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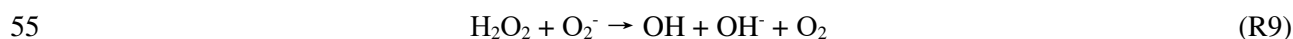
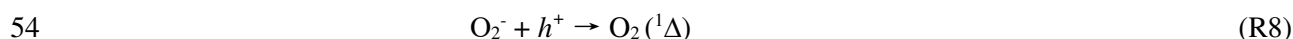
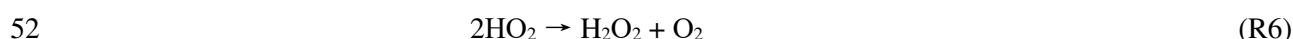
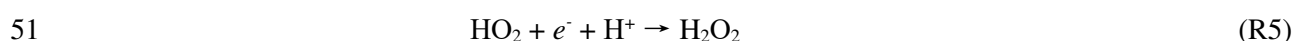
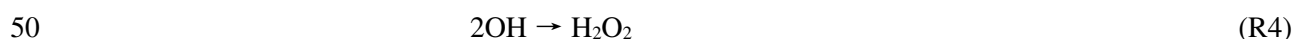
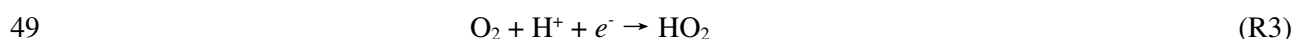
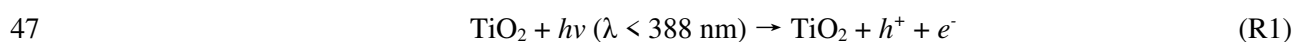
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32 high aerosol surface areas, and was attributed to the decomposition of H₂O₂ at the surface by
33 photogenerated electrons.

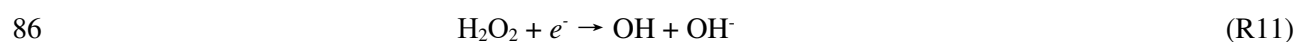
34 1. Introduction

35 The photocatalytic properties of TiO₂ are widely known ^{1, 2} and have been exploited in many
36 applications such as water and air purification and self-cleaning materials. ³ TiO₂ is a semiconductor
37 material and when illuminated with UV light an electron (*e*⁻) is promoted from its valance band into its
38 conduction band also creating a hole (*h*⁺) (R1). The magnitude of the band gap for TiO₂ nanoparticles
39 is ~ 3.2 eV, so there is a wavelength threshold of $\lambda < 388$ nm for TiO₂ to become electronically
40 conductive. ⁴ The *e*⁻ and *h*⁺ pair can migrate to the crystal surface and subsequently oxidise and reduce
41 adsorbed donor and acceptor molecules, respectively. ⁵ One reaction of interest is the oxidation of water
42 by *h*⁺ to produce highly reactive hydroxyl radicals (OH, R2) on the TiO₂ surface. ⁶ Other reactive
43 oxygenated species (ROS), such as the hydroperoxyl radical (HO₂), hydrogen peroxide (H₂O₂) and
44 singlet oxygen (O₂(¹Δ), R3-R10), can also be formed on the surface of TiO₂ materials. The detailed
45 reaction mechanism for the formation of these ROS on the surface of TiO₂ is not well understood,
46 however it is believed to be as follows ⁶:



57 ROS formed on the surface of the TiO₂ catalyst can react with and degrade adsorbed organic compounds
58 making it ideal for air and water purification applications. However, some laboratory studies have
59 shown that some ROS can also desorb from the surface of TiO₂ materials into the gas phase. Lee and
60 Choi ⁷ observed the degradation of soot particles that came within close proximity, but not into direct

61 contact, with an illuminated substrate partially covered with TiO₂. Tatsuma *et al.*⁸ saw the degradation
62 of organic films placed adjacent (up to 2.2 mm) from a TiO₂ film in the presence of light and air. Both
63 experiments indicate possible OH emissions from the surface. Murakami *et al.*⁹ conducted the first
64 study that directly observed gas phase OH radicals using low pressure laser induced fluorescence up to
65 8 mm from illuminated TiO₂ powders. They demonstrated that OH was produced from photocatalytic
66 activity on the surface of the TiO₂ powder through studies using deuterated water vapour, and observed
67 a decrease in OH signal as calcination temperatures of TiO₂ powders were increased. Vincent *et al.*¹⁰
68 and Thiebaud *et al.*¹¹ demonstrated experimentally the formation of OH radicals and H₂O₂ molecules
69 in the gas phase upon irradiation of TiO₂ surface in the presence of H₂O. HO₂ emissions from irradiated
70 TiO₂ surfaces in the presence of gas phase H₂O₂ at low pressures (50 and 200 Torr) were first observed
71 by Bahrini *et al.*⁶ In that study HO₂ was detected up to 44 mm away from the TiO₂ surface using Cavity
72 Ring Down Spectroscopy (cw-CDRS) which directly observed the decomposition of H₂O₂ and
73 production of HO₂ simultaneously. Bahrini *et al.*⁶ showed that significant concentrations of H₂O₂ (1.2
74 × 10¹⁴ molecule cm⁻³) decomposed over 140 s until a steady state concentration was reached. In one
75 example, it was demonstrated that 6.9 × 10¹¹ molecule cm⁻³ of HO₂ was generated in this way. It was
76 concluded that gas phase HO₂ was produced via the decomposition of H₂O₂ by irradiated TiO₂, however
77 the mechanism for the formation of HO₂ was unclear. This study was taken further by Yi *et al.*⁴ who
78 showed that gas phase HO₂ was only produced if H₂O₂ was also present within their system and that
79 using either N₂ or O₂ as carrier gas made little difference in gas phase HO₂ concentrations. This suggests
80 that HO₂ was created via H₂O₂ decomposition and not from photocatalytic reduction of O₂ and that
81 H₂O₂ serves as the electron acceptor as well as an electron donor (R11 – 12). Yi *et al.* also showed that
82 different polymorphs of TiO₂, such as anatase and rutile, perform very differently with some showing
83 rapid degradation of H₂O₂ but little HO₂ emissions and others with slower degradation but with higher
84 emissions of HO₂. Through studies with e⁻ and h⁺ scavengers it was shown that H₂O₂ decomposition is
85 initiated by reaction with e⁻ (R11) or h⁺ (R12) or OH (R13), produced via R2.

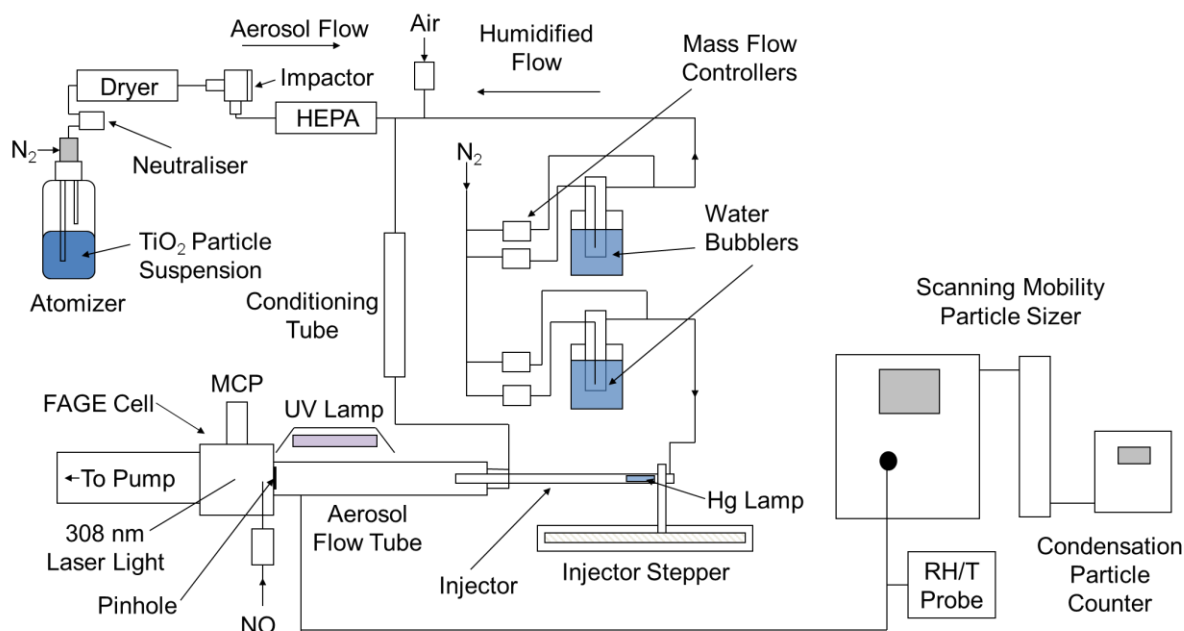


89 This study reports the first direct observation of HO₂ and OH emissions when airborne TiO₂
90 nanoparticles are irradiated with UVA light (320 to 400 nm) in the presence of water vapour and oxygen
91 alone (i.e. with no added H₂O₂) within an aerosol flow tube equipped with a highly sensitive laser
92 induced fluorescence (LIF) detector for OH and HO₂ (limit of detection ~ 1 × 10⁶ molecule cm⁻³).

93 2. Experimental

94 2.1 Overview

95 Figure 1 presents a schematic diagram of the apparatus, with all experiments undertaken at room
96 temperature (293 ± 3 K).



97

98 **Figure 1.** Schematic diagram of the aerosol flow tube experiment. MCP: Multi-Channel Plate
99 photomultiplier, HEPA: high-efficiency particulate air filter, FAGE: fluorescence assay by gas
100 expansion, RH/T: Relative Humidity/Temperature.

101

102 A detailed description of the apparatus, which has been used in a slightly different configuration for
103 uptake studies of HO_2 onto a variety of sub-micron aerosols, is provided elsewhere.¹² In summary, a
104 humidified flow of TiO_2 aerosols was introduced within a laminar aerosol flow tube reactor made from
105 borosilicate glass (107 cm length, 5.9 cm I.D.) held at atmospheric pressure. The TiO_2 aerosols were
106 irradiated with a UV lamp (see section 2.2) placed 5 cm above the aerosol flow tube. The HO_2 signal
107 was then measured at the end of the aerosol flow tube using a laser-induced fluorescence at low pressure,
108 a technique known as Fluorescence Assay by Gas Expansion (FAGE, see section 2.4), after chemical
109 conversion by its reaction with NO to OH .¹³ The size distribution of TiO_2 aerosols within the aerosol
110 flow tube was measured using a Scanning Mobility Particle Sizer (SMPS, see section 2.3) from a flow
111 sampled from the exhaust of the aerosol flow tube. All gas flows within the experiment were controlled
112 using mass flow controllers (Brookes and MKS). The RH and temperature of the flow was measured
113 using a calibrated probe (Rotronics Hygroclip2, accuracy $\pm 0.8\%$ RH and ± 0.1 K) in the exhaust of the
114 aerosol flow tube.

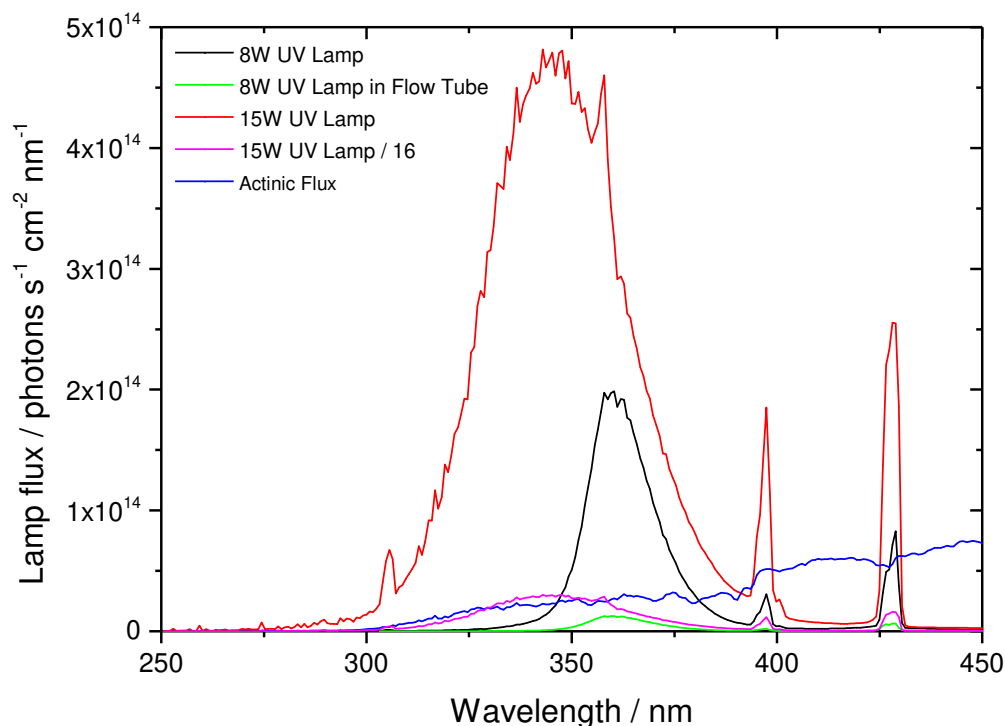
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116 **2.2 Aerosol Irradiation**

117 The aerosol flow tube was illuminated with a UV lamp located adjacent to the FAGE cell and
118 approximately 5 cm above the aerosol flow tube. Two UV lamps were used in this study; a 15 W UVA
119 bench lamp (which has two 420 mm length fluorescent tubes, UVP, XX-15) and an 8 W UVA lamp (1
120 \times 8 W 300 mm length fluorescent tube, Eterna, LFT58WH). The 15 W UVA lamp was used in all
121 studies unless otherwise stated. The absolute lamp fluxes of the lamps as a function of wavelength were
122 measured using a calibrated spectral radiometer (Ocean Optics QE500) as is shown in Figure 2. These
123 fluxes were measured outside the aerosol flow tube since it was not possible to fit the integrating dome
124 of the spectral radiometer within the aerosol flow tube due to space constraints. Both the aerosol flow
125 tube and the halocarbon wax film, which was applied to the walls of the aerosol flow tube to reduce
126 HO₂ wall losses, attenuates light entering the aerosol flow tube. An experiment was conducted where
127 the spectral output of the 8 W lamp whilst it was placed inside the aerosol flow tube was measured with
128 the integrating dome of the spectral radiometer placed outside the aerosol flow tube and positioned
129 where the UV lamps are usually placed (with the same distance from lamp to integrating dome). This
130 experiment showed that the total flux of UVA photons from the 8W lamp (integrated between 250 and
131 388 nm) placed inside the aerosol flow tube was 16 times lower than when the flux was measured with
132 the lamp outside the aerosol flow tube (as shown in Figure 2) for the same lamp to integrating dome
133 distance. Hence the light flux inside of the aerosol flow tube with the lamp placed outside is assumed
134 to be 16 times smaller than shown in Figure 2, although it is realised there are considerable uncertainties,
135 for example the circular nature of the flow-tube may create a heterogeneous light field within the aerosol
136 flow tube and there is an opposite lensing effect for the two cases. The attenuation factor from the
137 tube/wax was found to be approximately constant with wavelength across the spectral output of the 8
138 W lamp, and hence it was assumed for the 15 W lamp (which would not fit within the flow tube) that
139 the flux inside the flow tube would scale in a similar manner and be 16 times lower than shown in
140 Figure 2.

141 Figure 2 also compares the spectral variation of the flux of the lamps to a typical actinic flux spectrum
142 measured at a mid-latitude coastal site in the UK in summer. The amount of light with $\lambda < 388$ nm
143 (threshold for promotion of electron to the TiO₂ conduction band) from the 8W lamp entering the flow
144 tube was ~ 7 times smaller than that from typical actinic fluxes experienced within the troposphere and
145 ~ 5 times smaller than fluxes from the 15 W lamp. The amount of such light emitted from the 15 W
146 lamp entering the flow tube was comparable to typical actinic fluxes, which are 40% greater. There are
147 also notable differences in the emission spectra of the two lamps. The average wavelength emitted
148 from the 15 W lamp (340 nm) is smaller than the 8W lamp (365 nm) and the 15 W lamp emits a broader

149 range of wavelengths in the ultraviolet region (275 – 400 nm) compared to the 8 W lamp (325 – 400
150 nm).



151
152 **Figure 2.** UVA emission spectra for the 8 W UVA lamp inside (green line) and outside (black line) the
153 aerosol flow tube and the 15 W UVA lamp inside (purple line) and outside (red line) the aerosol flow
154 tube, in all cases with the spectral radiometer integrating dome outside the flow tube. In all cases the
155 distance from the lamp to the spectral radiometer integrating dome was constant. The actinic flux (blue
156 line) measured at the Weybourne Atmospheric Observatory (Norfolk Coast, UK, 52°57'N, 1°07'E) on
157 the 1st July 2015 is shown for comparison.

158

159 2.3 Aerosol Generation and Detection

160 A suspension of TiO₂ nanoparticles (Aldrich Chemistry 718467, 99.5% Degussa, 5 g in 500 ml of Milli-
161 Q water) was placed in a commercial atomizer (TSI 3076) which was in turn connected to compressed
162 nitrogen which produced a 3.5 L min⁻¹ flow entrained with TiO₂ particles, of which 1.5 L min⁻¹ was
163 introduced into the apparatus (referred to as the aerosol flow) and the rest left the apparatus through an
164 exhaust. The nanoparticles are composed of 80% anatase and 20% rutile, polymorphs of TiO₂. Similar
165 formulations of TiO₂, such as Degussa P25 (75% anatase and 25% rutile), are widely used in laboratory
166 studies², and have been shown to have enhanced photocatalytic activity as electrons can rapidly transfer
167 from the rutile to anatase crystallites which results in photoactivity occurring at visible wavelengths and
168 creates enhanced catalytic activity at the rutile-anatase interface.¹⁴ The aerosol flow was then passed
169 through a neutraliser to reduce static wall losses, a diffusion drier and an impactor (TSI 1034900) to

170 ensure larger aerosols beyond the detection range of the SMPS (~ 750 nm) do not enter the aerosol flow
171 tube. A high-efficiency particulate air (HEPA, PALL Life Sciences) filter situated within a by-pass
172 loop was used to control the number concentration of particles entering the aerosol flow tube. The
173 aerosol flow was then mixed with a humidified flow of nitrogen to control the RH within the system.
174 The RH of the humidified flow was altered by changing the ratio of dry nitrogen and nitrogen passed
175 through a water bubbler. Oxygen was introduced into the system via zero air (BOC UN1002, 20% O₂
176 and 80% N₂) before the aerosol and humidified flow enters the conditioning tube and controlled using
177 a calibrated mass flow controller (Alicat Scientific). This flow was then passed through a conditioning
178 tube (residence time ~ 5 s) before entering the aerosol flow tube to allow time for adequate mixing of
179 the three flows and water vapour adsorption onto the surface of the TiO₂ particles to equilibrate at the
180 given RH. The combined flow rate through the aerosol flow tube was 5.3 L min⁻¹.

181 The aerosol size distribution and number concentration was measured over a period of 180 s once during
182 each measurement using a Scanning Mobility Particle Sizer (SMPS, TSI 3081) and condensation
183 particle counter (CPC, TSI 3775), from which the total surface area and average radius of particles can
184 be calculated, assuming that particles are spherical. Scanning Electron Microscope images of the TiO₂
185 particles used within the experiments showed that these particles are indeed spherical.¹² Measurements
186 of the size distribution of the TiO₂ aerosols were made at the beginning and end of the aerosol flow tube
187 which showed that there only a small loss of aerosols during transit of the flow tube (< 5%).

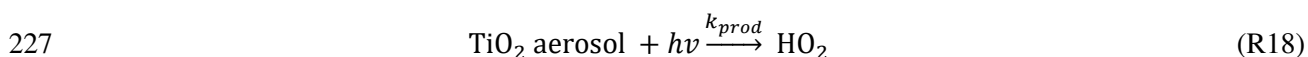
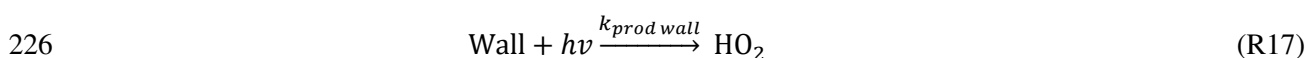
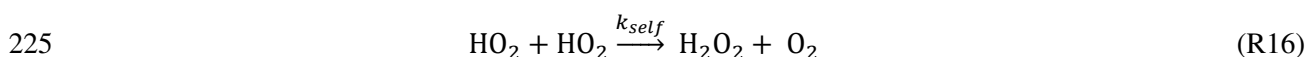
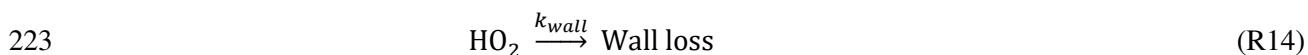
188 **2.4 HO₂ and OH Radical Detection**

189 OH and HO₂ (HO_x) radicals were detected by Fluorescence Assay by Gas Expansion (FAGE, detection
190 limit 10⁶ molecule cm⁻³).¹⁵ HO_x radicals entered the FAGE cell placed at the end of the flow tube
191 through a 0.7 mm diameter pinhole. In order to detect HO₂, it was chemically converted to OH by
192 injecting 50 sccm of NO (BOC, 99.5 %) into the resulting jet on the low pressure side of the pinhole.
193 The Q₁(2) line of the OH ($A^2\Sigma^+ - X^2\Pi_{1/2}v' = 0 - v'' = 0$) transition at ≈ 308 nm was used to
194 electronically excite the OH in the FAGE cell. A Nd:YAG pumped dye laser (JDSU Q201-HD Q-
195 series, Sirah Cobra Stretch) was used to produce the required 308 nm radiation (line width ≈ 0.1 cm⁻¹)
196 at a pulse repetition rate of 5 kHz. The FAGE cell was continuously evacuated using a combination of
197 a rotary pump (Edwards, model E1M80) and a roots blower (EH1200), and was kept at 0.8–0.9 Torr,
198 which was monitored using a capacitance monitor (Tylan General, CDC 11). The FAGE signal was
199 calibrated using a turbulent flow tube calibration method¹⁶ which has been developed for field
200 measurements of OH and HO₂ radicals, meaning the LIF signal could be converted into an absolute
201 concentration. The calibration experiment involves generating known concentrations of OH and HO₂
202 from photolysis of H₂O vapour in zero air in a turbulent flow tube placed immediately adjacent to the
203 FAGE sample inlet.

204 2.5 Experimental Procedure and Data Analysis

205 At the beginning of all experiments the FAGE background measurements without the UVA lamp on
 206 were taken without and with NO injected into the FAGE cell and subtracted from the OH and HO₂
 207 signals respectively, to correct for laser scatter and photolysis of any impurities in the NO which may
 208 form OH. The FAGE signal was averaged over 20 s (average of twenty 1 s data points, each
 209 corresponding to 5000 laser shots) for each measurement. Eight 20 s measurements were taken during
 210 each run. Measurements were made in the absence of aerosols and in the presence of aerosols.
 211 Measurements of HO_x concentrations produced from TiO₂ aerosols under varying conditions were made
 212 at different total surface area densities of TiO₂ aerosols, RH, light flux and oxygen concentration. The
 213 laser power was recorded for each measurement and used to normalise the HO₂ signal to correct for any
 214 fluctuations in laser power (< 5% during an experiment).

215 The HO₂ signal measured at the end of the aerosol flow tube results from several radical production and
 216 loss processes, namely wall loss (R14), aerosol uptake (R15), HO₂ self-reaction in the gas-phase (R16),
 217 production of HO₂ from aerosols which have been deposited on the walls of the aerosol flow tube (R17)
 218 and HO₂ production from airborne TiO₂ aerosol surfaces (R18). To obtain the rate coefficient k_{prod} for
 219 HO₂ production from processes occurring on airborne aerosol surfaces, reactions (R14)-(R18) were all
 220 included in a numerical model developed within the Kintecus integrator package (Windows Version
 221 2.80).¹⁷ The HO₂ concentration measured at the end of the flow tube after illumination for a known
 222 period of time was used as the target parameter for the model.



228 The HO₂ wall loss rate coefficient (k_{wall}) used in the model was determined at the beginning and end of
 229 each experiment using a methodology previously described¹² in which a sliding injector emitting HO₂
 230 was translated down the flow tube in the absence of aerosols (but after the walls have been conditioned
 231 in the presence of aerosols). Wall losses increased as RH was increased during experiments. The HO₂
 232 concentration as a function of time along the flow tube when determining k_{wall} (as k_{self} is negligible in at
 233 the HO₂ concentrations of these experiments) can be expressed as:

$$234 \quad \ln[\text{HO}_2]_t = \ln[\text{HO}_2]_0 - k_{wall}t \quad (\text{E2})$$

235 where $[\text{HO}_2]_t$ and $[\text{HO}_2]_0$ are concentrations of HO_2 at time t and $t = 0$ (i.e. $[\text{HO}_2]$ at initial injector
 236 position) respectively, and k_{wall} is the observed pseudo-first-order rate coefficient for HO_2 wall losses.
 237 This rate constant was determined in independent experiments where HO_2 was generated in the injector
 238 as in previous work ⁹ in the absence of aerosols. Similar HO_2 concentrations were used in these
 239 experiments and in HO_2 generation experiments.

240 The aerosol loss rate coefficient, $k_{\text{aerosol loss}}$, was calculated using E3:

$$241 \quad k_{\text{aerosol loss}} = 0.25 S_a \omega_{\text{HO}_2} \gamma(\text{HO}_2) \quad (\text{E3})$$

242 where $\gamma(\text{HO}_2)$ is the reactive uptake coefficient of HO_2 onto TiO_2 , which was previously measured in
 243 this laboratory in the absence of light ¹², S_a is the surface area density of TiO_2 aerosols and ω_{HO_2} is the
 244 molecular speed of HO_2 . The self-reaction of HO_2 (R16) in the gas-phase contributes a negligible HO_2
 245 loss pathway ($\sim 0.01\%$) at the HO_2 concentrations used. The production of HO_2 from the surfaces of
 246 the flow tube walls and TiO_2 aerosols was characterised in Kintecus using equations (E4) and (E5),
 247 respectively:

$$248 \quad \frac{d[\text{HO}_2]}{dt} = k_{\text{wall prod}} [\text{Wall}] \quad (\text{E4})$$

$$249 \quad \frac{d[\text{HO}_2]}{dt} = k_{\text{prod}} S_a \quad (\text{E5})$$

250 where $[\text{Wall}]$ is the surface area concentration ($\text{cm}^2 \text{cm}^{-3}$) of the illuminated walls of the aerosol flow
 251 tube (i.e. surface area of the interior walls of the aerosol flow tube divided by the internal volume of
 252 aerosol flow tube) and S_a is the surface area density of the TiO_2 aerosols, determined by the SMPS.
 253 Using $[\text{Wall}]$, S_a , k_{self} , k_{wall} , and $k_{\text{aerosol loss}}$ as constraints, which are all known for a given experiment, the
 254 Kintecus model was used to calculate $[\text{HO}_2]$ at the appropriate illumination time, which is also known
 255 for a given lamp. With the lamp illuminating the flow tube, but in the absence of aerosols ($S_a = 0$), the
 256 value of $k_{\text{prod wall}}$ within Kintecus was optimised to give the best fit with measured $[\text{HO}_2]$ at the end of
 257 the flow-tube after the known illumination time. Using this value of $k_{\text{wall prod}}$, but now in the presence of
 258 aerosols at a given S_a , the value of k_{prod} was optimised within Kintecus to match $[\text{HO}_2]$ at the end of the
 259 flow tube. k_{prod} describes the rate of HO_2 production per unit surface area of TiO_2 aerosols, and is
 260 expected to depend on experimental variables such as $[\text{O}_2]$, RH and lamp radiation flux (which itself is
 261 a function of S_a). In the following section, the HO_2 concentration was measured at the end of the flow
 262 tube whilst changing a number of variables, and Kintecus was used to obtain an optimised value of k_{prod}
 263 for each set of experimental conditions.

264 3. Results

265 3.1 HO₂ production by irradiated airborne TiO₂ nanoparticles

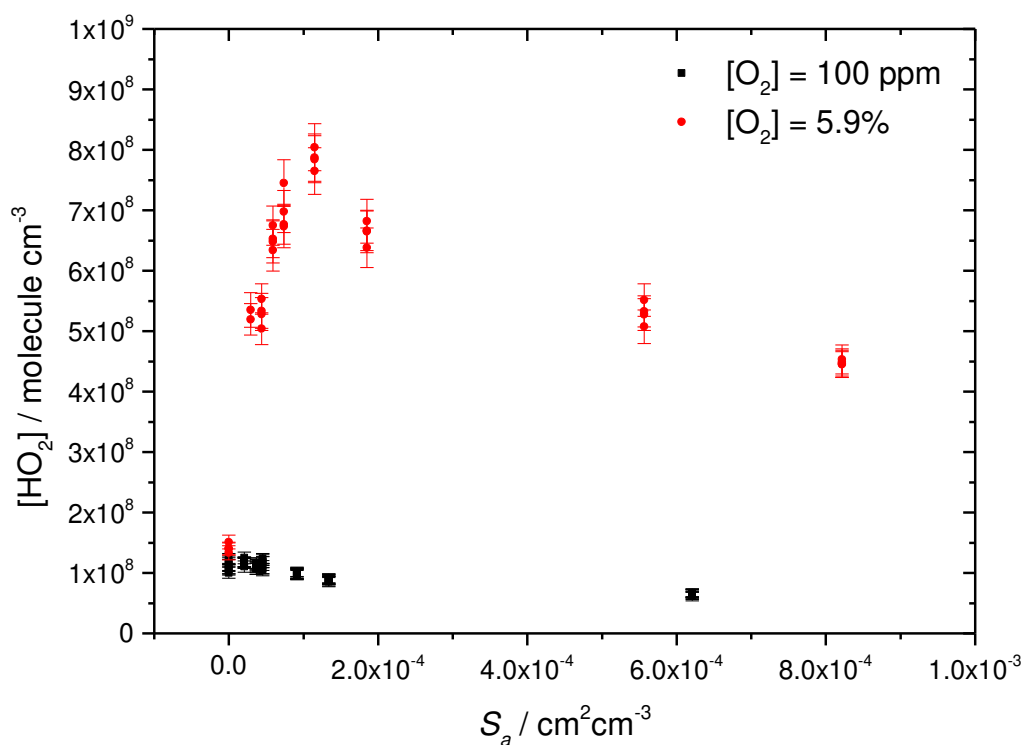
266 3.1.1. Variation with aerosol surface area and lamp flux

267 Initial experiments were performed using a carrier gas consisting of either pure nitrogen or 5.9% O₂ in
268 nitrogen. Figure 3 displays the concentration of HO₂ measured at the end of the aerosol flow tube
269 (corresponding to 14 s of exposure to the lamp radiation) as a function of the surface area density of
270 airborne TiO₂ nanoparticles, S_a . In the presence of O₂ a significant increase of gas-phase HO₂ was
271 measured as S_a was increased, however when the carrier gas was composed of solely compressed
272 nitrogen at similar RH no significant change was observed. These experiments suggest that the HO₂
273 produced was from the surfaces of irradiated airborne TiO₂ nanoparticles via a photocatalytic
274 mechanism involving adsorbed molecular oxygen. A small HO₂ signal was detected at $S_a = 0$ (i.e. when
275 airborne TiO₂ nanoparticles were not present in the aerosol flow tube) likely associated with production
276 from previously deposited TiO₂ nanoparticles on the walls of the aerosol flow tube and O₂ impurities
277 in the nitrogen (estimated at ~ 100 ppm). No such HO₂ signal was observed after the aerosol flow tube
278 had been cleaned. The small concentration of HO₂ produced from the walls at $S_a = 0$ was included
279 within the Kintecus model using (R17) and $k_{prod\ wall}$ (E4).

280 Figure 3 shows that HO₂ increases as more airborne TiO₂ nanoparticles enter the system until a
281 maximum was reached, after which adding more particles results in a decrease in the HO₂ concentration.
282 Two processes may account for this. TiO₂ aerosols have a large refractive index (2.5 at 500 nm)¹⁸,
283 therefore lamp radiation entering the aerosol flow tube will be Mie scattered by the aerosols shading
284 those aerosols below and which may result in a drop in the overall photocatalytic activity of TiO₂
285 aerosols, and hence the total rate of production of HO₂. Moreover, as the aerosol loading of the flow
286 tube increases the rate of reactive heterogeneous uptake of HO₂ by TiO₂ aerosols via reaction (R15)
287 also increases and will compete with HO₂ production.

288

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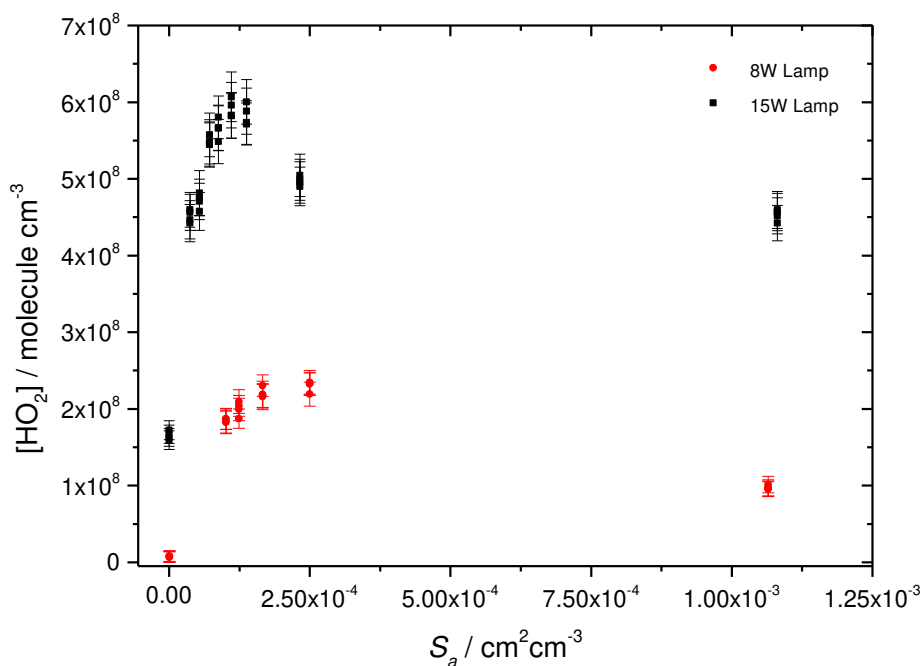


290

291 **Figure 3.** Gas phase HO₂ produced by airborne irradiated TiO₂ nanoparticles as a function of surface
 292 area density, S_a , with a carrier gas composed of compressed nitrogen with $\sim [\text{O}_2] = 100 \text{ ppm}$ impurity
 293 (solid black squares) at RH = 24.0%, and for a 5.9 % mixture of O₂ (balance N₂) (filled red squares) at
 294 RH = 16.4%. At $S_a = 0$, the HO₂ is due to production at the flow tube walls. The aerosol flow tube was
 295 illuminated with the 15 W lamp. The illumination time = 14 s.

296

297 Figure 4 compares the HO₂ produced as a function of S_a when the 8 W and 15 W UVA lamps were used
 298 to illuminate the aerosol flow tube. As expected, the use of the higher-powered lamp resulted in more
 299 gas-phase HO₂ being produced, however the 15 W UVA lamp is also longer by 12 cm (40%) resulting
 300 in aerosols being irradiated for 4 s longer than with the 8 W lamp and will also account for the higher
 301 concentrations of HO₂ produced. A similar dependence of HO₂ production with varying S_a was
 302 observed.



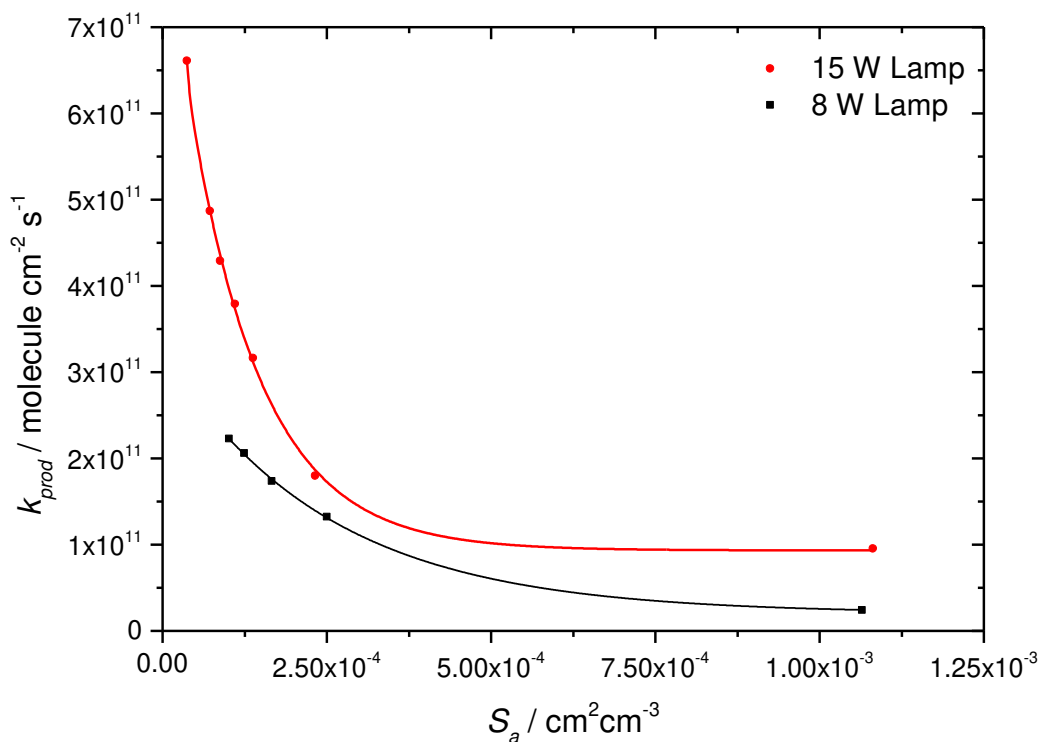
303

304 **Figure 4.** Gas phase HO₂ produced from airborne irradiated TiO₂ nanoparticles as function of total
 305 surface area density (S_a) at RH = 8.0% and [O₂] = 5.9% using an 8 W UVA lamp (red circles) and a
 306 15 W UVA lamp (black squares) to illuminate the aerosol flow tube. The illumination time for 15 W
 307 lamp = 14 s and 8 W lamp = 10 s. The ratio of flux with $\lambda < 388$ nm that enters the flow tube emitted
 308 from the 8 W and 15 W lamp was 1:5.

309

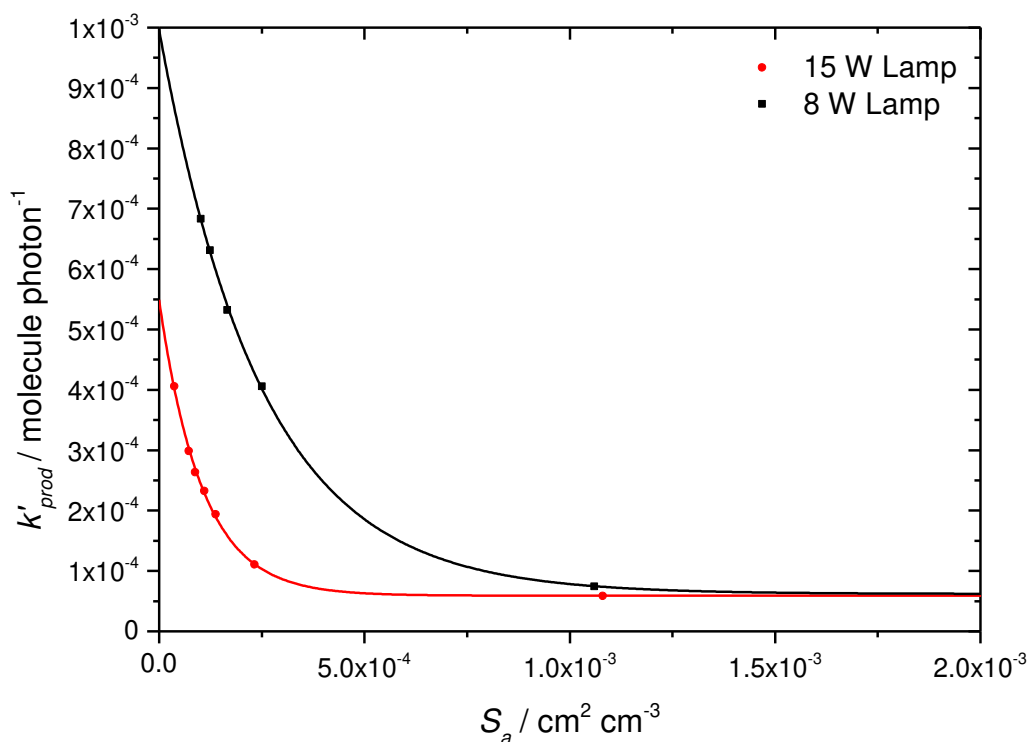
310 Using the constrained model described by reactions (R14) – (R18), the optimised value of k_{prod} (the
 311 number of HO₂ molecules emitted per cm² of particle surface per second) was calculated to give the
 312 best fit to the measured [HO₂] at the end of the flow tube after illumination. The variation of k_{prod} as a
 313 function of S_a is shown in Figure 5 for both lamps, and shows k_{prod} decreases rapidly with S_a , which is
 314 expected given the decreasing rate of production of HO₂ with S_a seen in Figure 4. The inverse
 315 dependence of k_{prod} with S_a is consistent with aerosol light scattering reducing the photons per unit
 316 surface area interacting with the TiO₂ surface. At low S_a , k_{prod} using the 15 W lamp was significantly
 317 greater than k_{prod} using the 8 W lamp, which is expected owing to the larger light flux, although the
 318 production of HO₂ below 388 nm may also be wavelength dependent. However, as the aerosol loading
 319 within the aerosol flow tube was increased, k_{prod} using the 15 W lamp decreases ~ 3 times faster than
 320 for the 8 W lamp, suggesting light from the 15 W lamp is more affected by aerosol scattering. At high
 321 S_a , k_{prod} reaches a minimum value which is ~ 5 times larger for the 15 W lamp than the 8 W lamp,
 322 consistent with the ratio of lamp fluxes for $\lambda < 388$ nm of the two lamps entering the flow tube. As seen
 323 in Figure 2 the 15 W lamp emits UV light across a much broader range of wavelengths (275 – 400 nm)
 324 with an average wavelength of 340 nm compared to the 8 W lamp which emits across a smaller range
 325 of wavelengths (325 – 400 nm) with an average wavelength of 365 nm. As the refractive index of a

326 material and the Mie scattering are inversely proportional to the wavelength of light, the 15 W lamp
 327 radiation may be more efficiently scattered.



328
 329 **Figure 5.** The variation of k_{prod} as function of total surface area density (S_a) of TiO₂ nanoparticles at RH
 330 = 8.0% and [O₂] = 5.9% using the 8 W UVA lamp (black squares) and the 15 W UVA lamp (red circles)
 331 to illuminate the aerosol flow tube. Solid lines represent exponential decays as a guide to the eye. The
 332 lamps have different fluxes (see text for details).

333
 334 The value of k_{prod} depends on several factors, including the lamp flux $\lambda < 388$ nm, F , and a flux-
 335 independent rate coefficient, k'_{prod} , can be defined as $k_{prod} = F k'_{prod}$. Figure 6 shows that values of k'_{prod}
 336 decayed exponentially as the aerosol loading was increased in the aerosol flow tube. At the lowest
 337 value of S_a ($\sim 1 \times 10^{-4}$ cm² cm⁻³) and using the lamp flux appropriate for within the flow tube, the values
 338 of k'_{prod} for the 8W and 15 W lamps were determined to be 6.4×10^{-4} and 2.3×10^{-4} HO₂ molecule
 339 photon⁻¹ respectively (see Figure 6), with an average value of 4.4×10^{-4} HO₂ molecule photon⁻¹. This
 340 shows that HO₂ production was 2.8 times more efficient when using 8 W lamp, likely due to greater
 341 levels of scattering or lesser levels of absorbance of light from the 15 W lamp. However, at the highest
 342 S_a ($\sim 1 \times 10^{-3}$ cm² cm⁻³) where k_{prod} reaches a minimum and scattering reaches its maximum level the
 343 values of k'_{prod} for the 8 W and 15 W were broadly consistent and determined to be $(7.4 \pm 0.3) \times 10^{-5}$
 344 and $(5.9 \pm 0.4) \times 10^{-5}$ HO₂ molecule photon⁻¹ respectively, with an average value of 6.7×10^{-5} HO₂
 345 molecule photon⁻¹. .



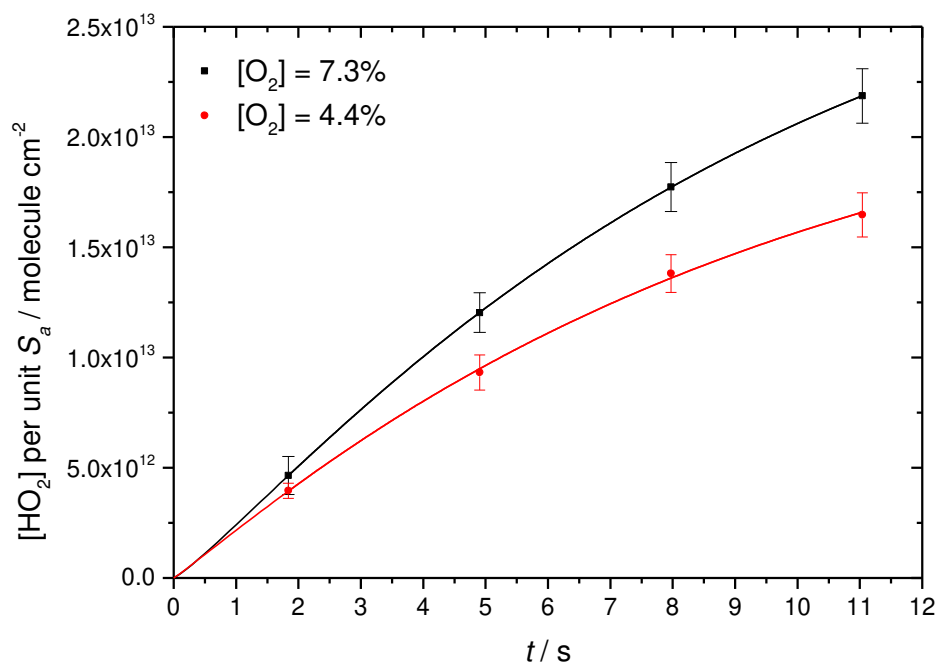
346

347 **Figure 6.** The variation of k'_{prod} as function of total surface area density (S_a) of TiO_2 nanoparticles at
 348 $\text{RH} = 8.0\%$ and $[\text{O}_2] = 5.9\%$ using the 8 W UVA lamp (black squares) and the 15 W UVA lamp (red
 349 circles) to illuminate the aerosol flow tube. Solid lines represent exponential decays as a guide to the
 350 eye.

351

352 3.1.2. Variation with illumination time, $[\text{O}_2]$ and RH

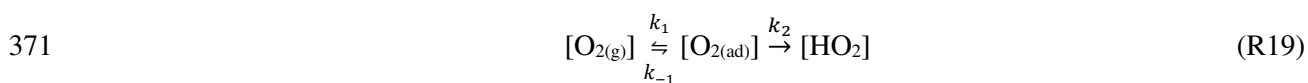
353 Further experiments were conducted at low aerosol surface area densities ($\sim 1 - 2 \times 10^{-5} \text{ cm}^2 \text{ cm}^{-3}$) to
 354 reduce the effects Mie scattering and aerosol uptake of HO_2 , and Figure 7 shows the HO_2 concentration
 355 per unit surface area measured at 4 different illumination times, which was varied by masking different
 356 lengths of the 15 W lamp, and for two different $[\text{O}_2]$. The rate of production of HO_2 appears to slow
 357 down with irradiation time (although not observed it is expected HO_2 production would reach a steady-
 358 state value at longer time) and increases with the O_2 mixing ratio. The observed slowdown of HO_2
 359 produced is associated with wall loss and aerosol uptake.



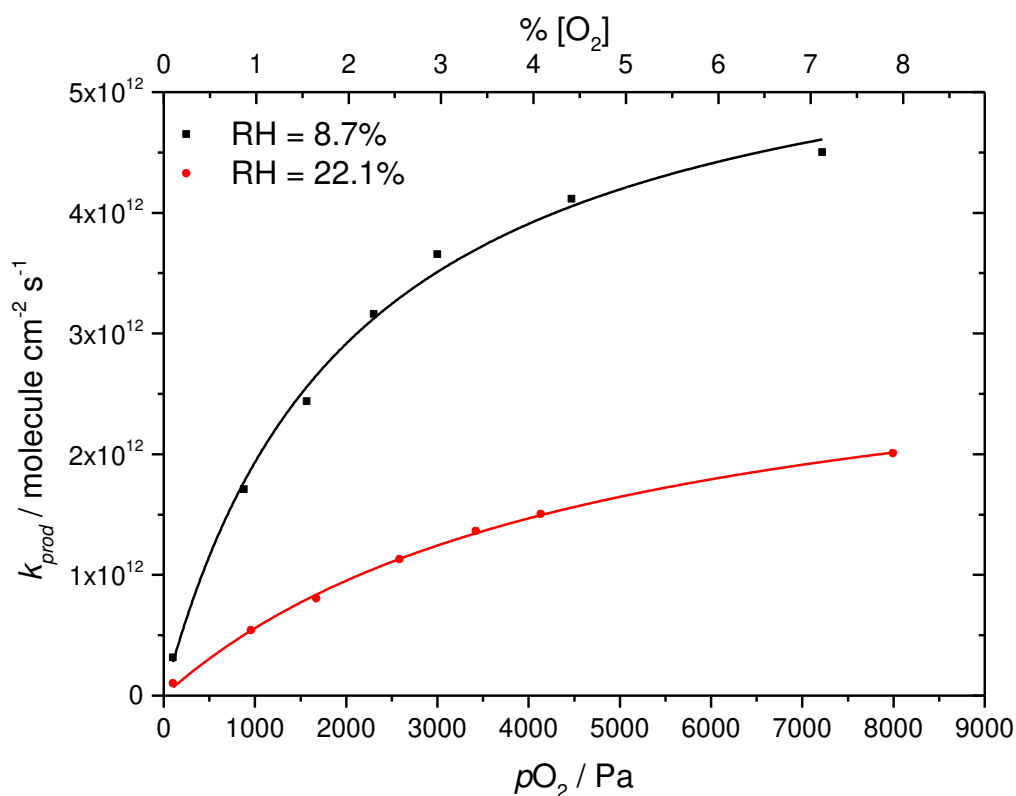
360 **Figure 7.** Time dependence of HO₂ produced by the 15 W UVA lamp at 4 illumination times for S_a =
 361 1.6 × 10⁻⁵ cm² cm⁻³, RH = 11.0% and at [O₂]_{t=0} = 7.3% (black squares) and 4.4% (red circles) RH =
 362 11.0%. The solid lines are a polynomial fit as a guide to the eye. Error bars represents 1σ of the data
 363 points taken over the 20 s averaging period.

364

365 For a fixed illumination time of 14 s (the lamp was unmasked), the dependence of [HO₂] at the end of
 366 flow tube was measured as a function of [O₂] over the mixing ratio range 0-8 %. Using the Kintecus
 367 model described above, k_{prod}, the rate coefficient for HO₂ production from illuminated aerosols was
 368 calculated and is shown as a function of the partial pressure, pO₂, in Figure 8 for two different RH. The
 369 relationship between k_{prod} and pO₂ in Figure 8 shows typical Langmuir adsorption behaviour, described
 370 by the reaction scheme:



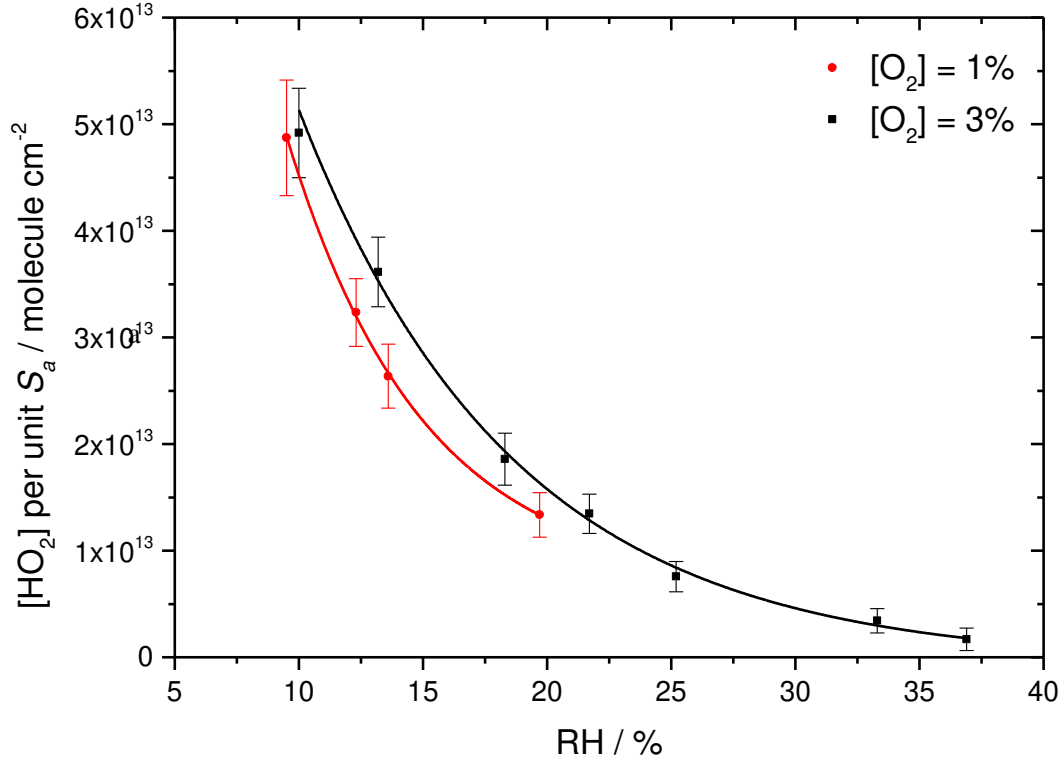
372 with HO₂ postulated as being generated from the oxidation of adsorbed water vapour by a
 373 photogenerated hole (h⁺) (R2) to form H⁺, and reaction of H⁺ with O₂ and a photogenerated e⁻ (R2 –
 374 R3).



375

376 **Figure 8.** k_{prod} , the rate coefficient for the production of gas-phase HO₂ from irradiated airborne TiO₂
 377 nanoparticles as a function of O₂ partial pressure and for RH = 8.7% (black squares) and 22.1% (red
 378 circles). The solid lines represent fits of the Langmuir expression equation (E7) to the data, see text for
 379 details. Light intensity $\lambda < 388 \text{ nm} = 1.63 \times 10^{15} \text{ photons cm}^{-2}$.

380 The relationship between the rate of HO₂ formation and the amount of water vapour within the aerosol
 381 flow tube was investigated more extensively. Figure 9 shows that the concentration of HO₂ produced
 382 per unit surface area decreases significantly as the relative humidity was increased within the aerosol
 383 flow tube. As expected from Figure 8, tripling the concentration of O₂ only resulted in a modest increase
 384 in HO₂ production. Beyond a RH of ~ 40% k_{prod} appears to approach a minimum value and H₂O no
 385 longer has an inhibiting effect to HO₂ production. From FTIR studies of TiO₂ aerosols in the presence
 386 of various RH this corresponds to a H₂O surface coverage of 1.6 monolayers.¹⁹



387 **Figure 9.** Gas-phase HO₂ concentration per unit of S_a for airborne TiO₂ nanoparticles at an illumination
 388 time of 14 s as a function at different RH for [O₂] = 1% (red circles) and 3% (black squares). Solid
 389 lines represent exponential decay fits to experimental data as a guide to the eye. Error bars represents
 390 1σ of the data points taken over the 20 s averaging period.

391

392 Figures 8 and 9 suggests adsorption of water vapour inhibits HO₂ production by reducing the effective
 393 surface area of the particle and therefore reducing the number of available sites on the TiO₂ particle
 394 surface that O₂ can adsorb and react on. The total concentration of active sites, [S₀], is given by:

$$395 \quad [S_0] = [S] + [H_2O_{(ad)}] + [O_{2(ad)}] \quad (E4)$$

396 where [S] is the concentration of unoccupied sites, and [H₂O_(ad)] and [O_{2(ad)}] are the density of sites
 397 inhibited or occupied by water vapour and O₂, respectively. The equilibrium constant for adsorption of
 398 O₂ or water vapour is defined by:

$$399 \quad K_A = \frac{k_1}{k_{-1}} = \frac{[A_{(ad)}]}{p_A[S]} \quad (E5)$$

400 where k₁ and k₋₁ is the rate of adsorption and desorption respectively, A = O₂ or H₂O, p_A is the partial
 401 pressure of A and [A_(ad)] is the concentration of A adsorbed on the surface. For Langmuir adsorption
 402 within the presence of an inhibiting species, the fractional coverage of O₂, θ_{O₂}, defined as the fraction
 403 of active sites on the TiO₂ nanoparticle surface occupied by O₂, is given by:

$$404 \quad \theta_{O_2} = \frac{[O_{2(ads)}]}{[S_0]} = \frac{K_{O_2} p_{O_2}}{1 + K_{O_2} p_{O_2} + K_{H_2O} p_{H_2O}} \quad (E6)$$

405 where K is the adsorption equilibrium constant for O_2 or H_2O vapour on TiO_2 , and p is the partial
 406 pressure of O_2 or H_2O vapour. From experiments using IR spectroscopy Goodman *et al.*¹⁷ showed that
 407 at RH = 8.7% and 22.1% the number of monolayers of H_2O is 0.9 and 1.2 respectively on TiO_2 .
 408 Assuming reaction (R3) is the rate determining step, the rate of production of HO_2 from the TiO_2
 409 aerosols (k_{prod}) is then given by:

$$410 \quad k_{prod} = k_2 \theta_{O_2} = \frac{k_{prod\ max} K_{O_2} p_{O_2}}{1 + K_{O_2} p_{O_2} + K_{H_2O} p_{H_2O}} \quad (E7)$$

411 where $k_{prod\ max}$ is the maximum rate coefficient of production of HO_2 at high partial pressures of O_2 .
 412 Figure 8 also includes a fit of E7 to the experimental data which yielded best-fit values for $k_{prod\ max}$, K_{O_2}
 413 and K_{H_2O} , which are summarised in Table 1.

414

415 **Table 1.** Parameters yielded from fitting E7 to the experimental data in Figure 8 (error = 2σ). Average
 416 $S_a = 1.5 \times 10^{-5} \text{ cm}^2 \text{ cm}^{-3}$. Light intensity $\lambda < 388 \text{ nm} = 1.63 \times 10^{15} \text{ photons cm}^{-2}$

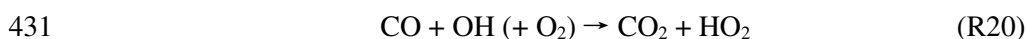
Parameter	RH = 8.7%	RH = 22.1%
$k_{prod\ max} / \text{molecule cm}^{-2} \text{ s}^{-1}$	$(5.93 \pm 0.07) \times 10^{12}$	$(3.21 \pm 0.02) \times 10^{12}$
$k'_{prod\ max} / \text{molecule photon}^{-1}$	$(3.64 \pm 0.04) \times 10^{-3}$	$(1.97 \pm 0.03) \times 10^{-3}$
K_{O_2} / Pa^{-1}	0.269 ± 0.016	0.184 ± 0.004
$K_{H_2O} / \text{Pa}^{-1}$	2.16 ± 0.12	1.33 ± 0.04

417

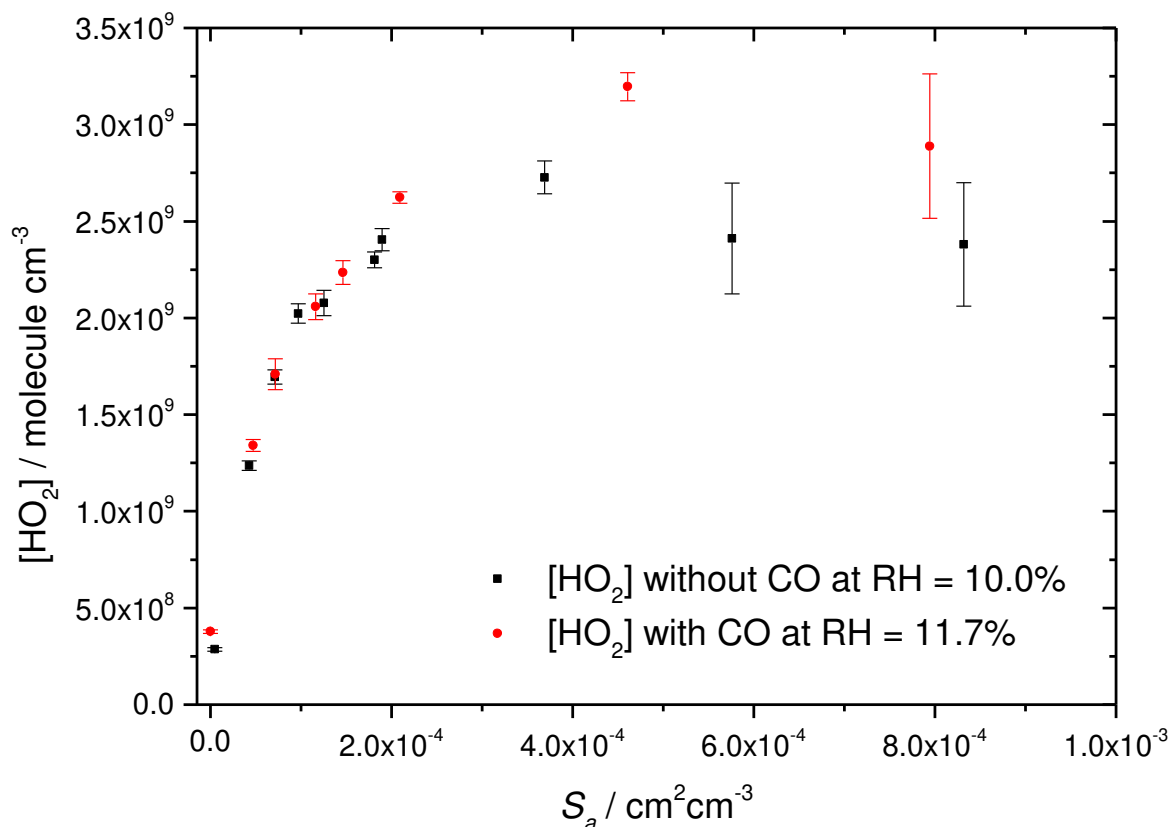
418 A measurement of K_{H_2O} onto a TiO_2 surface has previously been conducted via a study of the
 419 photocatalytic reduction of CO_2 with H_2O .²⁰ However, key discrepancies between the studies make
 420 the measurements incomparable; i.e., the measurements in this study were regarding surfaces of
 421 airborne Degussa TiO_2 nanoparticles, whereas that study concerned a graphene oxide-supported
 422 oxygen-rich TiO_2 hybrid, which was used to coat the walls of a flow tube. There are no previous
 423 measurements of K_{O_2} on TiO_2 surfaces to our knowledge.

424 3.2 OH formation by irradiated airborne TiO_2 nanoparticles

425 OH production from irradiated TiO_2 aerosols was also investigated. The FAGE instrument operated
 426 with no added NO in the fluorescence cell did not see any OH signal from TiO_2 aerosols illuminated
 427 within the aerosol flow tube. However, this observation might be explained by OH losses to the walls
 428 of the flow tube or via reactions of OH with impurities before entering the FAGE sampling nozzle. To
 429 test this hypothesis, CO (0.5 L min^{-1} , 5% in air) was added to the carrier gas prior to the conditioning
 430 tube to rapidly scavenge any OH generated from the aerosol surface via the reaction:



432 Any additional OH signal when CO was added would provide evidence for aerosol production of OH.
 433 In the flow tube $[CO] = 1.1 \times 10^{17}$ molecule cm^{-3} , giving an OH lifetime of $= 5.5 \times 10^{-5}$ s, during which
 434 it only moves $\sim 1.4 \times 10^{-4}$ cm along the flow tube, and other loss processes should not compete. Figure
 435 10 shows that for aerosol surface areas (S_a) lower than 2×10^{-4} $cm^2 cm^{-3}$ there was no discernible
 436 difference between HO_2 produced with and without CO present, for RH = 10 – 12%. However, for $S_a >$
 437 2×10^{-4} $cm^2 cm^{-3}$, a noticeable difference ($[OH] \sim 8 \times 10^8$ molecule cm^{-3}) was observed, providing
 438 some evidence for OH production, although the uncertainties are quite high at the largest S_a .



439
 440 **Figure 10.** Gas-phase HO_2 produced by irradiated airborne TiO_2 nanoparticles at an irradiation time =
 441 14 s as a function of S_a for $[O_2] = 5.9\%$ without added CO (black squares, RH=10.0%) and with added
 442 CO (red circles, RH=11.7%).

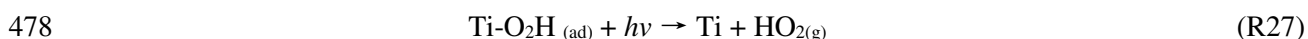
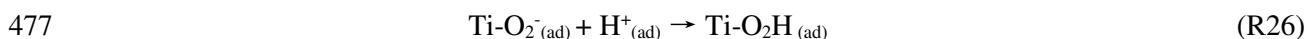
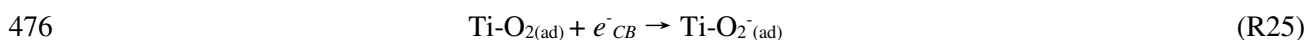
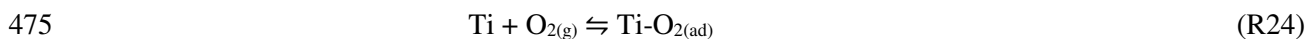
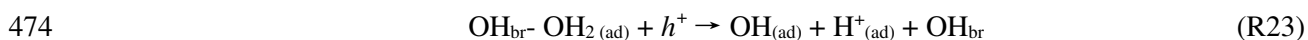
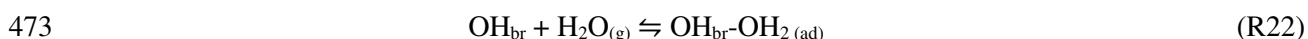
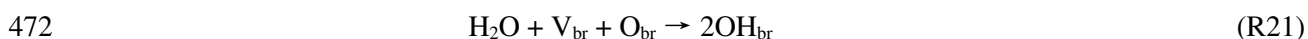
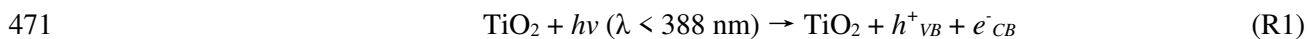
443 OH is likely produced by the decomposition of H_2O_2 (R11) formed by HO_2 uptake, which is more
 444 prevalent at high $[HO_2]$ and S_a . The mechanism of H_2O_2 decomposition producing OH and the resulting
 445 OH reacting with H_2O_2 , may explain the HO_2 observed by Yi *et al.* ⁴ (R11 and R13). Murikami *et al.* ⁹
 446 directly observed gas-phase production of OH from irradiated TiO_2 surfaces. OH may be associated
 447 with H_2O_2 decomposition rather than from water oxidation, and a theoretical study ²¹ has shown that
 448 OH formed by water oxidation on anatase is likely to remain adsorbed on the surface rather than
 449 desorbing into the gas-phase and on rutile peroxy intermediates are formed rather than OH.

450

451 **4. Discussion**

452 Sources of HO_x radicals in the condensed phase that have been previously suggested include the uptake
 453 of OH and HO₂ from the gas-phase, followed by the formation of aqueous H₂O₂ and subsequent
 454 decomposition, as well as Fenton reactions of reduced metal ions and H₂O₂, and direct photolysis of
 455 H₂O₂, nitrite, nitrate, hydroperoxides, light-absorbing secondary aerosols and iron (III) complexes.²²
 456 Although the formation of HO₂ from illuminated aerosols containing a photo-sensitizer (imidazole-2-
 457 carboxaldehyde) has been measured indirectly by converting gas-phase NO to NO₂, this study presents
 458 the first direct observations of HO₂ radicals generated on aerosol surfaces. These are the first
 459 observations of HO₂ production from illuminated TiO₂ surfaces in the presence of light and O₂, but
 460 without the presence of added H₂O₂, which was needed by Yi *et al.*⁴ in order to see HO₂ from TiO₂
 461 films. Unlike heterogeneous reactions involving surfaces or films, heterogeneous reactions involving
 462 airborne nanoparticles are not limited by diffusion of gas-phase reactants to the particle surface. To
 463 overcome diffusion limitations production from solid surfaces or thin film experiments are often
 464 performed at low pressure, however this will not favour adsorption of species with a high vapour
 465 pressure, such as water vapour. Yi *et al.* used pure forms of TiO₂ polymorphs which has been shown to
 466 enhance photocatalytic activity¹⁴ rather than a blend, and surface or thin film experiments often take a
 467 number of minutes, so surface saturation and product accumulation may occur on the surface of the
 468 sample and could change its chemical characteristics.

469 The mechanism generating HO₂ on irradiated TiO₂ surfaces in the presence of O₂ is postulated to be
 470 (where V_{br}, O_{br} and OH_{br} are bridging vacancy, oxygen and hydroxyl groups):

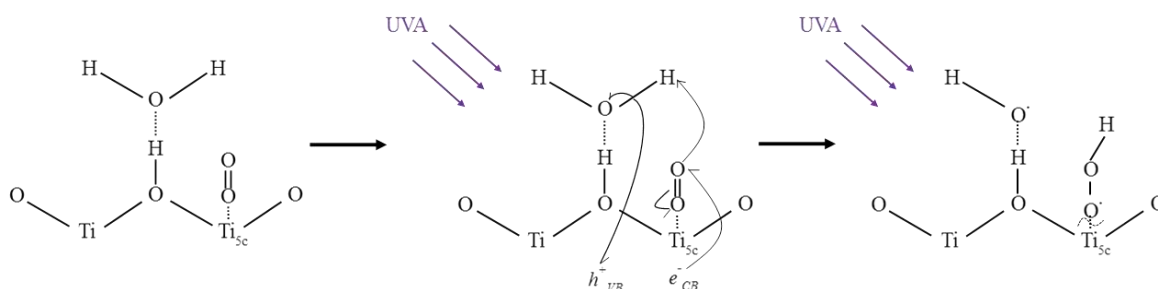


479

480 The reaction is initiated by the production of photogenerated electrons in the conduction band (e^-_{CB}) and
 481 holes within the valence band (h^+_{VB}), which can either recombine or reside in a trapped state or within

482 the respective band. O_2 is an effective electron scavenger forming either O_2^- or O_2^{2-} . A study of this
 483 process on TiO_2 (101) surfaces²³ showed that photogenerated e^- can exist on paramagnetic Ti^{3+} sites or
 484 delocalise within the conduction band. At room temperature, most photogenerated e^- remain stable
 485 within the conduction band rather than in trapped Ti^{3+} states, however at lower temperatures e^- can
 486 reside in these traps which could lead to a higher rate of O_2^- formation. That study observed the efficient
 487 production of long-lived O_2^- , with all photoexcited e^- being transferred to adsorbed O_2 . It is likely that
 488 the mechanism for HO_2 production would therefore have to involve the reduction of adsorbed O_2 with
 489 e^-_{CB} forming adsorbed O_2^- (R25). O_2^- can then go on to react with a proton (R26) formed by the oxidation
 490 of adsorbed water via its reaction with a photogenerated h^+ (R23) located at bridging oxygen sites (O_{br})
 491 for TiO_2 (110) and OH_{br} groups for TiO_2 (101)^{24,25} to form adsorbed HO_2 . This mechanism highlights
 492 the contradictory role that water plays in the photocatalytic activity of TiO_2 , on the one-hand producing
 493 active species on the surface of photocatalytically active TiO_2 available for reaction (R21) and, on the
 494 other hand, reducing the availability and effectiveness of active sites and therefore reducing adsorption
 495 of gas-phase species, as shown in Figures 8 and 9. It is also likely that desorption of HO_2 could be
 496 augmented by photodesorption (R27) as shown below in Figure 11:

497



498

499 **Figure 11.** Mechanism for the production of gas-phase HO_2 from the surfaces of airborne TiO_2
 500 nanoparticle. Ti_{5c} refers to fivefold coordinated Ti sites. h^+_{VB} refers to valence band holes and e^-_{CB} refers
 501 to conduction band electrons.

502

503 Adsorption of water vapour may inhibit the reaction by blocking adjacent O_2 adsorption sites reducing
 504 the effective surface area available and by reducing the O_2 adsorption binding energy and hence
 505 desorption lifetime. The value of K_{H_2O} (obtained from Figure 8) shows that $K_{H_2O} > K_{O_2}$ suggesting that
 506 the H_2O adsorption enthalpy onto TiO_2 is larger than for O_2 adsorption and many more water molecules
 507 are adsorbed on the surface of the TiO_2 particle than O_2 . This is consistent with studies that have shown
 508 TiO_2 surfaces become super-hydrophilic when irradiated with UV light.²⁶ Both K_{O_2} and K_{H_2O} decrease
 509 as RH was increased (Table 1) suggesting that the enthalpy of adsorption of both species is decreasing
 510 with RH. Bridging hydroxyl groups (OH_{br}), formed in R21 by dissociation of water at oxygen vacancy

511 defects in bridging sites (V_{br})²⁷, provide an anchoring point for water molecules to adsorb onto TiO_2
512 surfaces forming $OH_{br}-H_2O$ complexes (R22) which are acidic in character (i.e. OH_{br} groups act as H-
513 donors).^{27, 28} The enthalpy of water adsorption on these sites is $\sim 70 \text{ kJ mol}^{-1}$. As RH is increased
514 beyond 11% (RH for one monolayer of H_2O on TiO_2 ¹⁹) a second monolayer of H_2O begins to form and
515 H_2O binds to the $OH_{br}-H_2O$ complexes, reducing their acidity and resulting in the water binding
516 structure being more characteristic of bulk water²⁸ and a lowering of the H_2O adsorption enthalpy, and
517 hence K_{H_2O} . Density functional theory (DFT) calculations²⁹ have shown that O_2 adsorption onto TiO_2
518 (110, i.e. the rutile polymorph of TiO_2) surfaces is also entirely dependent on the presence of OH_{br}
519 groups. These calculations show that the most stable configuration for O_2 adsorption is onto two
520 adjacent fivefold coordinated Ti sites (Ti_{5c}) adjacent to an OH_{br} group with an adsorption enthalpy of \sim
521 77 kJ mol^{-1} . However, many other configurations have an adsorption enthalpy which is only slightly
522 less ($\sim 58 \text{ kJ mol}^{-1}$), e.g. adsorption to a single Ti_{5c} site adjacent to an OH_{br} group. The calculations also
523 show that the adsorption enthalpy of O_2 is dependent on the coverage of OH_{br} , with higher coverage of
524 OH_{br} resulting in a higher enthalpy of adsorption and hence a longer adsorption lifetime for O_2 . The
525 distance between adsorbed O_2 and OH_{br} does not significantly affect the adsorption enthalpy, meaning
526 OH_{br} exerts a long-range influence on O_2 adsorption via the donation of electrons to TiO_2 which
527 delocalise amongst $Ti_{(5c)}$ atoms. Upon O_2 adsorption, there is a charge transfer from the $Ti_{(5c)}$ atoms to
528 O_2 (R24), the magnitude of which determines the enthalpy of adsorption. The same mechanism was
529 found for calculations of O_2 adsorption onto TiO_2 (101, anatase).³⁰ The decrease of K_{O_2} with RH and
530 the inhibiting effects of H_2O adsorption to the rate of HO_2 production observed in this work are likely
531 associated with the formation of $OH_{br}-H_2O$ complexes which inhibits the ability of OH_{br} groups to
532 donate electron density to Ti_{5c} atoms thereby reducing the adsorption enthalpy of O_2 or alternatively,
533 adsorption of H_2O blocks more favourable O_2 adsorption sites near OH_{br} . When the surface coverage
534 of H_2O reaches ~ 1.6 monolayers (at RH = 40%) further adsorption of H_2O does not result in further
535 inhibition of HO_2 formation (Figure 9). At sufficiently high RH large amounts of water may condense
536 around the particle forming a liquid layer which may either block access of O_2 to all binding sites or
537 any HO_2 formed remains solvated within the liquid layer.

538 A laboratory study investigating the photocatalytic performance of cement-based TiO_2 -containing
539 materials for reduction of gas-phase oxides of nitrogen ($NO_x = NO + NO_2$),³⁴ showed that upon
540 illumination of the material within a standard flow reactor, concentrations of NO decreased from 100
541 ppm to 20 ppm and continued to fall over the period of a couple of hours until a steady-state
542 concentration of 10 ppm was reached. During this time, gas-phase NO_2 was formed in the flow reactor
543 and remained at a constant concentration of 10 ppm, with NO_2 potentially being produced via the gas-
544 phase reaction of HO_2 generated at surfaces and NO. Furthermore, NO reduction showed a similar
545 dependence to O_2 concentration and RH seen in this study.

546

547 **5. Atmospheric Implications**

548 TiO₂ surfaces are present in the troposphere, occurring naturally as a component of mineral dusts and
549 artificially as building materials, such as self-cleaning glass or environmental catalysts, or from
550 industrial sources, including the nanotechnology industry. TiO₂ nanoparticles are also a candidate for
551 application within Solar-radiation Management (SRM) schemes to mitigate global warming due to their
552 high refractive index and relative affordability.¹⁸ It is proposed that TiO₂ nanoparticles could be injected
553 into the dynamically stable lower stratosphere in order to back-scatter incoming solar-radiation to space
554 resulting in a cooling effect to the Earth's climate. However, this SRM method carries significant risk,
555 as the photocatalytic production of HO₂ radicals from TiO₂ surfaces may have the potential to perturb
556 atmospheric chemistry, particularly in the lower stratosphere where HO₂ is involved in a HO_x catalytic
557 cycle responsible for about 40% of O₃ depletion.³¹ Also, heterogeneous processes are known to
558 influence levels of active chlorine and NO_y partitioning in the stratosphere.

559 During the Saharan Mineral Dust Experiment (SAMUM-2) field campaign held at sea-level in the Cape
560 Verde islands, typical dust concentrations ranged from 10 – 200 µg m⁻³ which correspond to surface
561 areas of $2.2 \times 10^{-7} - 4.4 \times 10^{-6} \text{ cm}^2 \text{ cm}^{-3}$, respectively.³² In this same region, the proportion of TiO₂
562 in mineral dusts was measured to be 4.5% using energy dispersive X-ray spectroscopy,³³ from which
563 we have estimated a range of effective surface areas for TiO₂. The measured values of k'_{prod} presented
564 in section 3.1 above, which are the light flux and surface area independent rates of HO₂ production from
565 TiO₂ aerosol surfaces, were used to calculate the HO₂ production rate from TiO₂ photocatalytic aerosol
566 processes for a typical ambient sunlight flux (using the values at Weybourne, UK shown in Figure 2)
567 and for a 20% mixing ratio of O₂ and RH ~20%. For the above range of TiO₂ surface areas, the rate of
568 heterogeneous HO₂ production is estimated to range from $4.5 \times 10^4 - 1.6 \times 10^6 \text{ molecule cm}^{-3} \text{ s}^{-1}$.
569 However, there is considerable uncertainty in this estimate owing in particular to difficulties in
570 obtaining the absolute flux of the lamp within the flowtube. For comparison, the production rate of HO₂
571 from the gas-phase reaction between OH and CO, and assuming typical concentrations of [OH] = $2 \times$
572 $10^6 \text{ molecule cm}^{-3}$ (0.08 parts per trillion) and [CO] = $5 \times 10^{12} \text{ molecule cm}^{-3}$ (200 parts per billion),
573 typical of the unpolluted troposphere, is $1.6 \times 10^6 \text{ molecule cm}^{-3} \text{ s}^{-1}$. Hence, during periods of significant
574 loading of mineral dust the aerosol production mechanism could represent a significant source of HO₂
575 in the troposphere. However, further studies of HO₂ production from morphologies of TiO₂ typically
576 found in mineral dust are required to provide a more accurate estimate.

577 Considering the potential impact on stratospheric ozone chemistry of the production of HO₂ from TiO₂
578 aerosols used in SRM schemes, it is important to note that the HO₂ production rate is likely to
579 demonstrate a strong temperature dependence, as adsorption is an exothermic process. Further studies
580 which investigate the temperature dependence of HO₂ production from TiO₂ aerosols at
581 stratospherically relevant partial pressures of H₂O and O₂ are required to further quantify any impact.

583 **6. Conclusions**

584 Upon illumination of airborne TiO₂ nanoparticles with near-UV light (~ 300 – 400 nm) in an aerosol
585 flow tube in the presence of O₂ and water vapour, significant quantities of HO₂ was observed in the gas-
586 phase. The dependence of HO₂ production on O₂ shows typical Langmuir adsorption behaviour
587 suggesting O₂ is a reactant in the process generating HO₂. The addition of further H₂O vapour inhibits
588 the production of HO₂ and reduces the adsorption equilibrium coefficient for both O₂ and H₂O,
589 demonstrating the contradictory role of H₂O within the photocatalytic mechanism. Reduction of O₂ by
590 photogenerated electrons is likely to be the initial step for HO₂ production followed by reaction of O₂⁻
591 with a proton produced via oxidation of adsorbed water with a photogenerated hole. The maximum
592 rate coefficient (i.e. when [O₂] is projected to atmospherically relevant levels) for production of gas-
593 phase HO₂ normalised for surface area and light intensity was found to be $k'_{prod} = (3.64 \pm 0.04) \times 10^{-3}$
594 HO₂ molecule photon⁻¹ at a RH of 8.7% for the 80% anatase and 20% rutile formulation of TiO₂ used
595 here, although this decreased to $k'_{prod} = (1.97 \pm 0.03) \times 10^{-3}$ molecule photon⁻¹ as the RH was increased
596 to 22.1%. From surface areas of mineral dust observed at Cape Verde and assuming a TiO₂ fraction of
597 4.5%, the rate of heterogeneous production of HO₂ from TiO₂ surfaces was calculated to be in the range
598 $5 \times 10^4 - 1 \times 10^6$ molecule cm⁻³s⁻¹, with the upper end of this range being similar to the rate of HO₂
599 production from the gas-phase reaction of OH with CO typical of unpolluted regions of the troposphere.
600 Production of gas-phase OH radicals could only be observed for the largest concentrations of TiO₂
601 aerosols used, and are postulated to be formed from the photo-decomposition of H₂O₂ formed via self-
602 reaction of HO₂ on the surfaces of the TiO₂ aerosols.

603

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