 region of high aerosol and even extend to the upper stratosphere. It is possible that their simulations, although nudged,
410 also include some dynamical feedback which enhances an otherwise small signal. Figure 8 also shows that the
411 resulting impact on O₃ is small with changes less than 0.02%. The model produces a region of slight decrease in the
412 very low stratosphere, with a region of slight increase above.

413 Figure 9 shows results from the simulation which also included the loss of HO₂ on stratospheric TiO₂ particles, and
414 using $\gamma(\text{HO}_2) = 1$ (a simulation using the measured value of $\gamma(\text{HO}_2) = 0.021$ at 295 K led to no impact on O₃ or HO₂).

415



416

417 **Figure 9.** Annual mean change (%) in atmospheric O₃ (a) and HO₂ (b) calculated using the TOMCAT 3-D model
418 from inclusion of heterogeneous loss of HO₂ on TiO₂ particles for 2008, and using $\gamma(\text{HO}_2) = 1$.

419

420 It is evident that HO₂ loss due to heterogeneous reaction between HO₂ and TiO₂ particles in 2008 is < 1% and is
421 confined to the lower stratosphere where it is assumed TiO₂ particles are located. Figure 9 also shows that the
422 subsequent effect of the TiO₂ particles on the O₃ concentrations through the effects of this reaction is also small
423 (< 0.1%), with a small decrease in the tropical upper troposphere/lower stratosphere and a small increase at all
424 latitudes in the lower stratosphere. This small effect of TiO₂ particles on stratospheric HO₂ and O₃ concentrations is

425 due to the reactive nature and short lifetime of HO₂. The species readily reacts with other gas phase species (e.g. O₃)
426 and so loss on TiO₂ surfaces does not compete significantly.

428 **4. Conclusions and further work**

429 The reactive uptake coefficients for the heterogeneous reaction of HO₂ onto TiO₂ particles were measured at different
430 RH and at room temperature for the first time using an aerosol flow tube reactor coupled with a sensitive FAGE HO₂
431 detection system. A range of HO₂ uptake coefficients on TiO₂ particles were measured varying from $\gamma(\text{HO}_2) = 0.021$
432 ± 0.001 to 0.036 ± 0.007 for RH over the range 11% to 66%, respectively. The HO₂ uptake coefficient showed a
433 positive dependence on RH which correlated well with the number of monolayers of water adsorbed onto the TiO₂
434 particle. These results suggest a mechanism by which HO₂ adsorbs to the surface of the TiO₂ particle by forming
435 complexes with water molecules bound to bridging OH groups. As the number of water layers increases so does the
436 network of hydrogen bonds that stabilises HO₂ leading to a longer adsorption lifetime and increased $\gamma(\text{HO}_2)$. The
437 TOMCAT chemical transport model was used to evaluate the possible effects of HO₂ uptake (using an upper limit of
438 $\gamma(\text{HO}_2) = 1$) onto the surface of TiO₂ particles on the stratospheric concentrations of HO₂ and O₃. The amount of
439 TiO₂ used was chosen to achieve a similar cooling to that following the Mt. Pinatubo eruption, but the model predicted
440 a very small loss of both stratospheric HO₂ and O₃. TiO₂ possesses photocatalytic properties and water adsorbed
441 onto its surface may dissociate under stratospheric illumination providing a source of radicals (Chen et al.,
442 2012; Romanias et al., 2012). Production of OH and HO₂ from irradiated TiO₂ surfaces should be evaluated in future
443 studies [together with studies of uptake at lower temperature](#) to fully understand the consequences of injection of TiO₂
444 particles into the stratosphere.

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