We thank the two reviewers for their very helpful comments, which have helped to improve the manuscript. The detailed point-by-point responses to the referees' comments are given below in blue and we have indicated the changes made in the manuscript in response to each comment. The marked up revised manuscript (changes are given in red) is then appended after the responses.

Anonymous Referee #1
Received and published: 24 May 2016
The manuscript entitled, "The effect of viscosity on the HO2 uptake by sucrose and secondary organic aerosol particles," by Lakey et. al. describes new measurement of the uptake coefficient of HO2 onto model organic aerosol surfaces (sucrose and SOA). The HO2 loss rate onto aerosol surfaces may have important ramifications for the HO_x cycle in the atmosphere. The experimental measurements are interpreted using a kinetic multi-layer model. The experimental measurements are carefully done with the appropriate checks and associated error analysis. The following aspects should be addressed by the authors in a revised manuscript.

1. There are a number of studies not cited in the manuscript that have generally discussed and observed the evolution of uptake coefficients with particle viscosity. These should be included and discussed in light of their relevance for the present study. For example, Slade and Knopf (Geophys. Res. Lett., 41, 5297–5306), Davies and Wilson (Chem Sci, 2015,6, 7020-7027) Houle et al. (Phys. Chem. Chem. Phys., 2015, 17, 4412), observed similar relationships as shown in Fig. 5 albeit for OH radical uptake. All of these studies interpret the relationship between gamma and viscosity mathematically using diffusoreactive lengths and such an analysis should be conducted in order to connect the present study with the larger body of literature on the subject.

    We have now included these references within the manuscript. We have calculated the reacto-diffusive length as varying between ~ 4 – 7 nm at the highest relative humidity that we used (71 % RH) down to ~0.006 – 0.05 nm at the lowest relative humidity that we used (17 % RH). The range of values for the reacto-diffusive length is due to the difference of the parameterizations of the diffusion coefficient given by (Price *et al.*, 2014) and (Zobrist *et al.*, 2011). These reacto-diffusive lengths indicate that at all relative humidities HO_2 radicals are limited to the outermost molecular layers of the particle, which is in agreement with our model. In these previous studies, it was shown that as the reacto-diffusive length increased, the uptake of gas-phase species would also increase as the gas-phase species could travel further into the bulk of the aerosol. Similarly, in our work, as the reacto-diffusive length increases and the HO_2 can travel further into the aerosol bulk an increase in the HO_2 uptake coefficient is observed until the uptake coefficient is limited by surface mass accommodation. The effect of diffusion and the reacto-diffusive length is large, as can be observed by the dashed-lines in Figure 5. However, at the lower relative humidities where the reacto-diffusive length is significantly smaller than the diameter of HO_2 a surface reaction is required for the uptake coefficient to not be underestimated. It should also be noted that in contrast to the case of OH, the slower and more complex chemistry of HO_2 requires explicit modelling and cannot be treated with a simplified resistor model.

    This discussion has been added to the results section of the manuscript with the added text shown below:
    "The HO_2 reacto-diffusive length (Schwartz and Freiberg, 1981, Hanson et al., 1994) varied from between ~ 4 – 7 nm at the highest relative humidity that was used (71 % RH) down to ~0.006 – 0.05 nm at the lowest relative humidity (17 % RH). The range of values for the reacto-diffusive length at a given RH is due to the difference between the parameterizations of the diffusion coefficient in Price et al. (2014) and Zobrist et al. (2011). These reacto-diffusive lengths indicate that at all relative humidities HO_2 radicals will be limited to the outermost molecular layers of the particle

before reacting away, which is in agreement with the model. Note that it was shown in previously that the uptake of gas-phase species generally increases with increasing reacto-diffusive length, which is consistent with our HO2 uptake coefficient measurements (Slade and Knopf, 2014, Davies and Wilson, 2015, Houle et al., 2015)."

"In contrast to traditional resistor models, the KM-SUB model enables efficient treatment of complex chemical mechanisms."

2. On lines 275-279 the authors say that the Henry's law constant and HO2 diffusion constant are both terms contained within the bulk HO2 bulk accommodation coefficient. This statement should be clarified in the manuscript. Does this mean that the two quantities cannot be separated independently in the model?

We have now changed bulk accommodation to mass accommodation within the manuscript. Mass accommodation, which is the mass transfer from the gas phase to the bulk of the aerosol, contains two different sub-processes: surface accommodation and surface-to-bulk transfer. The surface-to-bulk transfer rate describes transport from the surface of the aerosol particle into bulk layer 1 and is a derived input parameter in our model. It is dependent upon both the Henry's law constant and the HO_2 diffusion coefficient (Pöschl *et al.*, 2007, Berkemeier *et al.*, 2013). These two quantities can still be independently changed within the model and would both affect the HO_2 uptake coefficient. It makes sense that the rate at which a molecule is incorporated into the bulk of a solution is inversely dependent on viscosity ((Behr *et al.*, 2009), and references therein), similarly to the diffusivity being inversely dependent upon the viscosity as stated by the Stokes Einstein equation. Therefore, the Henry's law constant and HO_2 diffusion coefficient are coupled within the process of mass accommodation.

The text has been reworded to show that the Henry's law constant and HO_2 diffusion coefficient can be changed independently. The clarified text is shown below:

"At intermediate relative humidities with $\gamma < \alpha_{s,0}$, the uptake is limited by surface-to-bulk transport, which is related to both solubility (Henry's law coefficient) and diffusivity (diffusion coefficient) in the kinetic model. Under both conditions, the uptake is driven by chemical reaction in the near-surface bulk and effectively limited by mass accommodation, which includes both surface accommodation and surface-to-bulk transport (Behr et al., 2009, Berkemeier et al., 2013)."

3. The authors should clarify the geometry of the simulation, spherical shells?

Yes, the shells used within the model were spherical. This has now been clarified within the manuscript by modifying the following sentence:

"It is a multi-layer model comprising a gas phase, a near-surface gas phase, a sorption layer, a near-surface bulk layer and a number of bulk layers arranged in spherical geometry."

4. As diffusion becomes slower as RH decreases for sucrose, will any of the rate coefficients for R4-R10 be limited by this slow diffusion. In other words, while diffusion of species between shells decreases with RH, do the reactions occurring within a single shell have to be slowed due to diffusion? This should be clarified why this is or is not needed to accurately simulate the experimental data.

The rate coefficients for reactions R4-R10 were assumed constant over the entire range of relative humidities. However, it is expected that if the reactions are diffusion limited, decreasing the diffusion coefficients would decrease the collision rates between molecules and thus the rate coefficients would also decrease. Currently, our model predicts that at low relative humidity the uptake is limited by mass accommodation due to slow surface-to-bulk transfer and at high relative

humidity it is limited by surface mass accommodation. We therefore performed sensitivity tests to check whether a decrease in the rate constants would affect the outputted uptake coefficient. We found that when decreasing all reaction rate constants by a factor of 100, the largest effect was observed when the HO_2 diffusion coefficients were in the range of $10^{-10} - 10^{-9}$ (equivalent to a RH of $\sim 40 - 55$ %) with a decrease in the uptake coefficient of slightly less than 10 %. The model predicts that for this range of diffusion coefficients, when decreasing the rate constants by a factor of 100, the HO_2 uptake goes from being mass accommodation limited to bulk reaction limited. At the lower relative humidities the uptake would still be mass accommodation and surface reaction limited and thus independent of the bulk reaction rate, whereas at the higher relative humidities the uptake coefficient is still limited by surface mass accommodation. It should also be noted that in the hypothetical case of no surface reaction, if we were to further decrease the reaction rates at the lower relative humidities (< 35 % RH) such that the uptake was limited by bulk reaction rather than mass accommodation, the difference between the measurements and the model output would become larger. This indicates the importance of the surface reaction.

The caption of Table 1 has been updated to show that the parameters shown in Table 1 are for all relative humidities. The updated caption is shown below:
"The parameters used in the KM-SUB HO_2 uptake model over all relative humidities."
The following text has also been added to show the impact of decreasing the rate constants by a factor of 100.
"A two order of magnitude decrease in the rate constants affects the uptake coefficient marginally by reducing it by less than 10 % in the 40 – 55 % relative humidity range, but has no impact at the lower or higher relative humidities."

5. The desorption lifetime of HO2 appears unphysically long (1.5 ms) compared to MD simulations results presented in Vieceli et al. (J. Phys. Chem. B 2005, 109, 15876-15892). The desorption lifetimes from MD for OH, O3 and H2O range from 35-140 ps, orders of magnitude faster than the HO2 value used in the present study. While these are different species, I can't imagine a molecular reason for such a large difference for HO2. The value used here for the desorption lifetime of HO2 (Shiraiwa, 2010) is from a previous simulation study of ozone + oleic acid and appears to be a fit parameter, which is also orders of magnitude different than the MD results of Vieceli et al. for the ozone desorption lifetime. The reason for this discrepancy should be addressed and if possible simulations be run with a more realistic value for t_d.

Much discussion was spent in the past on desorption lifetimes of reactive molecules in kinetic flux models. In early studies (Pfrang *et al.*, 2010, Shiraiwa *et al.*, 2010), desorption lifetimes in the millisecond range were used, a value determined by manual fitting. In follow-up studies, much shorter desorption lifetimes of ozone physisorption were used to be compliant with the results from MD simulations (Shiraiwa *et al.*, 2011). However, in this study, the effective residence time of atmospheric oxidants on aerosol surfaces also remained high through inclusion of long-lived reactive oxygen intermediates. Berkemeier *et al.* (2013) showed that when using desorption lifetimes in the nanosecond range, not including reactive oxygen intermediates, surface reaction is way too slow to reach observed uptake coefficients in heterogeneous reaction systems and never influences reactivity: A desorption lifetime in that range effectively disables Langmuir-Hinshelwood type surface reactions as surface concentrations are too low to have impact on total reactivity with reasonable surface reaction rate coefficients. This stands in contrast to several studies showing the importance of surface reactions on aerosols. Nanosecond desorption lifetimes hence also effectively disable the possibility of surface saturation effects commonly observed in aerosol kinetics. Steimer *et al.* (2015a) show a strong gas phase concentration dependence of ozone uptake onto shikimic acid films with a Langmuir constant of $\sim 6 \times 10^{-13}$ cm^3. Such a high Langmuir constant cannot be obtained with a nanosecond desorption lifetime. The surface adsorption of

reactive trace gases on aerosol surfaces must thus be a process that goes beyond simple physisorption. Possibly, aerosol surface chemistry has to include chemical reaction occurring after partial dissolution of reactants in the uppermost layer of organics, like discussed in the case of oleic acid ozonolysis in Hearn *et al.* (2005), or be some kind of chemisorption process as discussed in Shiraiwa *et al.* (2011) and Berkemeier *et al.* (2016). MD simulations look at mere physically adsorbed, and hence weakly bound, molecules desorbing from a flat surface. We are not sure about the process extending the effective desorption lifetime of atmospheric trace species and hence HO_2 in our model, but we are confident that the effective desorption lifetimes to be used in models employing a in Langmuir-Hinshelwood-type surface reaction scheme must lie in the range of at least several microseconds to describe all the surface effects that can be observed in laboratory experiments. Uptake of HO_2 onto mineral dust particles (where only surface reaction is possible) would not be significant if HO_2 molecules would only reside on the surface for a few nanoseconds. We will follow-up on this issue in future publications and added the following clarifying comment to the manuscript:

"Note however that for a relevant surface reaction in kinetic flux models, it is necessary to use an effective desorption lifetime τ_d in the millisecond to second time range (Shiraiwa et al., 2010, Berkemeier et al., 2016). This is many orders of magnitude longer than would be expected due to pure physisorption as estimated by molecular dynamic simulations (Vieceli et al., 2005), indicating that the adsorption process should involve chemisorption or formation of long-lived intermediates that would have the potential to extend these effective desorption lifetimes (Shiraiwa et al., 2011, Berkemeier et al., 2016)."

6. To account for the finite value of the gamma at low RH the authors invoke a surface reaction (R11) catalyzed by Cu+2. It is unclear what the rate law is for this catalyzed reaction, the authors should make this clear in the manuscript. Furthermore, why would this reaction only occur at the surface? This assumes that HO2, which is fairly unreactive will not diffuse even into the subsurface region. It seems more reasonable to me, since surface rate coefficients are rarely measured, to allow this reaction to occur in the subsurface with a rate coefficient that has bulk units. This will allow the reader to more closely evaluate the magnitude of the rate coefficient needed to account for the measurements.

The surface reaction was required to describe the experimental data at the lower relative humidities due to it being independent of the bulk diffusion coefficients. For this surface reaction we assume a bimolecular self-reaction, $HO_2 + HO_2$. The actual reaction mechanism remains unclear and could potentially be $Cu + HO_2$ or an even more complex mechanism. However, the model results are insensitive to the true mechanism occurring at the surface of the aerosol particle which is thus beyond the scope of this work. We have used a simple mechanism to demonstrate that a surface reaction must be occurring. By multiplying the diameter of HO_2 (0.4 nm) by the surface rate constant (1×10^{-8} cm^2 s^{-1}) we can estimate an equivalent bulk reaction rate constant of ~ 4×10^{-16} cm^3 s^{-1} (which is equivalent to 2.4×10^5 M^{-1} s^{-1}).

In the particle bulk however, a Cu-catalyzed reaction (reactions R7 and R9) is explicitly treated in addition to the bimolecular self-reaction of HO_2 (reaction R5). HO_2 diffusion into the sub-surface (or bulk layer 1 within our model) is included within the model and may exhibit the mass accommodation-limited uptake discussed in the manuscript (Berkemeier *et al.*, 2013). It should be noted that the reaction rate coefficients within bulk layer 1 would be the same as in all other bulk layers. Mass accommodation will still occur at the lower relative humidities but to a much lesser extent due to the lower diffusion coefficients.

4

We have specified within the text that the reaction included at the surface is the HO_2 self-reaction but that the mechanism remains unclear. The following text has been slightly modified to include these points:

"For example, at 17 % RH and without a surface reaction, γ values as low as ~5 × 10⁻⁴ and ~3 × 10⁻⁵ would be expected using the Zobrist et al. (2011) and Price et al. (2014) parameterisations, respectively. However, by including the following self-reaction of HO_2 at the surface of the sucrose particles, much better agreement with the observed values of around ~10⁻² could be obtained (Fig. 5)."

"Although the true mechanism for reaction at the surface remains unclear, the large rate constant for this reaction suggests that copper could potentially be catalyzing the destruction of HO_2 at the surface of the sucrose particles which is consistent with the higher HO_2 uptake coefficients measured onto solid aerosol particles containing transition metals compared to solid aerosol particles containing no transition metal ions (Bedjanian et al., 2013, George et al., 2013, Matthews et al., 2014, Lakey et al., 2015)."

7. The authors interpret their data solely in terms of the diffusion of HO2 into sucrose. However, it is not clear whether this captures the complete picture. Wouldn't the diffusion of Cu+2, and O2- to the surface be equally important as HO2 diffusion at low RH for determining gamma? The authors should include these diffusing species in the simulation or clearly justify why it is not necessary to explicitly include the diffusion of all species (including sucrose) in their simulation.

We explicitly treat diffusion of O_2^- and Cu^{2+} in the model and use the same diffusion coefficients for these species as for HO_2. However, sensitivity studies with independent diffusion coefficients showed that only changing the diffusion rate of HO_2 affected modelling results. A range of values were tested, however, the HO_2 uptake coefficient outputted by the model did not change when setting the diffusion coefficient of O_2^-, Cu^{2+} and Cu^+ to zero or changing it to be 1000 times faster than the diffusion coefficients of HO_2 and over the whole range of relative humidities. For O_2^- the diffusion coefficient is unimportant due to the rates of reaction with copper being so rapid that it is produced in situ and consumed locally. The diffusion of Cu^+ and Cu^{2+} would only be important within the model if the reaction with HO_2/O_2^- permanently removed them or if their rate coefficients with HO_2 were significantly different such that the equilibrium between the two ions was important. However, as the reactions with HO_2/O_2^- are catalytic and cause Cu^{2+} and Cu^+ to rapidly interconvert they are still available at high concentrations in the upper layers of the aerosol particle. Similarly, as sucrose does not react with any species in the model, its diffusion within the model is unimportant to the outputted HO_2 uptake coefficient.

This discussion has been added to the model description section as shown below.
"Sensitivity tests showed that the diffusion rate constants of O_2^-, Cu^+ and Cu^{2+} did not influence calculation results. The reaction rate coefficients involving copper ($k_{BR,3} - k_{BR,6}$) are so large that O_2^- is produced in situ and consumed locally. The catalytic nature of these reactions cause Cu^+ and Cu^{2+} to rapidly interconvert meaning that they remain available at high concentrations in the upper layers of the aerosol particle. Similarly, as sucrose does not react with any species within the model, its diffusion within the model is unimportant to the outputted HO_2 uptake coefficient."

Anonymous Referee #2
Received and published: 22 May 2016
This manuscript provides an important step towards understanding the uptake of HO2 by secondary organic aerosol (SOA) and the influence of the viscous/glassy nature of the SOA on the reactive uptake

kinetics. The manuscript is well-written, concise, and the data are clearly presented. I have only minor suggestions for the authors to consider before the manuscript can be accepted for publication.

Line 269: "There is good agreement between the model and the measurements suggesting that the change in HO2 uptake over the range of humidities is indeed due to a change in the HO2 diffusion coefficient which is in turn due to a change in the viscosity of the aerosol particles." Given that the viscosity of aqueous/sucrose aerosol changes by more than >8 orders of magnitude over this experimental RH range (10 Pa s to >109 Pa s), things are clearly more complex than this sentence suggests with uptake coefficients only changing by a little over 1 order of magnitude. The authors do go on to discuss this more fully and they seem to attributed it to a combination of increasing viscosity, which suppresses diffusion rates into the particle bulk, coupled with an efficient surface reaction. In effect, the surface reaction means the uptake coefficient doesn't decrease as much as it might based on the increase in viscosity (see the dashed and solid lines in Figure 5). The near-surface chemistry is attributed to the presence of catalysing Cu2+ ions near the surface. It would be helpful to the reader to compare directly the relative change in viscosity expected over this range to the change in the uptake coefficient (see for example the recent paper by Marshall et al., Diffusion and Reactivity in Ultraviscous Aerosol and the Correlation with Particle Viscosity, Chem. Sci., 7, 1298–1308, doi:10.1039/C5SC03223G, 2016 where they do something similar for previous measurements).

Although the viscosity changes by more than 8 orders of magnitude over this range of relative humidities the diffusion coefficients only change by ~ 5 – 7 orders of magnitude depending on whether the Zobrist *et al.* (2011) or Price *et al.* (2014) parameterizations are used. Uptake coefficients are dependent upon the square root of the diffusion coefficient (Davidovits *et al.*, 2006). Therefore, we expect (based purely on diffusion), that the uptake coefficients would change by 2.5 – 3.5 orders of magnitude over the range of relative humidities. However, measured HO_2 uptake coefficients change by ~ 1 order of magnitude due to the surface mass accommodation limiting the uptake coefficient at the higher relative humidities and a surface reaction becoming important at the lower relative humidities. In order to demonstrate how the uptake coefficient changes as a function of viscosity we have now added an extra panel to Figure 5 (see the modified figure and new caption after another response below).

Indeed, many of the studies referenced in the introduction have shown that the uptake coefficients for OH, O3 and N2O5 etc do not vary nearly as strongly with viscosity as would be expected and do infact only decrease by an order of magnitude, even though the viscosity/diffusivity changes by many more orders of magnitude. In these earlier studies, it is not clear that there is any special surface enhanced chemistry that keeps the uptake coefficient larger than would be expected. Further clarification/discussion is needed. How can the authors be sure that that the inclusion of a surface reaction is what is needed to "correct" for a diminishing bulk diffusion inferred from water diffusion constants and does anything other than provide an additional parameter (degree of freedom) with which to ensure good agreement between the measurements and model? How legitimate do the authors believe it is to use of the diffusion constant for water (a stable molecule forming 2 hydrogen bonds etc) to represent the much more reactive, less strongly interacting HO2 in viscous sucrose? In the other measurements of reactive uptake coefficients, must similar enhancements in surface reaction rates be included to explain why the uptake coefficients do not fall as much as would be expected based on viscosity and water diffusivity?

Sensitivity tests showed that at the lower relative humidities the HO_2 uptake coefficient was only limited by three parameters: the HO_2 Henry's law constant, the HO_2 diffusion coefficient and the rate coefficient of the surface reaction. As already discussed in the manuscript the effective Henry's law constant is very sensitive to the pH of the aerosol due to the equilibrium between HO_2 and O_2^- (R4). The pH of the aerosols would have to increase significantly to almost neutral pH values and greater than 7 for the parameterization of (Zobrist *et al.*, 2011) and (Price *et al.*, 2014), respectively, in order to obtain HO_2

uptake coefficients that could reproduce the measured HO_2 uptake coefficient at the lowest relative humidity. It seems extremely unlikely that the pH would increase significantly at the lower relative humidities as pH measurements of the expected copper sulfate concentrations within the aerosol particles showed that the pH should be ~ 4.1. It should also be noted that in case of a higher pH, the measurements at the intermediate relative humidities could no longer be reproduced by the model. We have also not found any evidence in the literature for salting in of HO_2 as the organic fraction increases at low relative humidity, but if this does occur the effect is likely to be minimal and would change the uptake coefficient by less than 1 order of magnitude. Hydrogen bonding of water with sucrose could reduce the diffusion coefficients of water through a sucrose particle whilst HO_2, which is less strongly interacting, would have comparatively larger diffusion coefficients. However, it is also possible that hydrogen bonding could aid the diffusion process by smoothing out diffusion barriers. However, we see no evidence of this happening at the higher relative humidities (RH > 40%) where the HO_2 uptake coefficients can be reproduced well using HO_2 diffusion coefficients based upon the diffusion coefficients of water. The shape of the data in Figure 5 suggests a surface reaction as the decrease in the uptake coefficient at the low relative humidities is much smaller than would be expected from a constant decrease in the diffusion coefficients. It should also be noted that the effect and importance of surface reactions is consistent with previous work by Gržinić *et al.* (2015) and Berkemeier *et al.* (2016) for the uptake of N_2O_5 to citric acid and the uptake of O_3 to shikimic acid over a range of relative humidities. For these examples the surface reaction was rate limiting under certain conditions so that its extent could be better quantified than in the present case.

We have clarified within the results section that the inclusion of a surface reaction is consistent with previous studies by adding the following text:

"The effect and importance of surface reactions is consistent with previous work by Gržinić et al. (2015), Steimer et al. (2015b) and Berkemeier et al. (2016) for the uptake of N_2O_5 to citric acid and the uptake of O_3 to shikimic acid over a range of relative humidities."

We have also emphasized that the uptake coefficient varies less than might be expected based on the large change in viscosity:

"Although the viscosity changes by more than 8 orders of magnitude and the diffusion coefficients change by 5-7 orders of magnitude over the investigated range of relative humidity, the measured HO_2 uptake coefficients change by only ~ 1 order of magnitude. This can be explained to some extent by the uptake coefficient being proportional to the square root of the diffusion coefficient when the uptake is controlled by reaction and diffusion of HO_2 in the bulk (Davidovits et al., 2006, Berkemeier et al., 2013). If this were the only mechanism involved, however, one would still expect a change in the uptake coefficient by 2.5 – 3.5 orders of magnitude."

We have also added the following Figure to the manuscript in order to demonstrate the limiting cases within the model at different relative humidities.
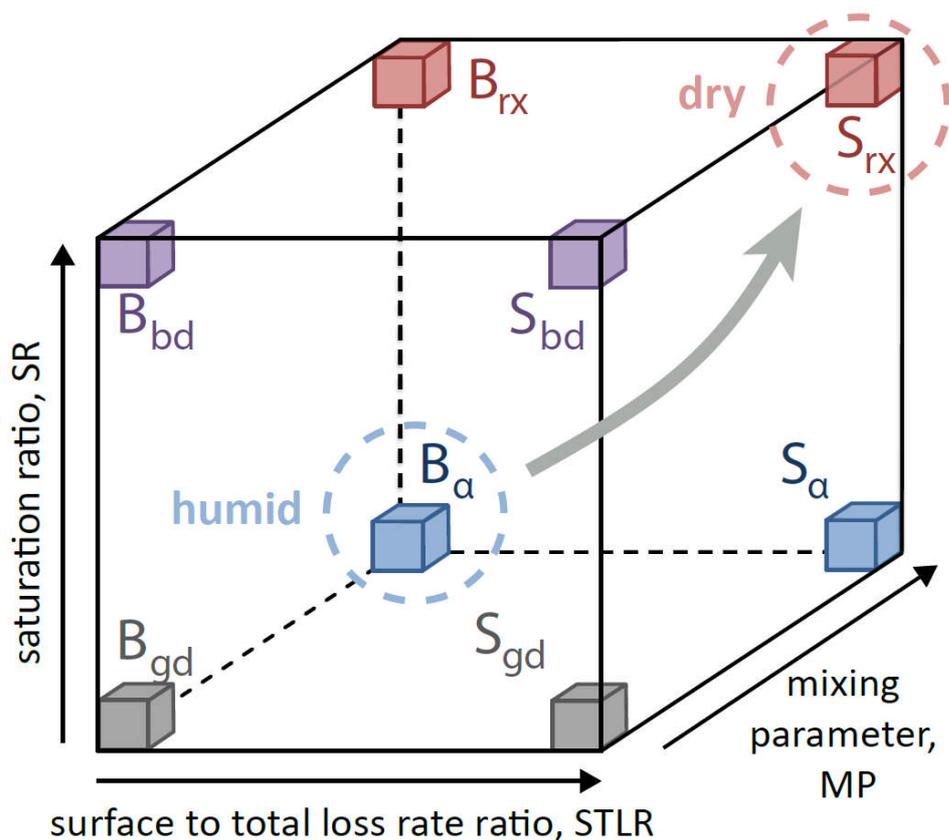
Figure 6: The kinetic cube representing the eight limiting cases for uptake of gases to aerosol particles (Berkemeier et al., 2013). B_{rx}: bulk reaction limited by chemical reaction, B_{bd}: bulk reaction limited by bulk diffusion of the volatile reactant and the condensed reactant, B_a: bulk reaction limited by mass accommodation, B_{gd}: bulk reaction limited by gas-phase diffusion; S_{rx}: surface reaction limited by chemical reaction, S_{bd}: surface reaction limited by bulk diffusion of a condensed reactant, S_a: surface reaction limited by surface accommodation, S_{gd}: surface reaction limited by gas-phase diffusion. For copper doped sucrose aerosol particles, the HO_2 uptake coefficient is limited by mass accommodation under humid conditions and by chemical reaction at the surface at low relative humidity.

Line 293: "Bones et al. (2012) measured that for 100 nm diameter sucrose aerosol
Particles to my knowledge, this paper does not report measurements of these timescales for size change for such small particles, it only inferred them from measurements on larger particles.
We have clarified within the text that this was inferred from measurements on larger particles as shown below:
"Bones et al. (2012) inferred from measurements on larger particles that for 100 nm diameter sucrose aerosol particles the equilibration time would be more than 10 seconds when the viscosity increased above $\sim 10^5$ Pa s, which would occur at $\sim 43\,\%$ RH (Power et al., 2013)."

Line 309: The two bulk concentrations of copper sulfate were chosen to span the expected range based on RH. Does this mean the concentration is expected to be 0.1 M at 17 % RH? How might the pH be expected to vary for supersaturated solutions of sucrose containing copper sulfate at such low water activity?

Yes, our calculations predicted a concentration of copper of 0.1 M at 17 % RH. Unfortunately, we cannot directly measure the aerosol pH within the supersaturated solutions of sucrose. However, as

sucrose within water has a pH of 7 and a very high pKa of 12.6, we expect the pH to be dominated by the presence of copper sulfate within the aerosol particles.

The following text has been added to the manuscript:

"*It is expected that the pH would be dominated by the presence of copper sulfate rather than sucrose which has a pH of 7 in water and a very high pKa of 12.6.*"

Line 366: "effect of aerosol viscosity upon HO2 uptake coefficients was systematically investigated with a combination of HO2 uptake coefficient measurements" as suggested, it might be helpful to show the dependence of uptake coefficient on viscosity explicitly.

We agree that it is interesting to show the dependence of the uptake coefficient upon the viscosity explicitly and we have now added an extra panel to Figure 5 as shown below based upon the data and fitting shown in Power *et al.* (2013) and Marshall *et al.* (2016):
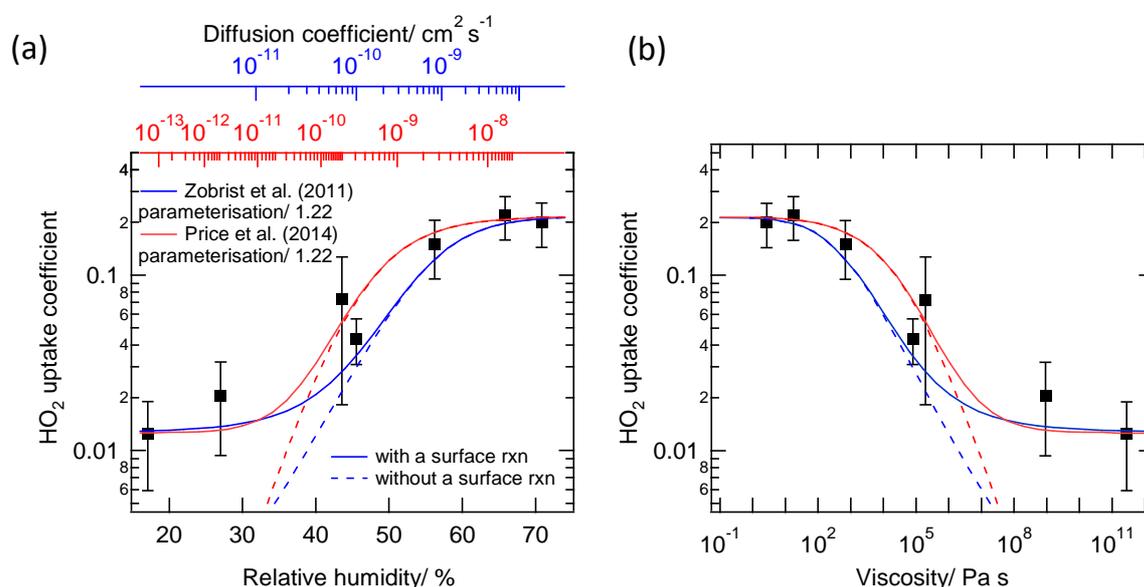

Figure 5: The HO_2 uptake coefficient onto copper (II) doped sucrose aerosol particles as a function of (a) relative humidity and (b) aerosol particle viscosity. The lines represent the expected HO_2 uptake coefficient calculated using the KM-SUB model using the Price et al. (2014) (red) and Zobrist et al. (2011) (blue) diffusion parameterisations (see model description section) and with (solid) and without (dashed) the inclusion of a surface reaction (Reaction R11). The viscosity within sucrose aerosol particles is based upon the data and fitting shown in Power et al. (2013) and Marshall et al. (2016) whilst the red and blue axes in panel (a) are the Price et al. (2014) and Zobrist et al. (2011) diffusion parameterisations, respectively. The error bars represent two standard deviations of the propagated error in the gradient of the *k'* against aerosol surface area graphs.

Minor Points for Clarification/Additional Information

Line 188: What is the timescale for HO2 concentration to stabilise once mercury lamp turned on?

The HO_2 concentration within the flow tube will stabilize in less than 1 minute when the mercury lamp is switched on. We always wait for the HO_2 concentration to be stable before starting a HO_2 decay.

This has been clarified within the manuscript by adding the following text:

"Data acquisition was only started once HO₂ concentrations within the flow tube were stable which occurred within 1 minute of switching on the mercury lamp."

Line 210: Magnitude of RO2 interference signal in HO2 detection is shown to be significant for TMB SOA measurements but not a-pinene – this is different from expectations based on box model simulations. Why is this the case? Some more detailed discussion would be helpful.

As stated in the manuscript, the expected interference from TMB RO_2 and α-pinene RO_2 would have been equivalent to $0.59 \times [HO_2]$ and $0.44 \times [HO_2]$, respectively. The RO_2 interference for the TMB experiments is likely to be due to a tiny fraction of the precursors, oxidation products and ozone passing through the denuders. Due to working at ppm concentrations the amount making it through the denuders could be enough to lead to a RO_2 signal. However, for the α-pinene experiments it seems that the denuders were more efficient at removing these precursors and oxidation products although the reasons for this remain unclear.

The following discussion was added to the text:

"Although the denuders are efficient at removing gas phase species (Arens et al., 2001), it can be hypothesised that the signal was due to the formation of HO₂ and RO₂ radicals due to a small fraction of ozone, precursors and oxidation products passing through the denuders for the TMB experiments."

"The lack of interference for the α-pinene experiments suggests that the denuders were more efficient at removing the gas phase precursors and oxidation products from the chamber and that negligible concentrations of RO₂ species were present in the flow tube."

Line 219: Discussion of correction for wall loss and non-plug flow would benefit from indicating directly the level of correction typically required beyond what can be inferred from Figure 3.

The average correction due to wall loss and non-plug flow was 22 %.

This has been clarified within the manuscript by adding the following text.

"The average correction was 22%."

Line 238: "which is only slightly larger than the diameter of HO2 (0.4 nm)." – is there any significance to this?

It is important to show that the model resolves the diffusion gradient of HO_2 despite its very small length scale. It was significant that the HO_2 only had to travel approximately the distance of its own diameter to go from being an adsorbed radical on the surface of the aerosol particle to a dissolved aqueous radical. It also only had to travel the distance of approximately its own diameter to move between bulk layers. This is really important when the reactions within the aerosol particles are extremely fast leading to large concentration gradients within the particle.

This has been clarified within the manuscript by adding the following text to the manuscript.

"The bulk layer number was set to 100 corresponding to a bulk layer thickness of 0.5 nm which is only slightly larger than the diameter of HO₂ (0.4 nm) and implies that HO₂ only needs to travel approximately the distance of its own diameter to go from being an adsorbed radical on the surface of the aerosol particle to a dissolved aqueous radical. The same short distance must be overcome by HO₂ to move between bulk layers, which is important for convergence of the numerical model, especially when the chemical reactions within the aerosol particles are very fast compared to the diffusion time scales, leading to steep concentration gradients within the particle."

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The effect of viscosity and diffusion on the HO_2 uptake by sucrose and secondary organic aerosol particles

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Abstract

We report the first measurements of HO_2 uptake coefficients, γ, for secondary organic aerosol particles (SOA) and for the well-studied model compound sucrose which we doped with copper (II). Above 65% relative humidity (RH), γ for copper (II) doped sucrose aerosol particles equalled the surface mass accommodation coefficient $\alpha = 0.22 \pm 0.06$ but decreased to $\gamma = 0.012 \pm 0.007$ upon decreasing the RH to 17 %. The trend of γ with RH can be explained by an increase in aerosol viscosity and the contribution of a surface reaction, as demonstrated using the kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB). At high RH the total uptake was driven by reaction in the near-surface bulk limited by mass accommodation whilst at low RH it was limited by surface reaction. SOA from two different precursors, α-pinene and 1,3,5- trimethylbenzene (TMB), was investigated, yielding low uptake coefficients of $\gamma < 0.001$ and $\gamma = 0.004 \pm 0.002$, respectively. It is postulated that the larger values measured for TMB derived SOA compared to α-pinene derived SOA are either due to differing

viscosity, a different liquid water content of the aerosol particles or a $HO_2 + RO_2$ reaction occurring within the aerosol particles.

Introduction

OH and HO_2 radicals play a vital role in atmospheric chemistry by controlling the oxidative capacity of the troposphere, with HO_2 acting as a short-lived reservoir for OH. Oxidation by the OH radical determines the lifetime and concentrations of many trace gases within the troposphere such as NO_x (NO and NO_2), CH_4 and volatile organic compounds (VOCs). The reaction of HO_2 with NO also constitutes an important source of ozone, which is damaging to plants, a respiratory irritant and a greenhouse gas (Pöschl and Shiraiwa, 2015;Fowler et al., 2009). It is therefore important to have a thorough understanding of the reactions and processes that affect HO_x concentrations. However, during field campaigns HO_2 concentrations have sometimes been measured as being lower than the concentrations predicted by constrained box models implying a missing HO_2 sink, which has often been attributed to HO_2 uptake by aerosol particles (e.g. (Kanaya et al., 2007;Mao et al., 2010;Whalley et al., 2010)).

SOA is generated from low-volatility products formed by the oxidation of VOCs, and it accounts for a large fraction of the organic matter in the troposphere. For example, in urban areas it can account for up to 90 % of the organic particulate mass (Kanakidou et al., 2005;Lim and Turpin, 2002). Lakey et al. (2015a) previously measured the HO_2 uptake coefficient onto single component organic aerosol particles as ranging from $\gamma < 0.004$ to $\gamma = 0.008 \pm 0.004$ unless elevated transition metal ions, that catalyse the destruction of HO_2, were present within the aerosol. Taketani et al. (2013) and Taketani and Kanaya (2010) also measured the HO_2 uptake coefficient onto dicarboxylic acids ($\gamma = 0.02 \pm 0.01$ to $\gamma = 0.18 \pm 0.07$) and levoglucosan ($\gamma < 0.01$ to $\gamma = 0.13 \pm 0.03$) over a range of humidities. However, there are currently no measurements of the HO_2 uptake coefficient onto SOA published in the literature.

Using the kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB), Shiraiwa et al. (2011b) have shown that the bulk diffusion of a species within an aerosol matrix can have a large impact on a measured uptake coefficient. Diffusion coefficients of a particular species within a particle are related to the viscosity of that particle with larger diffusion coefficients in less viscous particles. Traditionally, the relationship between viscosity and diffusion coefficients is given by the Stokes-Einstein equation, although this relation was found to break down for concentrated solutions and solutions near their glass transition temperature or humidity (Champion et al., 1997;Power et al., 2013). Zhou et al. (2013) have also shown that the rate of heterogeneous reaction of particle-borne benzo[a]pyrene (BaP) with ozone within SOA particles was strongly dependent upon the bulk diffusivity of the SOA. Along the same lines, Steimer et al. (2015) and Steimer et al. (2014)

demonstrated a clear link between the ozonolysis rates of shikimic acid and the changing diffusivity in the transition between liquid and glassy states. Previous measurements of both N_2O_5 uptake coefficients and HO_2 uptake coefficients onto humic acid aerosol particles and N_2O_5 uptake coefficients onto malonic acid and citric acid aerosol particles have shown much lower uptake coefficients at low relative humidities compared to higher humidities (Badger et al., 2006;Thornton et al., 2003;Lakey et al., 2015a;Gržinić et al., 2015). However, viscosity effects have not been investigated systematically for HO_2 uptake, and the first aim of this paper was to investigate whether a change in aerosol viscosity, exemplified using the well-studied model compound sucrose (Berkemeier et al., 2014;Price et al., 2014;Zobrist et al., 2011), could impact the HO_2 uptake coefficient. The second aim of this study was to measure the HO_2 uptake coefficient onto two different types of SOA representative of biogenic and anthropogenic SOA. α-pinene is the major terpene that forms biogenic SOA, while 1,3,5-trimethylbenzene (TMB) is representative of alkyl benzenes which are the most abundant aromatic hydrocarbons and form anthropogenic SOA (Calvert et al., 2002;Qi et al., 2012). SOA is known to be highly viscous with viscosities of $10^3 – 10^6$ Pa s at 50 % RH (Renbaum-Wolff et al., 2013).

Experimental

The general experimental setup for the Leeds aerosol flow tube and the data analysis methodology to determine values of γ have previously been discussed in detail by George et al. (2013). This is the same experimental setup and data analysis methodology that was used for the copper (II) doped sucrose experiments, which were also performed at the University of Leeds. Therefore, only a brief description of the setup is included below, with the emphasis being on changes made to the apparatus for the SOA experiments undertaken at the Paul Scherrer Institute (PSI), for which a schematic is shown in Figure 1. For all experiments the HO_2 radical was released at the end of an injector which was moved backwards and forwards along an aerosol flow tube. The flow from the injector was 1.32 ± 0.05 slpm. For the copper doped sucrose experiments the humid aerosol flow was 1.0 ± 0.1 slpm, and was mixed with a much drier flow (with the humidity of this flow being controlled by mixing a flow from a water bubbler with a dry flow in different ratios) of 3.0 ± 0.3 slpm within a conditioning flow tube for approximately ten seconds before entering the aerosol flow tube. Nitrogen was used for all of these flows. For the SOA experiments the flow from the smog chamber or Potential Aerosol Mass (PAM) chamber at PSI was 4.0 ± 0.3 slpm. Decays of the HO_2 radical along an aerosol flow tube were measured using a Fluorescence Assay by Gas Expansion (FAGE) detector in both the absence and presence of different concentrations of aerosol particles. All experiments were performed at room temperature (293 ± 2 K).

The HO$_2$ radical was formed via Reactions 1 – 2, by passing a humidified flow over a mercury penray lamp (L.O.T. Oriel, model 6035) in the presence of trace amounts (20 – 30 ppm) of oxygen in the nitrogen flow.

$$H_2O + h\nu \rightarrow OH + H \tag{R1}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{R2}$$

Data acquisition was only started once HO$_2$ concentrations within the flow tube were stable which occurred within 1 minute of switching on the mercury lamp. The HO$_2$ radicals entered the FAGE cell through a 0.7 mm diameter pinhole, and were then converted to OH by reacting with added NO. The FAGE cell was either kept at a pressure of ~ 0.85 Torr or ~ 1.5 Torr using a combination of a rotary pump (Edwards, model E1M80) and a roots blower (EH1200). The OH radicals were detected by laser induced fluorescence at 308 nm (Heard and Pilling, 2003;Stone et al., 2012). Initial HO$_2$ concentrations (obtained by calibration) exiting the injector were measured as ~ 1×10^9 molecule cm^{-3} for all experiments (following mixing and dilution with the main flow), and the concentration was then measured as a function of distance along the flow tube.

For the experiments using copper doped sucrose aerosol particles, 3.42 grams of sucrose (Fisher, > 99%) and 0.125 grams of copper (II) sulphate pentahydrate were dissolved in 500 ml of milliQ water. These solutions were then placed in an atomiser (TSI, 3076) in order to form aerosol particles. The aerosol particles passed through a neutraliser (Grimm 5522) and an impactor before entering the conditioning flow tube. The size distribution of the aerosol particles were then measured at the end of the reaction flow tube using a Scanning Mobility Particle Sizer (SMPS, TSI, 3080).

The experimental setup used to measure previous HO$_2$ uptake coefficients (George et al., 2013;Matthews et al., 2014;Lakey et al., 2015a;Lakey et al., 2015b) was transported from the University of Leeds, UK, to the Paul Scherrer Institute, Switzerland, where it was connected to the Paul Scherrer Institute (PSI) smog chamber and, for some of the experiments, also to a Potential Aerosol Mass (PAM) chamber (see Figure 1). The PSI smog chamber has a volume of 27 cubic metres, it is made from 125 μm Teflon fluorocarbon film and has been described elsewhere (Paulsen et al., 2005). To initiate photochemical reactions four 4 kW xenon arc lamps (light spectrum >280 nm, OSRAM) and eighty black lights (100W tubes, light spectrum between 320 and 400 nm, Cleo Performance) were used. For most experiments the chamber was first humidified to 50% relative humidity, but for two experiments this was increased to 80%, after which the precursor gases were added. The concept, design and operation of a PAM chamber has also previously been described (Kang et al., 2007). The PAM chamber

at PSI is a flow tube of 0.46 m in length and 0.22 m internal diameter. Two low pressure Hg lamps mainly emitting at 185 and 254 nm produce ozone in the chamber. Water vapour was photolysed by the 185 nm radiation to produce OH and HO_2 and also photolysed O_2 to produce O_3, whereas the 254 nm light could also photolyse O_3 to produce OH following the reaction of $O(^1D)$ with water vapour. Upper-limit OH production rates are in the range of 1×10^{12} - 2×10^{12} molecule cm^{-3} s^{-1} (Bruns et al., 2015). The composition and oxidation state of SOA formed within PAM chambers has previously been shown to be similar to SOA generated within environmental chambers (Bruns et al., 2015;Lambe et al., 2011a) and SOA in the atmosphere (Ortega et al., 2015).

Four different types of experiments were performed.

(i) α-pinene ozonolysis in the PSI smog chamber (600 ppb α-pinene, 280 ppb ozone: ozone was added first to the chamber; after injection of α -pinene particle nucleation and growth rapidly occurred).

(ii) OH initiated α-pinene photochemistry in the smog chamber (500 ppb α-pinene, 350 ppb NO_2: Xenon and black lights where used to initiate photochemical reactions).

(iii) OH initiated α-pinene photochemistry in the PAM chamber (500 ppb α-pinene was filled into the large smog chamber at 50 or 80 % RH to supply a constant concentration of α-pinene to the PAM chamber, all SOA was formed within the PAM chamber).

(iv) OH initiated TMB photochemistry in the PAM chamber (2 ppm TMB was filled into the large smog chamber at 50 % RH to supply a constant concentration of TMB to the PAM chamber, all SOA was formed within the PAM chamber).

These precursor concentrations were chosen in order to obtain a large enough aerosol surface area in the flow tube to be able to measure a HO_2 uptake coefficient. Experiments were performed only once the aerosol surface area within the aerosol flow tube exceeded 5×10^{-5} cm^2 cm^{-3}, and in the case of the smog chamber experiments once a maximum aerosol concentration had been reached (as summarised in the Results Section). Prior to entering the flow tube, the aerosol flow from the smog or PAM chamber (4.0 slpm) was passed through either two or three cobalt oxide denuders in series (each 40 cm long, 0.8 cm inner diameter quartz tubes coated with cobalt oxide prepared by thermal decomposition of a saturated $Co(NO_3)_2$ solution applied to its inner walls at 700°C as described in Ammann (2001)), which in turn were in series with a charcoal denuder (length = 16.4 cm, diameter = 0.9 cm, 69 quadratic channels) in order to remove NO_x species, RO_2, VOC's and ozone that had been present in the chamber. These denuders have previously been shown to be extremely efficient at removing gas phase NO_x and VOCs (Arens et al., 2001). It should be noted that the flows were drawn through the aerosol flow tube using a pump instead of the normal procedure whereby the flows are pushed through the experimental setup using mass flow controllers. The pumping setup led to slightly

reduced pressures (904 – 987 mbar) in the aerosol flow tube, and so careful checks were performed to ensure that the flow tube was vacuum tight. The aerosol size distribution from which the surface area exiting the flow tube was calculated was measured using a Scanning Mobility Particle Sizer (SMPS), which consisted of a neutraliser (Kr-85), a Differential Mobility Analyser (DMA, length 93.5 cm, inner radius 0.937 cm and outer radius 1.961 cm) and a CPC (TSI, model 3022). A typical surface weighted aerosol size distribution for the α-pinene derived aerosol particles is shown in Figure 2. Note that an impactor was not used in the experimental setup for the SOA measurements as this restricted the flow that could be pumped through the flow tube and was also found to be unnecessary as the aerosol size distribution from the chambers fell entirely within the range of aerosol sizes that the SMPS could measure.

In order to check that the experimental setup used at PSI produced consistent results with those previously performed at the University of Leeds, an experiment was performed with ammonium sulphate aerosol particles. The ammonium sulphate aerosol particles were formed using an atomiser rather than aerosol particles being formed in a chamber, but were then passed through the same set up (including the denuders) as the SOA was passed through. The experiment was performed at a flow tube pressure of 915 mbar, due to the flows being pumped through the setup, (compared to pressures of 904 – 987 mbar for the SOA experiments), and a HO_2 uptake coefficient of 0.004 ± 0.002 was measured at 60% RH which is in agreement with previous experiments by George et al. (2013), which were performed at atmospheric pressure (~ 970 – 1040 mbar).

Data analysis

Experiments were performed by moving the HO_2 injector backwards and forwards along the flow tube either in the presence of or in the absence of aerosol particles, and recording the FAGE signal from HO_2 radicals. The background signal in the absence of HO_2 (mercury lamp in the injector switched off), but with the NO entering the FAGE cell, was recorded and was subtracted, from the signal during experiments. For α-pinene experiments this background signal was small and similar to previous experiments using dust, organic and inorganic salt aerosol particles (George et al., 2013;Lakey et al., 2015b;Lakey et al., 2015a;Matthews et al., 2014). However, for the TMB experiments this background signal varied from about half to two thirds of the signal from HO_2 with the mercury lamp in the injector switched on. The background signal disappeared when the NO added to the FAGE cell was switched off showing that it was not due to OH. The background signal within experiments did not change when aerosol particles were present compared to when they were completely filtered out (see Figure 1). Although the denuders are efficient at removing gas phase species (Arens et al., 2001), it can be

hypothesized that the signal was due to the formation of HO_2 and RO_2 radicals generated by a small fraction of ozone, precursors and oxidation products passing through the denuders for the TMB experiments. RO_2 species would have been observed as a HO_2 interference by the FAGE detection method. FAGE interferences have previously been observed for alkene, aromatic and > C3 alkane derived RO_2 (Fuchs et al., 2011;Whalley et al., 2013). A box model was run, utilising chemistry within the Master Chemical Mechanism (MCM 3.2), which is detailed further in Whalley et al. (2013)), and constrained to the experimental concentrations, and showed that the expected interference from TMB RO_2 and α-pinene RO_2 would have been equivalent to $0.59 \times [HO_2]$ and $0.44 \times [HO_2]$, respectively, at a NO flow of 50 ml min^{-1} into the FAGE cell, a FAGE pressure of 1.5 Torr and a flow through the FAGE pinhole of 4.2 slpm. However, for α-pinene experiments the background signal did not change between the NO being switched on and off with the mercury lamp switched off in the injector, indicating the absence of interferences in the FAGE cell for these experiments. The lack of interference for the α-pinene experiments suggests that the denuders were more efficient at removing the gas phase precursors and oxidation products from the chamber and that only negligible concentrations of RO_2 species were present in the flow tube. Nevertheless, since for the TMB experiments a significant background signal was observed, that signal was measured regularly throughout the experiment and used to correct the measurement data.

HO$_2$ decays along the flow tube in the presence and absence of aerosol particles were measured between ~ 10 and 18 seconds flow time after the point of injection to ensure thorough mixing. A previous calculation showed that the flows should be fully mixed by ~ 7 seconds (George et al., 2013). An example of the HO$_2$ decays in the presence and absence of aerosol particles for a TMB experiment is shown in Figure 3, plotted as the natural logarithm of HO$_2$ signal (proportional to concentration) against reaction time according to:

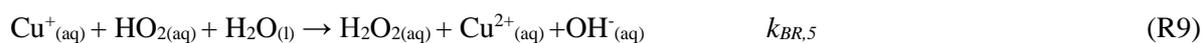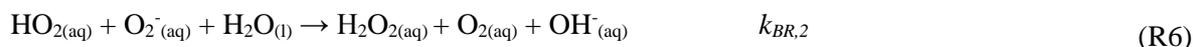$$ln\frac{[HO_2]_t}{[HO_2]_0} = -k_{obs}t \tag{E1}$$

There is clear uptake of HO$_2$ observed by the SOA derived from TMB. The pseudo first-order rate coefficients (k_{obs}) were then corrected for wall losses and non-plug flow conditions using the methodology described by Brown (1978). The average correction was 22%. These corrected rate constants (k') were related to the HO$_2$ uptake coefficient (γ_{obs}) by the following equation:

$$k' = \frac{\gamma_{obs}\omega_{HO2}S}{4} \tag{E2}$$

where ω_{HO2} is the molecular thermal speed of HO$_2$ and S is the total aerosol surface area. Examples of k' as a function of the aerosol surface area is shown in Figure 4. The HO$_2$ uptake coefficients were then corrected for gas-phase diffusion limitations using the methodology described by (Fuchs and Sutugin, 1970), although this correction changed the uptake coefficient by less than 1 % for all experiments.

Model description

The kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB) has been described in detail by Shiraiwa et al. (2010). It is a multi-layer model comprising a gas phase, a near-surface gas phase, a sorption layer, a near-surface bulk layer and a number of bulk layers arranged in spherical geometry. Processes that can occur within the model include gas-phase diffusion, adsorption and desorption, bulk diffusion, and chemical reactions in the gas phase, at the surface and in the bulk. In contrast to traditional resistor models, the KM-SUB model enables efficient treatment of complex chemical mechanisms. Input parameters to the model are summarised in Table 1 whilst the reactions that were included are shown below:

$$HO_{2(g)} + HO_{2(g)} \rightarrow H_2O_{2(g)} + O_{2(g)} \qquad\qquad k_{GP} \qquad\qquad (R3)$$

$$HO_{2(aq)} \rightleftharpoons H^+_{(aq)} + O_2^-{}_{(aq)} \qquad\qquad K_{eq} \qquad\qquad (R4)$$

$$HO_{2(aq)} + HO_{2(aq)} \rightarrow H_2O_{2(aq)} + O_{2(aq)} \qquad\qquad k_{BR,1} \qquad\qquad (R5)$$

$$HO_{2(aq)} + O_2^-{}_{(aq)} + H_2O_{(l)} \rightarrow H_2O_{2(aq)} + O_{2(aq)} + OH^-{}_{(aq)} \qquad\qquad k_{BR,2} \qquad\qquad (R6)$$

$$Cu^{2+}{}_{(aq)} + HO_{2(aq)} \rightarrow O_{2(aq)} + Cu^+{}_{(aq)} + H^+{}_{(aq)} \qquad\qquad k_{BR,3} \qquad\qquad (R7)$$

$$Cu^{2+}{}_{(aq)} + O_2^-{}_{(aq)} \rightarrow O_{2(aq)} + Cu^+{}_{(aq)} \qquad\qquad k_{BR,4} \qquad\qquad (R8)$$

$$Cu^+{}_{(aq)} + HO_{2(aq)} + H_2O_{(l)} \rightarrow H_2O_{2(aq)} + Cu^{2+}{}_{(aq)} + OH^-{}_{(aq)} \qquad\qquad k_{BR,5} \qquad\qquad (R9)$$

$$Cu^+{}_{(aq)} + O_2^-{}_{(aq)} + 2H_2O_{(l)} \rightarrow H_2O_{2(aq)} + Cu^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \qquad\qquad k_{BR,6} \qquad\qquad (R10)$$

The bulk layer number was set to 100 corresponding to a bulk layer thickness of 0.5 nm which is only slightly larger than the diameter of HO_2 (0.4 nm) and implies that HO_2 only needs to travel approximately the distance of its own diameter to go from being an adsorbed radical on the surface of the aerosol particle to a dissolved aqueous radical. The same short distance must be overcome by HO_2 to move between bulk layers, which is important for convergence of the numerical model, especially when the chemical reactions within the aerosol particles are very fast compared to the diffusion time scales, leading to steep concentration gradients within the particle. Reducing the bulk layer thickness further did not significantly impact the calculated uptake coefficients.

During experiments the average radius was observed to change by less than 10 % over the range of humidities, and therefore an assumption was made within the model that the average aerosol radius remained constant over the range of relative humidities. For the diffusion coefficient of HO_2 within aerosol particles we used the measured diffusion coefficients of H_2O within sucrose solutions, which we then corrected using the Stokes-Einstein equation to take into account the larger radius of HO_2 radicals compared to H_2O molecules (Price et al., 2014;Zobrist et al., 2011). The correction resulted in a factor of 1.22 decrease in the diffusion coefficients of HO_2 compared to the diffusion coefficients of H_2O. It should be noted that above a viscosity of 10 Pa s the Stokes-Einstein relationship starts to fail and that the effect of increasing molecular size may become much stronger (Power et al., 2013). Price et al. (2014) estimated diffusion coefficients of H_2O by using Raman spectroscopy to observe D_2O diffusion in high-viscosity sucrose solutions whilst Zobrist et al. (2011) used optical techniques to observe changes in the size of sucrose particles when exposed to different relative humidities.

Sensitivity tests showed that the diffusion rate constants of O_2^-, Cu^+ and Cu^{2+} did not influence calculation results. The reaction rate coefficients involving copper ($k_{BR,3}$ - $k_{BR,6}$) are so large that O_2^- is produced *in situ* and consumed locally. The catalytic nature of these reactions cause Cu^+ and Cu^{2+} to rapidly interconvert meaning that they remain available at high concentrations in the upper layers of the aerosol particle. Similarly, as sucrose does not react with any species within the model, its diffusion within the model is unimportant to the outputted HO_2 uptake coefficient.
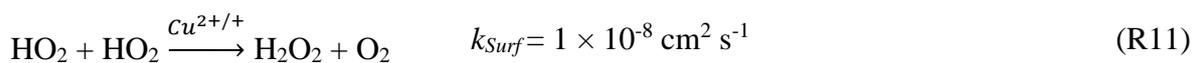
Results and Discussion

HO$_2$ uptake by copper doped sucrose aerosol particles

The results of the HO_2 uptake coefficient measurements onto copper doped sucrose aerosol particles as a function of relative humidity (RH) are shown in Figure 5. The results show a large dependence upon relative humidity with the HO_2 uptake coefficient increasing from 0.012 ± 0.007 at 17 ± 2 % RH to 0.22 ± 0.06 at relative humidities above 65%. The latter value is likely equal to the surface accommodation coefficient, and is consistent with many previous studies (Takahama and Russell, 2011;George et al., 2013;Lakey et al., 2015b). At lower humidities, the diffusion coefficients decrease which leads to slower transport of HO_2 within the bulk, and therefore to a slower overall rate of HO_2 destruction (Reactions 7 – 10). The HO_2 reacto-diffusive length (Hanson et al., 1994;Schwartz and Freiberg, 1981) varied from between ~ 4 – 7 nm at the highest relative humidity that was used (71 % RH) down to ~0.006 – 0.05 nm at the lowest relative humidity (17 % RH). The range of values for the reacto-diffusive length at a given RH is due to the difference between the parameterizations of the

diffusion coefficient in Price et al. (2014) and Zobrist et al. (2011). These reacto-diffusive lengths indicate that at all relative humidities HO$_2$ radicals will be limited to the outermost molecular layers of the particle before reacting away, which is in agreement with the model. Note that it was shown in previously that the uptake of gas-phase species generally increases with increasing reacto-diffusive length, which is consistent with our HO$_2$ uptake coefficient measurements (Slade and Knopf, 2014;Davies and Wilson, 2015;Houle et al., 2015). The red and blue lines in Figure 5 show the predicted HO$_2$ uptake coefficients using the KM-SUB model when using two different parameterisations for HO$_2$ diffusion coefficients as a function of RH (see the model description). There is good agreement between the model and the measurements suggesting that the change in HO$_2$ uptake over the range of humidities is indeed due to a change in the HO$_2$ diffusion coefficient which is in turn due to a change in the viscosity of the aerosol particles. Sensitivity tests showed that an increase in the rate constants of reactions R7 – R10 does not affect the HO$_2$ uptake coefficient. A two order of magnitude decrease in the rate constants affects the uptake coefficient marginally by reducing it by less than 10 % in the 40 – 55 % relative humidity range, but has no impact at the lower or higher relative humidities.

Using the kinetic framework and classification scheme of Berkemeier et al. (2013), Figure 6 illustrates how the change in relative humidity leads to a change in the kinetic regime of HO$_2$ uptake. At the highest relative humidities the uptake is limited by surface accommodation. At intermediate relative humidities with $\gamma < \alpha_{s,0}$, the uptake is limited by surface-to-bulk transport, which is related to both solubility (Henry's law coefficient) and diffusivity (diffusion coefficient) in the kinetic model. Under both conditions, the uptake is driven by chemical reaction in the near-surface bulk and effectively limited by mass accommodation, which includes both surface accommodation and surface-to-bulk transport (Behr et al., 2009;Berkemeier et al., 2013). At low relative humidities the HO$_2$ uptake coefficient was limited by chemical reaction at the surface as discussed below (Berkemeier et al., 2013).

Although the viscosity changes by more than 8 orders of magnitude and the diffusion coefficients change by 5-7 orders of magnitude over the investigated range of relative humidity, the measured HO$_2$ uptake coefficients change by only ~ 1 order of magnitude. This can be explained to some extent by the uptake coefficient being proportional to the square root of the diffusion coefficient when the uptake is controlled by reaction and diffusion of HO$_2$ in the bulk (Davidovits et al., 2006;Berkemeier et al., 2013). If this were the only mechanism involved, however, one would still expect a change in the uptake coefficient by 2.5 – 3.5 orders of magnitude. The most plausible explanation for the relatively high HO$_2$ uptake coefficients observed at low relative humidities is a surface reaction of HO$_2$. For example, at 17 % RH and without a surface reaction, γ values as low as ~5 $\times$ 10^{-4} and ~3 $\times$ 10^{-5} would be expected using the Zobrist et al. (2011) and Price et al. (2014) parameterisations, respectively. However, by including the following self-reaction of HO$_2$ at the surface of the sucrose particles, much better agreement with the observed values of around ~10^{-2} could be obtained (Fig. 5):

$$\text{HO}_2 + \text{HO}_2 \xrightarrow{Cu^{2+/+}} \text{H}_2\text{O}_2 + \text{O}_2 \qquad k_{Surf} = 1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1} \qquad \text{(R11)}$$

Although the true mechanism for reaction at the surface remains unclear, the large rate constant for this reaction suggests that copper could potentially be catalyzing the destruction of HO_2 at the surface of the sucrose particles which is consistent with the higher HO_2 uptake coefficients measured onto solid aerosol particles containing transition metals compared to solid aerosol particles containing no transition metal ions (Matthews et al., 2014;Lakey et al., 2015a;Bedjanian et al., 2013;George et al., 2013). Note however that for a relevant surface reaction in kinetic flux models, it is necessary to use an effective desorption lifetime τ_d in the millisecond to second time range (Berkemeier et al., 2016;Shiraiwa et al., 2010). This is many orders of magnitude longer than would be expected due to pure physisorption as estimated by molecular dynamic simulations (Vieceli et al., 2005), indicating that the adsorption process should involve chemisorption or formation of long-lived intermediates that would have the potential to extend these effective desorption lifetimes (Shiraiwa et al., 2011a;Berkemeier et al., 2016). The effect and importance of surface reactions is consistent with previous work by Gržinić et al. (2015), Steimer et al. (2015) and Berkemeier et al. (2016) for the uptake of N_2O_5 to citric acid and the uptake of O_3 to shikimic acid over a range of relative humidities. A second potential reason for the discrepancy at low humidities could be an incomplete equilibration of the aerosol particles with respect to RH, as they had only been mixed with the conditioning flow for ~ 10 seconds before entering the reaction flow tube. Bones et al. (2012) inferred from measurements on larger particles that for 100 nm diameter sucrose aerosol particles the equilibration time would be more than 10 seconds when the viscosity increased above ~ 10^5 Pa s, which would occur at ~ 43 % RH (Power et al., 2013). The actual diffusion coefficients would thus be higher than assumed in calculations which assume fully equilibrated particles. However, the near-surface bulk of the aerosol particles, where the reactions occur, would be much better equilibrated with respect to RH than the inner core of the aerosol particles (Berkemeier et al., 2014). This means that the lack of aerosol equilibration with respect to RH is likely to have a negligible impact upon the HO_2 uptake coefficient.

It should also be noted that the KM-SUB modelling results were very sensitive to the initial aerosol pH. For example, at a pH of 4.1 (used in Figure 5, the reason for this value is discussed below) the HO_2 uptake coefficient as predicted by the KM-SUB model at 50 % RH (using the Zobrist et al. (2011) H_2O diffusion coefficients) was $\gamma = 0.06$ compared to $\gamma = 0.11$ at pH 5 and $\gamma = 0.21$ at pH 7. The reason for this strong dependence upon pH has been discussed previously and is due to the partitioning of HO_2 with its conjugate base O_2^-, as shown by Reaction 4, affecting the effective Henry's law coefficient and the effective rate constants (Thornton et al., 2008). Although it was not possible to measure the actual pH of the aerosol particles, it was possible to estimate the concentration of copper

(II) sulphate (which is a weak acid) within the aerosol particles using the known growth factors of sucrose aerosol particles (Lu et al., 2014). The pH of 0.05 M and 0.1 M copper (II) sulphate solutions (which were calculated to be the extremes of the possible copper concentrations over the RH range) were then measured using a pH meter (Jenway, 3310) as being in the range of 4.10 ± 0.05. It is expected that the pH would be dominated by the presence of copper sulfate rather than sucrose which has a pH of 7 in water and a very high pKa of 12.6. Therefore, there is confidence that the correct initial aerosol pH was inputted into the model. Hence, while the HO_2 uptake coefficient might depend on further factors such as aerosol pH, a clear dependence on relative humidity, and hence particle viscosity could be observed, and it remains likely that at low humidity a surface loss process becomes dominating.

HO_2 uptake by SOA

A summary of all HO_2 uptake experiments performed on SOA is shown in Table 2. On average the HO_2 uptake coefficient was measured as 0.004 ± 0.002 onto TMB derived aerosol particles produced in the PAM chamber, whereas for α-pinene derived aerosol particles only an upper limit of 0.001 (obtained from the error in the slope of Figure 4(a)) could be placed on the HO_2 uptake coefficient at 50 and 80 % RH. It should be noted that for the α-pinene experiments the HO_2 uptake coefficient was non-measurable for both ozonolysis and photochemistry experiments using both the smog chamber and the PAM chamber as sources of the SOA, and therefore only upper limits of individual experiments are reported in

Table 2. There was some variability for the upper limits that were measured for individual α-pinene experiments which is likely to be due to the maximum aerosol surface-to-volume ratio that was obtained in each experiment.

There are several possible reasons for the larger HO_2 uptake coefficients being measured for the TMB derived aerosol particles compared to the α-pinene derived aerosol particles. These reasons will be summarised below, but include a differing particle viscosity, a different particle liquid water content or a $HO_2 + RO_2$ reaction occurring within the aerosol particles. Although the viscosity of α-pinene derived aerosol has been measured as $\sim 10^3$ Pa s at 70 % RH and $> 10^9$ Pa s for RH < 30 %, to our knowledge, there are currently no measurements of the viscosity of TMB derived aerosol published in the literature (Renbaum-Wolff et al., 2013). By running the KM-SUB model it can be estimated that the diffusion coefficient of HO_2 within the particles would need to be approximately 1×10^{-10} cm^2 s^{-1} for TMB derived aerosol particles and $< 5 \times 10^{-12}$ cm^2 s^{-1} for α-pinene derived aerosol particles. This range

of values seems to be consistent with the diffusion coefficients estimated by Berkemeier et al. (2014) and Lienhard et al. (2015) for water diffusion in low and medium O:C SOA.

Thornton et al. (2003) previously suggested that for malonic acid aerosol particles the liquid water content could be limiting the aqueous chemistry below 40 % RH. As can be seen by the HO_2 reaction scheme, the rate of Reaction R6 is dependent upon the liquid water concentration within the aerosol, and therefore the uptake coefficient could be limited by a low aerosol liquid water content. However, there remains some uncertainty as to whether the liquid water content of TMB derived aerosol particles would be higher than the liquid water content of α-pinene derived aerosol particles. Duplissy et al. (2011) measured a higher hygroscopicity parameter (κ_{org}) for TMB derived aerosol particles compared to α-pinene derived aerosol particles whereas Lambe et al. (2011b) and Berkemeier et al. (2014) stated the opposite. However, as well as being dependent upon the hygroscopicity parameter, the liquid water content of the aerosol particles would also be dependent upon the O:C ratio in the SOA.

If the viscosity and liquid water content of the α-pinene and TMB derived aerosol particles are similar, the larger HO_2 uptake coefficients measured for TMB derived aerosol particles could be due to a higher reactivity of these aerosol particles towards HO_2. This could be the case if the TMB derived aerosol particles contained reactive radical species such as organic peroxy radicals, RO_2, which partition into the aerosol or are formed within the aerosols by intra-particular reactions (Donahue et al., 2012;Lee et al., 2016). As previously stated in the Data Analysis section, during α-pinene experiments, no indication of RO_2 being present in the flow tube was observed by FAGE as a HO_2 interference. However, for TMB derived aerosol particles, a large background signal was observed by FAGE indicating that reactive radical species were likely to be present within the flow tube. If the reaction of HO_2 with these species at the surface or within the bulk of the aerosol was faster than the equivalent gas phase reaction, a larger HO_2 uptake coefficient would be observed.

Atmospheric implications and conclusions

The effect of aerosol viscosity upon HO_2 uptake coefficients was systematically investigated with a combination of HO_2 uptake coefficient measurements and a state-of-the-art kinetic model. A good correlation was obtained between measured HO_2 uptake coefficients onto copper doped sucrose aerosols as a function of RH and the KM-SUB model output. At higher relative humidities the uptake was limited by mass accommodation whilst at lower relative humidities the aerosol particles were viscous and the uptake was limited by surface reaction. These results imply that viscous aerosol particles will have very little impact upon gaseous tropospheric HO_2 concentrations.

The first measurements of the HO_2 uptake coefficient onto SOA have been reported in this work. The HO_2 uptake coefficient measured for α-pinene derived aerosol particles was below the limit of detection of the apparatus ($\gamma < 0.001$) whereas for TMB derived aerosol particles the uptake coefficient was measurable ($\gamma = 0.004 \pm 0.002$). These results are consistent with the copper doped sucrose results, and indicate that the impact of SOA on gaseous HO_2 concentrations would likely be small. However, it remains unclear as to the reasons for the larger HO_2 uptake coefficient measured onto TMB derived aerosol particles compared to α-pinene derived aerosol particles. The possibility that the larger uptake coefficient onto TMB derived aerosol particles was due to a lower viscosity of the aerosol particles or a higher liquid water content compared to α-pinene derived aerosol particles cannot be confirmed until further measurements of the viscosity and liquid water content of TMB derived aerosol particles are published in the literature. However, if the larger uptake coefficients are due to a $HO_2 + RO_2$ reaction within the aerosol, this could impact the HO_2 uptake coefficient for any aerosol containing RO_2. The actual increase would depend on a variety of factors such as the concentrations of RO_2, the partition coefficients of RO_2 to the aerosol particles, the reactivity of different RO_2 species with HO_2 radicals and the intra-particular formation of RO_2 and other reactive radicals (Lee et al., 2016;Donahue et al., 2012;Tong et al., 2016). The $HO_2 + RO_2$ reaction could potentially occur within the majority of aerosol particles within the atmosphere, this could have implications for the gaseous HO_2 and RO_2 concentrations in the troposphere which could then impact upon the concentrations of other species such as ozone.
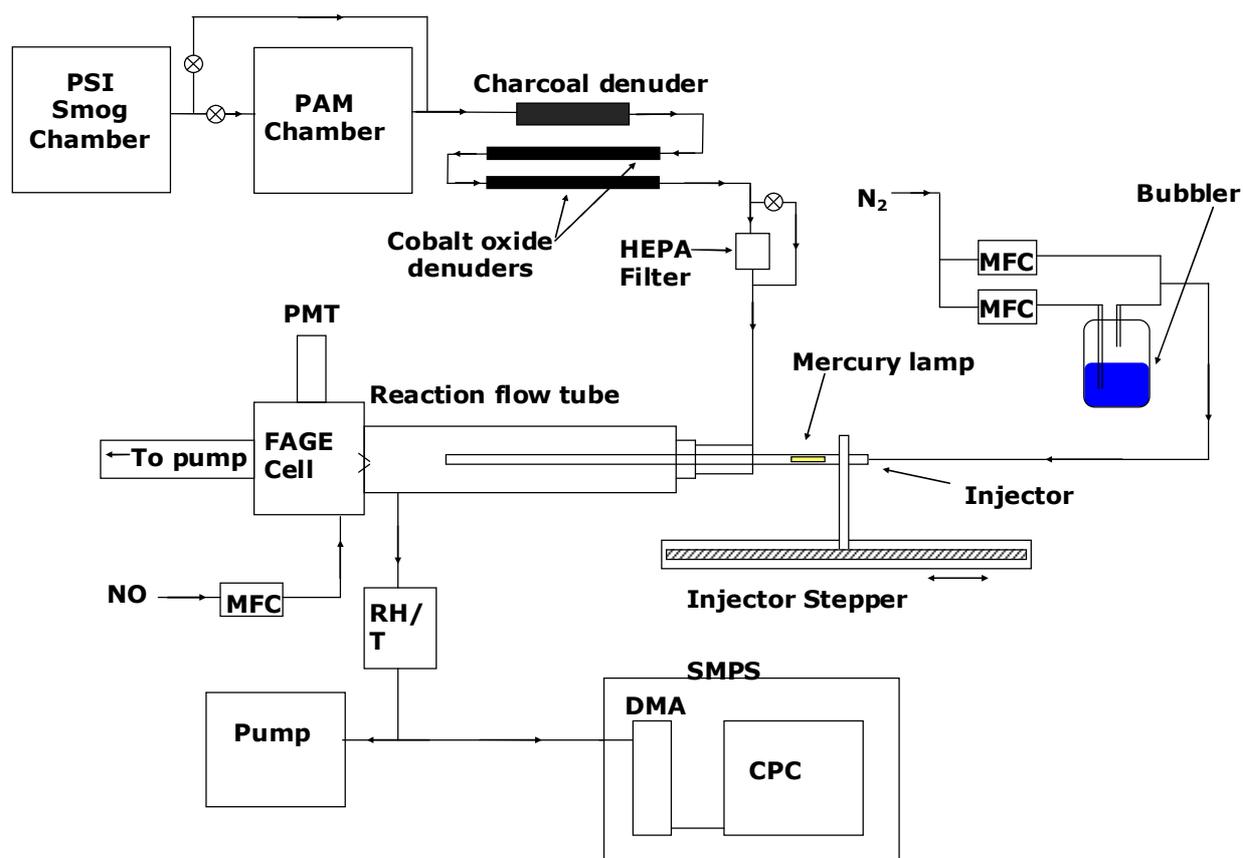
Acknowledgements

Figures

Figure 1: A schematic of the experimental setup used to measure HO_2 uptake coefficients onto SOA aerosol particles. Key: PAM- Potential aerosol mass, PMT- Photomultiplier tube, FAGE- Fluorescence Assay by Gas Expansion, MFC- Mass flow controller, RH/ T- relative humidity and temperature probe, SMPS- Scanning mobility particle sizer, DMA- Differential mobility analyser, CPC- Condensation particle counter.
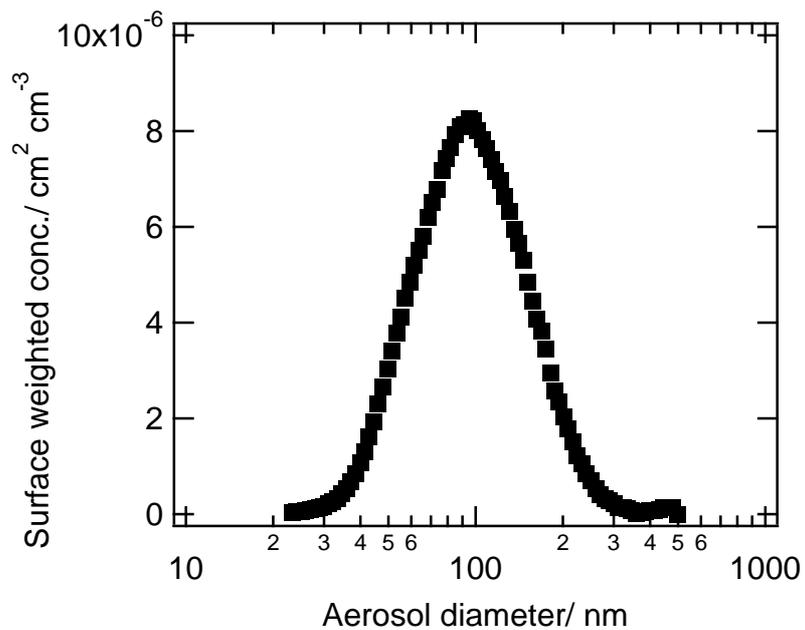
Figure 2: An example of the size distribution for α-pinene derived aerosol particles formed in the PAM chamber at a relative humidity of ~ 50 %.
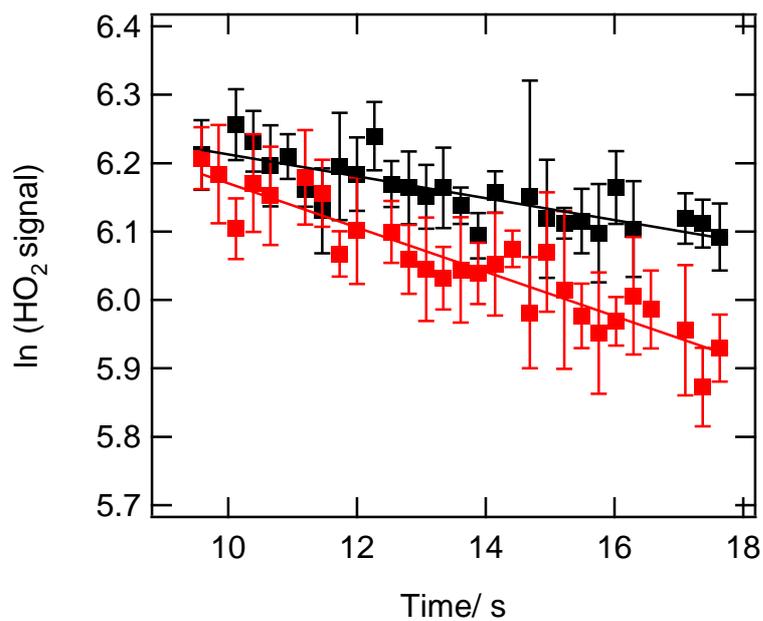
Figure 3: Examples of the HO_2 wall loss without any aerosol particles along the flow tube (black squares) and the HO_2 loss with an aerosol surface area of 2.2×10^{-4} cm^2 cm^{-3} for TMB derived aerosol particles at an initial HO_2 concentration of $\sim 1 \times 10^9$ molecule cm^{-3} (red squares) and for RH = 50 %. The error bars represent one standard deviation in the measured HO_2 signal for a measurement time per point of 3 seconds.
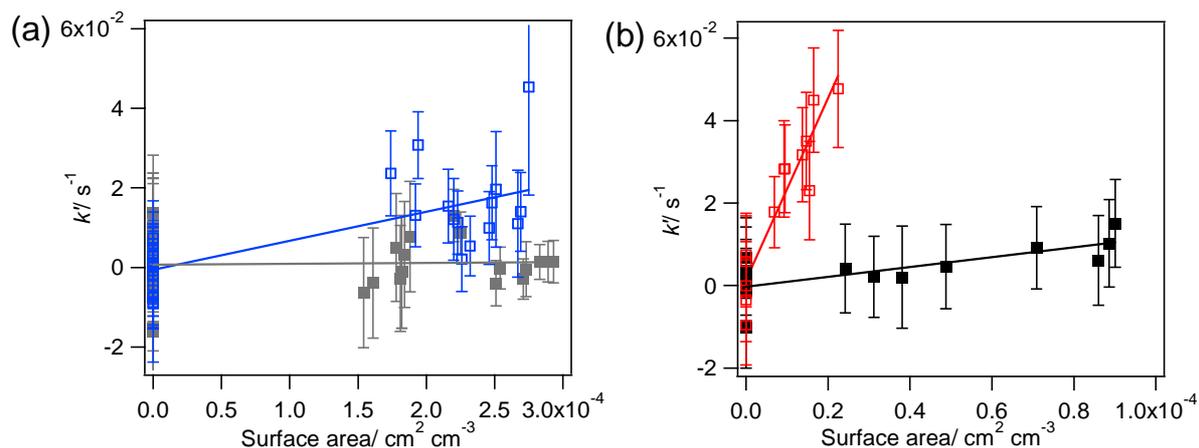
Figure 4: The pseudo-first-order rate constants with the wall losses subtracted as a function of aerosol surface area for (a) α-pinene derived aerosol particles (grey) and TMB derived aerosol particles (blue) at 50 % RH and a pressure of 904 – 929 mbar and (b) copper doped sucrose aerosol particles at 17% RH (black) and 71% RH (red) at atmospheric pressure. Experiments were performed at 293 ± 2 K. In panel (a) experiments were performed using the PAM chamber as the source of aerosol particles and represent experiments 5 and 6 in Table 2. Error bars represent the 1 standard deviation propagated uncertainty for individual determinations of k'. The data points at an aerosol surface area of 0 cm^2 cm^{-3} (no aerosol particles present) are repeats of the wall loss decays taken throughout the experiment and are within error of each other.
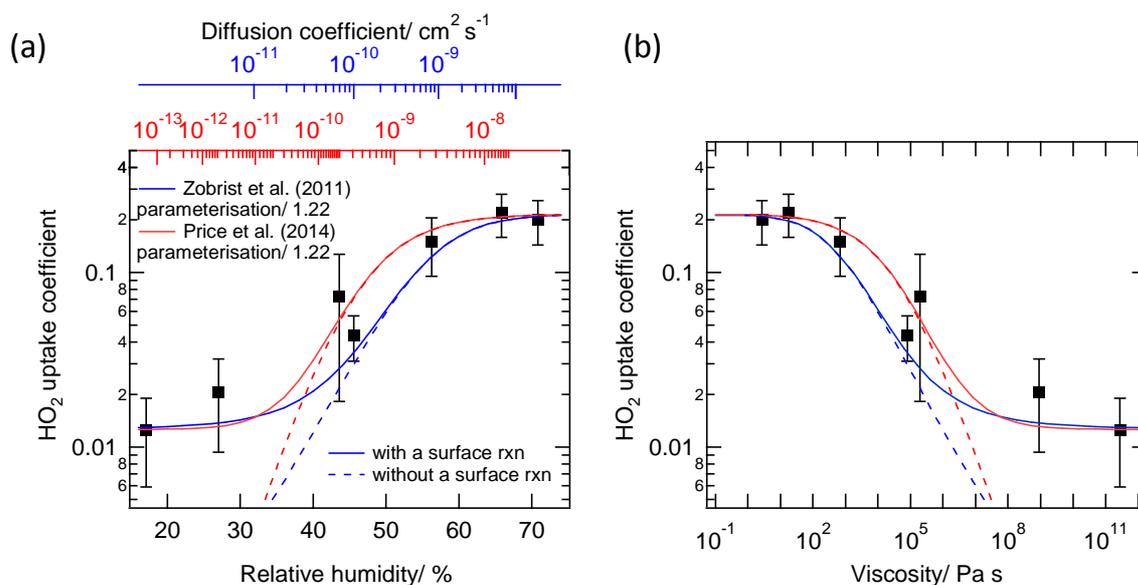
Figure 5: The HO₂ uptake coefficient onto copper (II) doped sucrose aerosol particles as a function of (a) relative humidity and (b) aerosol particle viscosity. The lines represent the expected HO₂ uptake coefficient calculated using the KM-SUB model using the Price et al. (2014) (red) and Zobrist et al. (2011) (blue) diffusion parameterisations (see model description section) and with (solid) and without (dashed) the inclusion of a surface reaction (Reaction R11). The viscosity within sucrose aerosol particles is based upon the data and fitting shown in Power et al. (2013) and Marshall et al. (2016) whilst the red and blue axes in panel (a) are the Price et al. (2014) and Zobrist et al. (2011) diffusion parameterisations, respectively. The error bars represent two standard deviations of the propagated error in the gradient of the *k'* against aerosol surface area graphs.
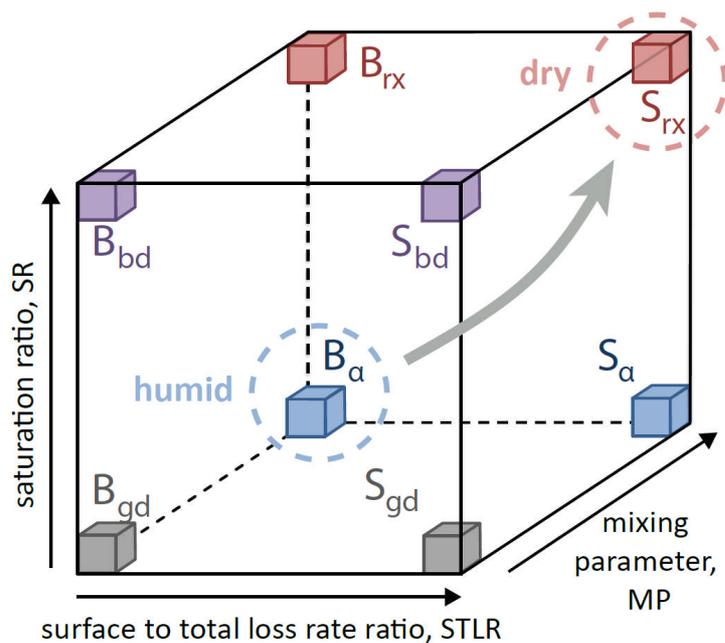
Figure 6: The kinetic cube representing the eight limiting cases for uptake of gases to aerosol particles (Berkemeier et al., 2013). B_{rx}: bulk reaction limited by chemical reaction, B_{bd}: bulk reaction limited by bulk diffusion of the volatile reactant and the condensed reactant, B_{α}: bulk reaction limited by mass accommodation, B_{gd}: bulk reaction limited by gas-phase diffusion; S_{rx}: surface reaction limited by chemical reaction, S_{bd}: surface reaction limited by bulk diffusion of a condensed reactant, S_{α}: surface reaction limited by surface accommodation, S_{gd}: surface reaction limited by gas-phase diffusion. For copper doped sucrose aerosol particles, the HO_2 uptake coefficient is limited by mass accommodation under humid conditions and by chemical reaction at the surface at low relative humidity.

Tables

Table 1: The parameters used in the KM-SUB HO_2 uptake model over all relative humidities.

Parameter	Description	Value at 293 K	Reference
$k_{BR,1}$	Rate constant, R5	1.3×10^{-15} cm^3 s^{-1}	Thornton et al. (2008)
$k_{BR,2}$	Rate constant, R6	1.5×10^{-13} cm^3 s^{-1}	Thornton et al. (2008)
$k_{BR,3}$	Rate constant, R7	1.7×10^{-13} cm^3 s^{-1}	Jacob (2000)
$k_{BR,4}$	Rate constant, R8	1.3×10^{-11} cm^3 s^{-1}	Jacob (2000)
$k_{BR,5}$	Rate constant, R9	2.5×10^{-12} cm^3 s^{-1}	Jacob (2000)
$k_{BR,6}$	Rate constant, R10	1.6×10^{-11} cm^3 s^{-1}	Jacob (2000)
k_{GP}	Rate constant, R3	3×10^{-12} cm^3 s^{-1}	Sander et al. (2003)
K_{eq}	Equilibrium constant, R4	2.1×10^{-5} M	Thornton et al. (2008)
H_{HO2}	HO_2 Henry's law constant	5600 M atm^{-1}	Thornton et al. (2008)
τ_d	HO_2 desorption lifetime	1.5×10^{-3} s	Shiraiwa et al. (2010)
$\alpha_{s,0}$	HO_2 surface accommodation at time 0	0.22	
$D_{g,HO2}$	HO_2 gas phase diffusion rate constant	0.25 cm^{-2} s^{-1}	Thornton et al. (2008)
$[Cu]$	Copper concentration (used when modelling copper doped sucrose aerosol particles)	5×10^{19} cm^{-3}	
T	Temperature	293 K	

Table 2: Summary of the reactants and conditions that were utilised and the HO_2 uptake coefficients that were measured during the experiments. Experiments 1 - 4 were performed using the smog chamber whereas experiments 5 - 9 utilised the PAM chamber.

Experiment number	Reaction type	Initial precursor concentrations	UV	Relative humidity in the chamber/ %	Pressure in the flow tube/ mbar	Maximum aerosol surface to volume ratio in the flow tube/ $cm^2 \, cm^{-3}$	HO_2 uptake coefficient (γ)
1	α-pinene ozonolysis	[α-pinene] = 600 ppb [O_3] = 280 ppb	Off	50	987	6.30×10^{-5}	< 0.01
2	α-pinene ozonolysis	[α-pinene] = 600 ppb [O_3] = 280 ppb	Off	50	965	1.30×10^{-4}	< 0.004
3	α-pinene ozonolysis	[α-pinene] = 200 ppb [O_3] = 310 ppb	Off	80	939	7.10×10^{-5}	< 0.006
4	α-pinene photochemistry	[α-pinene] = 500 ppb [NO_2] = 350 ppb	On	50	940	6.30×10^{-5}	< 0.018
5	α-pinene photochemistry	[α-pinene] = 500 ppb	On	50	929	2.93×10^{-4}	< 0.001
6	TMB photochemistry	[TMB] = 2 ppm	On	50	923	2.75×10^{-4}	0.004 ± 0.002
7	TMB photochemistry	[TMB] = 2ppm	On	50	918	2.32×10^{-4}	0.004 ± 0.003
8	α-pinene photochemistry	[α-pinene] = 500 ppb	On	50	927	1.88×10^{-4}	< 0.005
9	α-pinene photochemistry	[α-pinene] = 1 ppm	On	80	904	3.90×10^{-4}	< 0.001

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