Uptake of HO$_2$ radicals onto Arizona test dust particles using an aerosol flow tube

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Received: 30 January 2014 – Published in Atmos. Chem. Phys. Discuss.: 17 February 2014
Revised: 26 May 2014 – Accepted: 2 June 2014 – Published: 18 July 2014

Abstract. Uptake coefficients for HO$_2$ radicals onto Arizona test dust (ATD) aerosols were measured at room temperature and atmospheric pressure using an aerosol flow tube and the sensitive fluorescence assay by gas expansion (FAGE) technique, enabling HO$_2$ concentrations in the range 3–10 $\times$ 10$^8$ molecule cm$^{-3}$ to be investigated. The uptake coefficients were measured as 0.031 $\pm$ 0.008 and 0.018 $\pm$ 0.006 for the lower and higher HO$_2$ concentrations, respectively, over a range of relative humidities (5–76%). A time dependence for the HO$_2$ uptake onto the ATD aerosols was observed, with larger uptake coefficients observed at shorter reaction times. The combination of time and HO$_2$ concentration dependencies suggest either the partial saturation of the dust surface or that a chemical component of the dust is partially consumed whilst the aerosols are exposed to HO$_2$. A constrained box model is used to show that HO$_2$ uptake to dust surfaces may be an important loss pathway of HO$_2$ in the atmosphere.

1 Introduction

OH and HO$_2$ radicals, collectively known as HOx, are closely coupled and together are responsible for the majority of the oxidation in the troposphere. The OH radical controls the concentrations of many species in the atmosphere such as volatile organic compounds (VOCs), whilst the HO$_2$ radical can react with species such as NO, O$_3$ and halogen oxides to recycle OH radicals. Therefore, it is important to understand the processes and reactions that control the concentrations of HOx radicals. In a significant number of field studies a lower concentration of HO$_2$ has been measured than predicted using constrained box models (Brune et al., 1999; Cantrell et al., 1996; Carslaw et al., 1999, 2002; Haggerstone et al., 2005; Jaegle et al., 2000; Kanaya et al., 2000, 2007; Mao et al., 2010; Smith et al., 2006; Sommariva et al., 2004, 2006; Stevens et al., 1994; Stone et al., 2012; Whalley et al., 2010). The discrepancy between measured and predicted HO$_2$ concentrations has, in some cases, been attributed to heterogeneous uptake by aerosols, although some of the historical differences in the marine boundary layer (MBL) have now be accounted for by inclusion of the reactions of HO$_2$ with halogen oxides (Bloss et al., 2005; Kanaya et al., 2002; Sommariva et al., 2006).

Mineral dust is one of the most abundant aerosols in the atmosphere (Textor et al., 2006). Estimates suggest that 2000 Tg year$^{-1}$ are emitted into the troposphere and that it has an average residence time of 4 days before being removed by deposition (Textor et al., 2006). Mineral dust aerosols are formed from wind erosion over soil and deserts and are therefore composed of oxides and carbonates, which are found in Earth’s crust. Although the main sources of mineral dust particles in the atmosphere are the North African and Asian deserts, it can be carried over thousands of kilometres by wind (Textor et al., 2006). Mineral dust aerosols are formed from wind erosion over soil and deserts and are therefore composed of oxides and carbonates, which are found in Earth’s crust. Although the main sources of mineral dust particles in the atmosphere are the North African and Asian deserts, it can be carried over thousands of kilometres by wind (Textor et al., 2006). As well as being a major source of particulate matter in the troposphere, mineral dust plays an important role in processes controlling air quality, visibility, radiative forcing, biogeochemical cycles and atmospheric chemistry (Dentener et al., 1996; Seinfeld and Pandis, 2006). The heterogeneous uptake onto dust can influence...
the concentrations of several important species, for example NO₃, O₃ and HO₂ (Dentener et al., 1996; Tang et al., 2014).

Arizona test dust (ATD) is a proxy for atmospheric mineral dust as it contains many of the same metals which are found in naturally occurring mineral dust aerosols, for example Saharan and Asian dust (Karagulian et al., 2006), although its mineralogy is different. The composition of ATD (Powder Technology Inc.) is SiO₂ (68–76 %), Al₂O₃ (10–15 %), Fe₂O₃ (2–5 %), Na₂O (2–4 %), CaO (2–5 %), MgO (1–2 %), TiO₂ (0.5–1.0 %) and K₂O (2–5 %). An aerosol flow tube has been used to measure the uptake coefficient for N₂O₅ upon ATD aerosols (Tang et al., 2014) but to our knowledge, only one laboratory study has measured HO₂ uptake by ATD surfaces. ATD (0–3 µm) was chosen in this work rather than Saharan dust due to the smaller size of the ATD particles which reduces the risk of aerosol deposition along the flow tube. Bedjanian et al. (2013) recently measured initial HO₂ uptake coefficients onto ATD solid surfaces for HO₂ concentrations in the range of 0.35–3.30 molecule cm⁻³. However, there are currently no studies measuring HO₂ uptake coefficients onto ATD aerosols (rather than surfaces) or under atmospherically relevant HO₂ concentrations. Therefore, the aim of this study was to measure the HO₂ uptake coefficient for ATD aerosols at two different initial HO₂ concentrations (1 × 10⁹ and 3 × 10⁸ molecule cm⁻³), over a range of relative humidities (6–73 % RH) and as a function of the time that the ATD aerosol particles are exposed to the HO₂ radicals.

2 Experimental

2.1 Overview of the apparatus

The experimental apparatus used to measure HO₂ uptake coefficients onto ATD aerosols at atmospheric pressure and at 291 ± 2 K is shown in Fig. 1. The majority of the apparatus is described in detail by George et al. (2013) and is therefore only described briefly here. The dust disperser produced aerosol number concentrations which were unstable over time, and were measured using a condensation particle counter (CPC; TSI 3775). Half of the experiments were performed with the CPC before the aerosol flow tube and half were performed with it after the flow tube. It was found that the position of the CPC did not affect the measured uptake coefficient indicating that losses of dust in the flow tube were negligible. The total flow through the flow tube (107 cm length, 5.9 cm I.D.) was 5.4 ± 0.2 L min⁻¹ which resulted in a Reynolds number of ~130. Experiments were performed by placing a moveable injector (which introduced the HO₂ radicals into the flow tube) at different positions along the flow tube (30, 40, 50, 60, 70 and 80 cm) corresponding to reaction times between ~7 and 23 s. The distances were measured from the end of the flow tube to the injector position (a length of 0 cm would have represented the injector being at the end of the flow tube attached to the FAGE cell). For a given injector position, the HO₂ signal was then measured at the end of the flow tube using the fluorescence assay by gas expansion (FAGE) technique as a function of the aerosol concentration. The sensitivity of the FAGE cell towards HO₂ was calibrated and hence the signal could be converted into an absolute concentration (George et al., 2013).

2.2 HO₂ generation and detection

HO₂ radicals were produced by passing water vapour over a mercury lamp (L.O.T.-Oriel 6035) placed within a moveable injector (110 cm length, 1.9 cm O.D. (outer diameter), 1.6 cm I.D. (inner diameter)) via the following reactions:

\[
\text{H}_2\text{O} + h\nu \rightarrow \text{OH} + \text{H}, \quad (R1)
\]

\[
\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}. \quad (R2)
\]

The experiments were performed at two different initial HO₂ concentrations by setting the lamp current to either 20 or 2.5 mA, which produced initial HO₂ concentrations of 1 × 10⁹ and 3 × 10⁸ molecule cm⁻³ respectively, after dilution of the injector flow with the aerosol flow. A correction was applied to take into account any changes in the LIF (laser-induced fluorescence) signal owing to fluorescence quenching by water vapour if it was changed during experiments, using the methodology described by Vaughan et al. (2012). The maximum correction was an 8 % change in the HO₂ concentration. Initial HO₂ concentrations were calculated by propagating the measured HO₂ concentrations without aerosols present back to time zero (defined as the point of injection into the main flow tube). The HO₂ concentrations were also measured at the first injector position (30 cm along the flow tube, ~7 s) with no aerosols being present to take into account the wall loss in the first section of the flow tube.

HO₂ radicals were detected by FAGE (detection limit ~10⁶ molecule cm⁻³) which has previously been described (George et al., 2013). Briefly, the HO₂ radicals entered the FAGE cell placed at the end of the flow tube through a 0.7 mm diameter pinhole and were converted into OH by reacting with NO (BOC, 99.5 %). The Q₁(2) line of the OH \((A^2\Sigma^+ - X^2Π\nu' = 0 - \nu' = 0)\) transition at ~308 nm was utilised to excite the OH fluorescence in the FAGE cell. A Nd : YAG (neodymium-doped yttrium aluminium garnet)-pumped dye laser produced the required 308 nm radiation (line width ~0.1 cm⁻¹) and was operated at a pulse repetition rate of 5 kHz, with a pulse energy of ~2.4 µJ. The FAGE cell was continuously evacuated using a combination of a rotary pump (Edwards, model E1M80) and a roots blower (EH2100) and was kept at 0.8–0.9 Torr, which was monitored using a capacitance monitor (Tylan General, CDC 11). Mie scattering has previously been found not to contribute towards the FAGE cell signal and aerosols were found not to

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influence the LIF detection sensitivity towards HO$_2$ (George et al., 2013).

### 2.3 Arizona test dust generation and detection

The carrier gas used for these experiments was compressed nitrogen which first passed through a gas purification system (TSI 3074B) consisting of particle filters, a dryer and a carbon filter. The HO$_2$ flow, the humidified flow and the NO flow were controlled using five mass flow controllers (Brooks, model 5850S and MKS, model 1179A). The required relative humidity was obtained by mixing together and altering the ratio of a dry flow and a flow which had been passed through a water bubbler. This humidified flow, which was mixed with the aerosol flow in the conditioning flow tube, varied from 3.6 L min$^{-1}$ to 4.3 L min$^{-1}$ but was constant throughout each individual experiment. The aerosol flow was monitored and maintained at 1.35 ± 0.05 L min$^{-1}$ and the HO$_2$ flow was measured as 1.29 ± 0.02 L min$^{-1}$. The total flow passing through the flow tube, including the aerosol, dilution and HO$_2$ flows, was between 5.2 and 5.6 L min$^{-1}$. The FAGE instrument sampled 4.3 L min$^{-1}$ and the CPC sampled 0.3 L min$^{-1}$ with the remainder of the flow (0.6–1.0 L min$^{-1}$) exiting via an exhaust line.

The dust disperser consisted of a 500 mL high density polyethylene (HDPE) bottle (Thermo Scientific Nalgene) that had two holes drilled into it (one through the lid and one 5 cm from the base of the bottle, see Fig. 1). Two 1/4 in. O.D. tubes were placed through the holes and affixed to the bottle. Nitrogen entered the dust disperser through the tube on the side of the bottle and left through the tube at the top of the bottle. A magnetic stir bar (PTFE covered, 45 mm in length) was placed in the bottle and the bottle was placed on top of a magnetic stirrer, (Gallenkamp, 8640677) which was set to the maximum stirring speed. The combination of the stirring and the nitrogen flow produced a “dust cloud” in the bottle, which produced a non-stable aerosol concentration.

The flow of ATD aerosols passed through an impactor, which was used to stabilise the flow rate from the dust disperser. The concentration of aerosols entering the flow tube was controlled using a high efficiency particulate air filter.
(HEPA) filter and a bypass. The proportion of the flow passing through the bypass compared to the filter was controlled using a needle valve.

The aerosol number concentration was monitored using a CPC (TSI 3775). Measurements were also made under the same experimental conditions using a scanning mobility particle sizer (SMPS; TSI, 3080) and an aerodynamic particle sizer (APS; TSI, 3321) in order to measure the entire log-normal size distribution, as shown in Fig. 2. The APS measures the time of flight of particles over a fixed distance. Therefore, corrections were made to convert the aerodynamic diameters (Da) measured by the APS into a Stokes diameter (Ds) (measured by the SMPS) by taking into account the density of the dust particles (ρ) and the non-sphericity of the aerosols (β) (Hinds, 1982).

\[
Ds = \frac{Da}{\sqrt{\rho/\beta}} \tag{1}
\]

A value of ρ = 2.7 g cm\(^{-3}\) was used for the density of Arizona test dust, and β = 1.8 produced the best agreement between the SMPS and APS size distribution, and is close to the value for Saharan dust reported by Tang et al. (2012). From Fig. 2, the average radius of a single aerosol was calculated as 273 ± 10 nm. Checks determined that the average radius did not change over time or when sampling from before or after the flow tube.

2.4 Data analysis

A clear anti-correlation between the HO\(_2\) signal and the aerosol number concentration was observed, as shown in Fig. 3, showing that there is an interaction between HO\(_2\) and the aerosols. When the CPC was placed before the flow tube (for half of the experiments) a dilution factor had to be applied to the aerosol number concentration to take into account the flow from the injector mixing in to the rest of the flow.

\[
N_{flowtube} = \frac{N_{CPC}(F_{total} - F_{HO2})}{F_{total}}, \tag{2}
\]

where \(N_{flowtube}\) is the aerosol number concentration in the flow tube, \(N_{CPC}\) is the number concentration measured by the CPC, \(F_{total}\) is the total flow entering the flow tube and \(F_{HO2}\) is the total flow from the injector.

For each injector position along the flow tube, corresponding to a given value of the reaction time \(t\), the HO\(_2\) concentration is given by Wagner et al. (2008):

\[
-\ln \left[ \frac{[HO2]_t}{[HO2]_0} \right] = 0.25\gamma_{obs}wA_dN_d\delta + k_w t, \tag{3}
\]

where \(\gamma_{obs}\) is the observed HO\(_2\) uptake coefficient, \(N_d\) is the aerosol number concentration, \(A_d\) is the average surface area of an aerosol particle assuming a spherical shape, \(t\) is the reaction time which was calculated from the flow rate, injector position and dimensions of the flow tube, \(k_w\) is the pseudo first-order wall loss and \(w\) is the mean molecular speed of HO\(_2\) at room temperature given by

\[
w = \frac{8RT}{\pi M_w}, \tag{4}
\]

where \(R\) is the universal gas constant, \(T\) is the temperature and \(M_w\) is the molecular weight of HO\(_2\). Hence plotting the natural log of the HO\(_2\) LIF signal (with any background from scattered light subtracted) against \(N_d\), as shown in Fig. 4, yields a gradient of \(-0.25\gamma_{obs}wA_d\delta\). For each position along the flow tube, corresponding to a particular reaction time, the signal was obtained as a function of aerosol number concentration, and this included a signal with no aerosols present, and so for each reaction time the effect of wall loss was directly subtracted. Data obtained for aerosol number concentrations above \(4 \times 10^4\) particles cm\(^{-3}\) were not included in the analysis as the FAGE signal was usually close to background levels. A graph of the gradient of Fig. 4 \((0.25\gamma_{obs}wA_d\delta)\) plotted against \(t\) yields a gradient of \(0.25\gamma_{obs}wA_d\), as shown in Fig. 5, from which an observed uptake coefficient could be calculated. \(A_d\) was calculated from the average radius \((r_s)\) of the aerosols:

\[
A_d = 4\pi r_s^2, \tag{5}
\]

where

\[
r_s^2 = A_{total}/\left(4\pi N_{total}\right), \tag{6}
\]

where \(A_{total}\) is the total surface area measured in Fig. 2 and \(N_{total}\) is the total number of particles producing that surface area.

Unlike in previous experiments (George et al., 2013), the whole SMPS size distribution was not used to calculate the surface area, as the SMPS took 3 min to scan a distribution during which the dust aerosol number concentration varied significantly. The SMPS distribution shown in Fig. 2 is an average of many SMPS distributions, from which the average radius was obtained, and the CPC aerosol number density which was recorded with 1 s averaging period was used to calculate the average surface area with the same time distribution.

The observed uptake coefficient was corrected to take into account the effects of gas phase diffusion:

\[
\gamma_{corr} = \frac{\gamma_{obs}}{1 - \gamma_{obs}\lambda(r_s)} \tag{7}
\]

where the values of \(\lambda(r_s)\) are given by

\[
\lambda(r_s) = \frac{0.75 + 0.283Kn}{Kn(1 + Kn)}, \tag{8}
\]

where \(Kn\) is the Knudsen number defined by

\[
Kn = \frac{3D_s}{wr_s}, \tag{9}
\]
Figure 2. Normalised (a) number weighted and (b) surface weighted ATD aerosol size distributions recorded with the SMPS (open symbols) and the APS (closed symbols) positioned at the downstream end of the aerosol flow tube. The red line represents a log normal fitting to all the measured points from both instruments for the number-weighted distribution.

where $D_g$ is the gas phase diffusion constant of HO$_2$ ($0.25 \text{cm}^2\text{s}^{-1}$) at room temperature (Mozurkewich et al., 1987). The Brown correction (Brown, 1978) was then applied to the uptake coefficients, in order to take into account the laminar flow in the flow tube.

### 2.5 Measuring the time dependence of the uptake coefficient

In order to determine whether the HO$_2$ uptake coefficient was a function of the reaction time between HO$_2$ and the dust aerosol, the average uptake coefficient between the time that the HO$_2$ was released into the flow tube ($t_0$) and the time that it took to reach the FAGE cell ($t$) was measured. The analysis described above was used, however, instead of plotting $(0.25 \gamma_{\text{corr}} w_A g t)$ against $t$ (Fig. 5), uptake coefficients were calculated for each individual injector position by using $t - t_0$ as the time in Eq. (3). This is equivalent to measuring the gradient of a line that connects the origin with each data point in Fig. 5. If the uptake coefficient was constant over time, the linear-least squares fitted line to the data shown in Fig. 5 would be expected to pass through the origin. An intercept on the $y$ axis could indicate rapid uptake in the first few seconds of contact between the HO$_2$ radicals and the aerosols corresponding to a higher uptake coefficient, which then reduces over time.

### 3 Results and discussion

#### 3.1 The uptake coefficient dependence on humidity and HO$_2$ concentration

The HO$_2$ uptake coefficient onto ATD aerosols was measured over the RH range 5–76 % and at two initial HO$_2$ concentrations of $1 \times 10^9$ and $3 \times 10^8$ molecule cm$^{-3}$, the data for which are shown in Fig. 6. When averaged over the range of RH studied, HO$_2$ uptake coefficients of $\gamma_{\text{corr}} = 0.018 \pm 0.006$ and $0.031 \pm 0.008$ were obtained for $[\text{HO}_2] = 1 \times 10^9$ and $3 \times 10^8$ molecule cm$^{-3}$, respectively. Figure 6 shows a slight increase in the uptake coefficient as the RH increases. However, it should be noted that although the HO$_2$ concentration exiting the injector was the same for different RH, the HO$_2$ signal (which was corrected for fluorescence quenching) dropped more quickly along the flow tube at higher HO$_2$ concentrations because of higher wall losses observed at higher RH (George et al., 2013). It was observed that by 30 cm along the flow tube, corresponding to ~7 s reaction time, the HO$_2$ concentration at 7 % RH was approximately double that of the HO$_2$ concentration when working at 75 % RH, for both of the initial HO$_2$ concentrations used. At higher RH, uptake coefficients were effectively being measured at lower HO$_2$ concentrations. Therefore, the apparent small increase in uptake coefficient with RH may be due to the reducing HO$_2$ concentration.

Uptake coefficients were then measured for different concentrations of HO$_2$ generated in the injector. Figure 7 shows uptake coefficients determined from gradients of Fig. 5 (HO$_2$ loss as a function of aerosol number concentration measured for a variety of fixed injector positions between 30 and 80 cm) plotted against the HO$_2$ concentration at 30 cm along the flow tube. These results show clearly that the measured uptake coefficients increase as the initial HO$_2$ concentration is decreased. This concentration dependence would be expected if the HO$_2$ radicals (or the product of a reaction of HO$_2$ on the dust aerosol surface, which is assumed below to be H$_2$O$_2$) were binding to the active adsorption sites ($S$) of the aerosols and thereby blocking further adsorption of HO$_2$ radicals. A potential reaction scheme is shown in

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concentrations were $1 \times 10^2$ molecules cm$^{-3}$, and the relative humidity was 32% whereas for (b) the injector was positioned at 60 cm and the relative humidity was 53%.

Reactions (R3)–(R6):

\[ \text{HO}_2(g) + S \rightarrow \text{HO}_2 - S, \]  

\[ \text{HO}_2 - S + \text{HO}_2 - S \rightarrow \text{H}_2\text{O}_2(g) + \text{O}_2 + 2S, \]  

\[ \text{HO}_2 - S + \text{HO}_2 - S \rightarrow \text{H}_2\text{O}_2 - S + \text{O}_2 + S \]  

\[ \text{H}_2\text{O}_2 - S \rightleftharpoons \text{H}_2\text{O}_2(g) + S. \]  

If the surface were becoming partially saturated with HO$_2$ radicals (or the products of a reaction) and blocking the incoming HO$_2$ radicals, a decrease in the uptake coefficient with time would then be expected. Another possible explanation for an HO$_2$ concentration dependence would be if the HO$_2$ was reacting with a trace component of the aerosol ($X$), so that the concentration of that component decreased rapidly over a few seconds:

\[ \text{HO}_2 - S + X \rightarrow \text{products.} \]  

At higher HO$_2$ concentrations, $X$ would be used up much faster than at low HO$_2$ concentrations, again resulting in a time dependence of the uptake coefficient along the flow tube. It is not possible from these experiments alone to determine which of the two proposed mechanisms is responsible for the observed HO$_2$ concentration dependence of the uptake coefficient, both of which also predict a time dependence. However, a model is currently being developed to further interpret the trends that have been observed.

### 3.2 The time dependence of the uptake coefficient

Measurements of the average uptake coefficients between $t = 0$ (when the HO$_2$ is injected) and six different reaction times (using the methodology used in Sect. 2.5) are shown in Fig. 8, for two different initial concentrations of HO$_2$. The results show that the uptake coefficient decreases with increasing time, suggesting (as introduced above in Sect. 3.1) that there is either a higher uptake coefficient for fresh aerosols followed by a lower uptake onto aerosols that have a partially saturated surface (Reactions R3–R6), or that a component in the aerosol which reacts with HO$_2$ is being used up over time (Reaction R7). A dependence of $\gamma$ upon the HO$_2$ concentration can also be seen in Fig. 8, which also shows that the uptake coefficients do not approach zero at longer times, which would imply full equilibration (i.e. the rates of
adsorption and desorption of HO₂ are equal). These results suggest that surface saturation (Reaction R3) is not the only process occurring and that there is also reaction at the dust surface which removes HO₂ irreversibly. The reaction of the HO₂ at the surface of the aerosol would become the rate-determining step once the aerosol surface was saturated. It would also be expected that the uptake coefficient would tend to zero if Reaction (R7) was solely responsible for the observation of the HO₂ concentration dependence and time dependence. However, fitting an exponentially decaying function to the data shown in Fig. 8 gave \( \gamma = 0.042 \) and 0.024 as the limiting values at long reaction times for \([\text{HO}_2]=3 \times 10^8\) and \(1 \times 10^9\) molecule cm\(^{-3}\), respectively. These values are within

Figure 5. Plot of \(0.25\gamma_{\text{obs, } \text{wA}} t\) as a function of reaction time for uptake of HO₂ onto ATD aerosols. The linear least-squares fit to these point yields \(0.25\gamma_{\text{obs, } \text{wA}} t\) as the gradient. The intercept of the fit at \(t = 0\) \((1.9 \pm 0.4) \times 10^{-5} \text{ cm}^3\) suggests a higher gradient and hence a higher uptake coefficient occurring in the first few seconds of contact between the HO₂ and ATD aerosols. The error bars represent two standard deviations in the individual exponential fits, examples of which are given in Fig. 4.

Figure 6. HO₂ uptake coefficients onto ATD aerosols measured at different relative humidities and at an initial HO₂ concentration of \(1 \times 10^9\) (open symbols) and \(3 \times 10^8\) molecule cm\(^{-3}\) (closed symbols). The error bars represent one standard deviation of the average of a number of repeated experiments.

Figure 7. HO₂ uptake coefficients measured at different HO₂ concentrations, which were determined at an injector position of 30 cm when no dust aerosols were present in the aerosol flow tube. The error bars represent one standard deviation of a number of repeated experiments for a given HO₂ concentration.

Figure 8. HO₂ uptake coefficients measured at a number of HO₂-aerosol contact times (corresponding to different injector positions). Experiments were performed at 10 % RH and at initial HO₂ concentrations of \(1 \times 10^9\) (black squares) and \(3 \times 10^8\) molecule cm\(^{-3}\) (red circles). The uptake coefficients correspond to the average value between \(t = 0\) and the reaction time given. The error bars represent one standard deviation of the average of a number of repeated experiments. The solid lines are exponentially decaying functions \(\gamma = 0.58 \exp(-t/2.9) + 0.042\) and \(\gamma = 0.11 \exp(-t/5.4) + 0.024\) which are fitted to the data for \(3 \times 10^8\) and \(1 \times 10^9\) molecule cm\(^{-3}\), respectively.
the error bars of 0.031 ± 0.008 and 0.018 ± 0.006 measured as the average from Fig. 6.

3.3 Comparison of γ\textsubscript{\textit{HO}2} with literature values

Bedjanian et al. (2013) is the only published study to our knowledge reporting a HO\textsubscript{2} uptake coefficient onto solid ATD surfaces, which reported initial uptake coefficients (γ\textsubscript{i}) onto fresh ATD surfaces and for HO\textsubscript{2} concentrations in the range of 0.35–3.30 × 10\textsuperscript{12} molecule cm\textsuperscript{-3}. In the work reported here aerosols were used instead of a coated surface and HO\textsubscript{2} concentrations were approximately four orders of magnitude lower. Bedjanian et al. (2013) observed an order of magnitude decrease in the uptake coefficient (from γ\textsubscript{i} ~ 0.07 to γ\textsubscript{i} ~ 0.007 at 275 K) when increasing the relative humidity between 0.02 and 94 %, which was attributed to water molecules binding to the dust surface and blocking the active sites for incoming HO\textsubscript{2} radicals. A similar humidity dependence has also been observed by Remorov et al. (2002) for HO\textsubscript{2} uptake onto solid sodium chloride surfaces and by Loukhovitskaya et al. (2009) for HO\textsubscript{2} uptake onto MgCl\textsubscript{2}–6 H\textsubscript{2}O surfaces. However, Loukhovitskaya et al. (2009) did not see a humidity dependence for NaCl or NaBr surfaces. Contrastingly, Taketani and Kanaya (2010) and Taketani et al. (2008, 2013) reported a small increase in uptake coefficient with humidity for a variety of different solid aerosols which was attributed to HO\textsubscript{2}–H\textsubscript{2}O complexes being formed on the surface of the aerosols. In the work reported here, a small increase in uptake was also observed with increasing humidity. However, this apparent dependence was attributed to a HO\textsubscript{2} concentration effect, with higher humidities leading to lower HO\textsubscript{2} concentrations due to the higher wall losses and higher measured uptake coefficients.

Bedjanian et al. (2013) did not observe a HO\textsubscript{2} concentration dependence. However, this may be due to the fact that γ\textsubscript{i}, the initial uptake onto a fresh surface, was measured rather than uptake onto dust which had already been partially saturated by HO\textsubscript{2}. However, Bedjanian et al. (2013) did observe a time dependence over ~80 min that was attributed to deactivation of the dust surface. The deactivation of a solid surface has previously been suggested as being due to the by-products from reactions used to form HO\textsubscript{2} (e.g. HF as used by Bedjanian et al.) (Loukhovitskaya et al., 2009). However, as reported in this paper, HO\textsubscript{2} was formed from the photolysis of water vapour in the presence of trace levels of O\textsubscript{3} so, other than OH, which is completely removed within the injector, to our knowledge there should be no other products from our method of HO\textsubscript{2} generation that could deactivate the surface. An uptake coefficient dependence upon time and radical concentration has also been observed for other species onto solid surfaces and has been attributed to surface saturation or to a component of an aerosol being used up over time (Ammann and Pöschl, 2007; Shiraiwa et al., 2012; Slade and Knopf, 2013). Crowley et al. (2010) have also discussed the drawbacks of using bulk samples and the geometric area of sample holders to investigate heterogeneous reactions.

In this laboratory, George et al. (2013) previously measured uptake coefficients onto aqueous and dry salt aerosols using a very similar setup described in this paper and with an initial HO\textsubscript{2} concentration of 1 × 10\textsuperscript{9} molecule cm\textsuperscript{-3}. For dry salts, the uptake coefficient was below the limit of detection (<0.004) and for aqueous salts the uptake coefficient was measured as being between 0.003 and 0.016 depending on humidity and the type of salt. Therefore, the value of 0.018 ± 0.006 measured for [HO\textsubscript{2}] = 1 × 10\textsuperscript{9} molecule cm\textsuperscript{-3} for ATD aerosols shows that the HO\textsubscript{2} uptake coefficient of ATD is larger than for salt aerosols. The larger values for dust aerosols compared to solid dry salts may be due to the non-sphericity of the aerosols, leading to much larger surface areas for ATD (the Brunauer–Emmett–Teller (BET) surface area for ATD was determined by Bedjanian et al. (2013) as 85 ± 10 m\textsuperscript{2} g\textsuperscript{-1}), or may due to the chemical composition of the aerosols, for example the presence of transition metal ions.

4 Atmospheric implications

A box model which contains a near explicit chemical scheme for the oxidative degradation of C1–C5 hydrocarbons, taken from the master chemical mechanism (MCM) version 3.1 (Saunders et al., 2003) has been used to assess the atmospheric impact of heterogeneous loss of HO\textsubscript{2} concentrations to dust particles. The model was constrained with gas-phase data taken during the Reactive Halogens in the Marine Boundary Layer (RHaMBLe) project (Lee et al., 2010) that took place in 2007 at the Cape Verde Atmospheric Observatory (CVAO; Carpenter et al., 2010), which is situated on the island of Sao Vicente in the tropical Atlantic Ocean (23.96° S, 46.39° W). The model has been used previously to calculate OH and HO\textsubscript{2} concentrations for comparison with those measured at CVAO (Whalley et al., 2010). Hourly measurements of VOCs such as ethane, acetaldehyde, methanol, acetone and formaldehyde, NO\textsubscript{x}, O\textsubscript{3}, CO, CH\textsubscript{4}, j(O\textsubscript{1D}) and meteorological parameters were used to constrain the model. A halogen chemical scheme was also included in the mechanism (Whalley et al., 2010) and the model was constrained to average diurnal cycles of IO and BrO radicals which were measured by long-path differential optical absorption spectroscopy (DOAS) at the observatory in May 2007 (Read et al., 2008). A constant HCHO concentration of 328 pptv (parts per trillion by volume), based on average [HCHO] measured by LP-DOAS (Whalley et al., 2010), and a constant H\textsubscript{2} concentration of 500 ppb (parts per billion), typical of MBL concentrations, were used as constraints.
A simple scheme, based on a first-order loss of HO\textsubscript{2} to aerosol surfaces (Ravishankara, 1997) was considered in the model to determine the impact of dust particles:

$$k'_{\text{loss}} = \frac{wA\gamma}{4}, \quad (10)$$

where $w$ is the mean molecular speed of HO\textsubscript{2} molecules (cm s\textsuperscript{-1}), defined in Eq. (4), $k'_{\text{loss}}$ is the heterogeneous loss rate, $A$ is the aerosol surface area per unit volume and $\gamma$ is the uptake coefficient (determined from the experiments reported in this work). The model was run to steady state (~4 days) using the FACSIMILE integrator (Sweetenham and Curtis, 1987) at which point the diurnal variation of unmeasured model intermediates remained constant.

Cape Verde is predominantly affected by marine aerosols and is also seasonally affected by Saharan dust particles with more dust events observed during the winter (Müller et al., 2010). Although HO\textsubscript{2} uptake experiments have been performed in this work using ATD rather than Saharan dust, previous experiments for NO\textsubscript{2} and NO\textsubscript{3} uptake onto both types of surface have produced almost identical uptake coefficients, whilst for N\textsubscript{2}O\textsubscript{5} and HNO\textsubscript{3} the measured uptake was approximately a factor of 1.5–2 lower for ATD (Crowley et al., 2010; Tang et al., 2014).

When running the model it was assumed that no products, such as H\textsubscript{2}O\textsubscript{2}, generated from the uptake of HO\textsubscript{2} by dust surfaces, were released to the gas phase, and the temperature was inputted into the model and varied depending on the time of day with an average temperature of 296 K. The rate of uptake of other species onto dust aerosol surfaces was set to zero. The model calculated a maximum HO\textsubscript{2} concentration at solar noon of 1.9 \times 10\textsuperscript{8} molecule cm\textsuperscript{-3} (~7.5 pptv) with no aerosols present. The HO\textsubscript{2} uptake coefficient was then fixed to $\gamma = 0.031 \pm 0.008$, the value obtained in this work for ATD aerosols for the lower HO\textsubscript{2} concentrations used in the experiments. The value of $\gamma = 0.031 \pm 0.008$ was on the higher side of the observed range of HO\textsubscript{2} uptake coefficients measured in this work. Assuming an average aerosol diameter of 1 \mu m and a density of 2.7 g cm\textsuperscript{-3}, a typical range of dust aerosol concentrations of 10–200 µg m\textsuperscript{-3} observed in Cape Verde (throughout the SAMUM-2 field campaign) (Schladitz et al., 2011) corresponds to geometric surface areas of 2.2 \times 10\textsuperscript{-7}–4.4 \times 10\textsuperscript{-6} cm\textsuperscript{2} cm\textsuperscript{-3}, respectively. For this range of surface areas, the box model constrained by Cape Verde conditions calculated a decrease in the maximum HO\textsubscript{2} concentrations from the no aerosol value of between 0.3 and 6.5 %. The impact on the maximum noon HO\textsubscript{2} concentration due to varying the total dust surface area and $\gamma = 0.031$ is shown in Fig. 9. Given the variation of $\gamma$ with [HO\textsubscript{2}] as shown in Fig. 7, the percentage reduction in HO\textsubscript{2} due to heterogeneous uptake onto dust may be greater than shown in Fig. 9 in the morning and evening when [HO\textsubscript{2}] is lower. It should be noted that diffusive limitations due to the larger aerosol diameters were disregarded in these calculations.

![Figure 9. The decrease of the solar noon maximum HO\textsubscript{2} concentration (crosses with solid black line) with dust surface area calculated by a box model utilising the master chemical mechanism and constrained to conditions at the Cape Verde Atmospheric Observatory. An HO\textsubscript{2} uptake coefficient of 0.031 was used in these calculations, and the dashed red lines represent the HO\textsubscript{2} concentrations calculated with the ±0.008 error in the uptake coefficient.](image-url)

During the RHaMBLe campaign, which started in May 2007, high dust concentrations (40–69 µg m\textsuperscript{-3}) were only measured for the first 3 days of the campaign, although during a dust event in the previous week a dust concentration of 332 µg m\textsuperscript{-3} had been measured (Müller et al., 2010). During the remainder of the RHaMBLe campaign the dust concentrations were typically less than 10 µg m\textsuperscript{-3} (Müller et al., 2010). Whalley et al. (2010) reported that in order to obtain good agreement between HO\textsubscript{2} model predictions and observations during RHaMBLe, HO\textsubscript{2} aerosol uptake and deposition to the ocean had to account for 23 % of the total rate of HO\textsubscript{2} loss at noon. However, with dust concentrations of less than 10 µg m\textsuperscript{-3} during the model–measurement comparison period, the HO\textsubscript{2} concentrations would be affected by less than 0.3 %. The dust loading though at Cape Verde is highly variable, and the loading of 332 µg m\textsuperscript{-3} mentioned above would reduce HO\textsubscript{2} by over 10 % from uptake onto dust alone.

Soot and silicate particles have also been found in the fine particle modes in Cape Verde (Schladitz et al., 2011). The impact on HO\textsubscript{2} concentrations due to uptake onto these particles is unknown due to a lack of laboratory data. Sea-salt aerosols could also contribute significantly to the difference between the models and observations, especially if they contain small amounts of transition metal ions (Fitzsimmons et al., 2013), such as copper, which has been shown in laboratory studies to increase the HO\textsubscript{2} uptake coefficient significantly (George et al., 2013; Mozurkewich et al., 1987; Take-tani et al., 2008; Thornton and Abbatt, 2005). Uptake coefficients of N\textsubscript{2}O\textsubscript{5} to illite aerosols ($\gamma = 0.04–0.09$, dependent upon RH), which is one of the most abundant clay minerals in...
dust, were measured to be considerably larger than for uptake to ATD ($\gamma \sim 0.006$, weak if any dependence upon RH) (Tang et al., 2014). Hence future studies measuring the uptake of \( \text{HO}_2 \) onto illite and other components of dust aerosols, as well on Saharan or Asian dust samples, would be highly beneficial.

5 Conclusions

\( \text{HO}_2 \) uptake coefficients onto dust aerosols were measured for the first time using a flow tube reactor coupled with a sensitive \( \text{HO}_2 \) FAGE detection system. The \( \text{HO}_2 \) uptake coefficient on Arizona test dust aerosol was measured as $\gamma = 0.031 \pm 0.008$ and $\gamma = 0.018 \pm 0.006$ for initial \( \text{HO}_2 \) concentrations of $3 \times 10^8$ and $1 \times 10^9$ molecule cm$^{-3}$, respectively, with very little dependence upon relative humidity observed over a wide range ($6$–$76 \%$). Both a \( \text{HO}_2 \) concentration dependence and a time dependence on the uptake coefficient was observed, suggesting that the active sites on the dust surface were becoming blocked by either \( \text{HO}_2 \) or a reaction product, or that a component of the dust that removed \( \text{HO}_2 \) by reaction was being used up over time. However, for both the lower and higher \( \text{HO}_2 \) concentrations the time dependence of the uptake coefficient did not approach zero at long times, indicating that there was a slow reaction on the surface removing \( \text{HO}_2 \).

The atmospheric impact of the uptake onto dust aerosols on \( \text{HO}_2 \) concentrations was investigated for the conditions encountered at the Cape Verde Atmospheric Observatory in the tropical Atlantic Ocean. Over the range of dust aerosol concentrations encountered at Cape Verde there was a significant effect on \( \text{HO}_2 \) concentrations, lowering them by more than $10 \%$ for the higher loadings of aerosols that are common during winter. However, dust aerosols alone probably cannot account for the entire difference between measured and modelled \( \text{HO}_2 \) concentrations that was observed during the RHaMBLe field campaign in 2007. In order to be able to reduce the difference between measured and modelled concentrations from uptake onto aerosols, more information is needed about transition metal ion concentrations in marine aerosols as well as further measurements of \( \text{HO}_2 \) uptake coefficients onto other type or aerosols; for example, soot, silicate and other mineral particles. The modelling studies also showed that in regions with much higher dust concentrations (e.g. the sub-Saharan Africa), the impact on \( \text{HO}_2 \) concentrations may be even more important. Indeed, during a pre-monsoon dust storm in northern India, a study using the Weather Research and Forecasting model coupled with Chemistry (WRF-Chem) showed that uptake of \( \text{HO}_2 \) via heterogeneous reactions on dust surfaces led to a maximum reduction of about $40 \%$ over the Thar Desert study region (Kumar et al., 2014), using the value of $\gamma$ determined by Bedjanian et al. (2013).

Acknowledgements. This work was supported by the National Environment Research Council under grant NE/F020651/1. P. S. J. Matthews is grateful to NERC for the award of a studentship. L. K. Whalley and D. E. Heard are also grateful to the NERC funded National Centre for Atmospheric Science for ongoing support. We are grateful to the Centre for Atmospheric Science in the School of Earth Atmospheric and Environmental Sciences at the University of Manchester for the loan of the aerodynamic particle sizer used in this work.

Edited by: F. Keutsch

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Atmos. Chem. Phys., 14, 7397–7408, 2014

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