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Measurements of the HO_2 uptake coefficients onto single component organic aerosols

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Abstract

Measurements of HO_2 uptake coefficients (γ) were made onto a variety of organic aerosols derived from glutaric acid, glyoxal, malonic acid, stearic acid, oleic acid, squalene, mono ethanol amine sulphate, mono-methyl amine sulphate and two sources of humic acid, for an initial HO_2 concentration of 1×10^9 molecule cm^{-3}, room temperature and at atmospheric pressure. Values in the range of $\gamma < 0.004$ to $\gamma = 0.008 \pm 0.004$ were measured for all of the aerosols apart from the aerosols from the two sources of humic acid. For humic acid aerosols, uptake coefficients in the range of $\gamma = 0.007 \pm 0.002$ to $\gamma = 0.09 \pm 0.03$ were measured. Elevated concentrations of copper (16 ± 1 and 380 ± 20 ppb) and iron (600 ± 30 and 51000 ± 3000 ppb) ions were measured in the humic acid atomiser solutions compared to the other organics that can explain the higher uptake values measured. A strong dependence upon relative humidity was also observed for uptake onto humic acid, with larger uptake coefficients seen at higher humidities. Possible hypothesises for the humidity dependence include the changing liquid water content of the aerosol, a change in the mass accommodation coefficient or in the Henry's law constant.

Introduction

The HO_2 radical is important in the troposphere as it is closely coupled with OH, which initiates the removal of many trace gases via oxidation. However, a combination of field measurements of HO_2 and comparison with calculations from box modelling has indicated that the heterogeneous uptake of HO_2 by aerosols has the potential to be an important loss pathway of HO_2.[1-17] Global tropospheric models have also shown that in areas of high aerosol loadings, heterogeneous uptake can have a significant impact on gaseous HO_2 concentrations.[9, 18-22] Therefore, it is important to accurately measure the HO_2 uptake coefficient onto different aerosols and under different conditions in order provide data to constrain both box and global models. There are currently relatively few laboratory measurements of the HO_2 uptake coefficient onto aerosols and surfaces and these have concentrated on effloresced and deliquesced salts, dicarboxylic acids, levoglucosan, soot, copper doped aerosols ammonium sulphate and Arizona Test Dust.[23-37]

Organic aerosols are ubiquitous in the troposphere with 20 – 90 % of submicron particulate mass being attributable to organics.[38, 39] Many different organics have been observed or are predicted to be present in tropospheric aerosols, including both water insoluble organics (e.g. *n*-alkanes, *n*-alkanoic and n-alkenoic acids, diterpenoid acids, aromatic polycarboxylic acids, polycyclic aromatic hydrocarbons and oxygenated polyaromatic hydrocarbons) and water soluble organics (e.g. dicarboxylic acids, glyoxal, ketoacids, polyols, hydroxyamines, amino acids and nitrophenol).[40-42] Humic-like substances have also been identified as a major component of aerosols and have been measured in different aerosol types including marine aerosols, dust from soil and biomass burning aerosols.[43-48] Although there are high mass fractions of organics and many different types of organics present in tropospheric aerosols, only a few measurements of the HO_2 uptake coefficient have been made in the laboratory onto single component organic aerosols, and these have focused on dicarboxylic acids and levoglucosan.[32, 35] Therefore, the aim of this study was to extend the measurements to a variety of different single component organic aerosols that are representative of tropospheric aerosol components including both water insoluble (stearic acid, oleic acid and squalene) and water soluble organics (glutaric acid, glyoxal and malonic acid and two sources of humic acid). The first HO_2 uptake measurements were also made onto two aerosols containing amines, mono-methyl amine sulphate aerosols (MMS) and mono ethanol amine sulphate-H_2SO_4 (MEA-H_2SO_4). It should be noted that amines have previously been measured in the atmosphere.[49] MEA-H_2SO_4 has previously been suggested as suitable for carbon capture and would reduce the medium term CO_2 emissions into the troposphere.[50] If amines were to be used for carbon capture, it is likely that some of these amines would be released into the atmosphere where they could partition to the aerosol phase. It would therefore be important to understand the impact that these amines would have upon the concentrations of different species in the atmosphere, including HO_2 concentrations.

Experimental

An identical experimental setup was used in this work as described in detail by George et al. , [26] and is therefore only briefly summarised below. An glass aerosol flow tube (coated in halocarbon wax, 107 cm length, 5.9 cm inner diameter) coupled with a sensitive Fluorescence Assay by Gas Expansion (FAGE) instrument, capable of measuring HO_2 concentrations at ambient levels, which enabled HO_2 uptake coefficients to be measured at room temperature (293 ± 2 K), atmospheric pressure, and at an initial HO_2 concentration of 1×10^9 molecule cm^{-3}. By moving an injector (110 cm length, 1.9 cm outer diameter, 1.6 cm inner diameter) which released the HO_2 into the flow of aerosols along the flow tube, pseudo-first order decays of HO_2 were measured at different aerosol surface area concentrations. Experiments were performed over a range of relative humidities (32 - 80%) which was varied by using mass flow controllers that controlled the ratio of a dry flow and a humidified flow from a bubbler. Prior to entering the aerosol flow tube the aerosols were conditioned for ~ 5 seconds within a conditioning flow tube at the chosen relative humidity.

HO_2 production and detection

HO_2 radicals were formed through Reactions 1 – 2 by passing humidified nitrogen containing trace levels of O_2 over a mercury lamp that was placed at the end of the injector furthest away from the flow tube in order to avoid any local heating in the flow tube:

$$H_2O + hv \rightarrow OH + H \qquad \text{(R1)}$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad \text{(R2)}$$

The total flow exiting the injector was 1.32 ± 0.05 lpm that mixed into a 4.0 ± 0.3 lpm humidified flow containing aerosols. A sensitive FAGE cell enabled the HO_2 to be measured by firstly converting it to OH by reaction with added NO, and subsequently detected by utilising laser induced fluorescence from the $Q_1(2)$ transition of the OH ($A^2\Sigma^+$- $X^2\Pi_i$ v’=0 - v’’=0) band at ~308 nm.[14, 51] The FAGE cell was kept at a low pressure (0.85 Torr) using a rotary pump (Edwards, model E1M80) and roots blower (EH1200) combination to ensure a high flow velocity through the FAGE cell. There was no change in the LIF signal when the NO added to the fluorescence cell (to convert HO2 to OH) was switched off. In addition when the NO is switched off there is no difference in signal when the mercury lamp was either switched on or off. These results indicate that any OH radicals formed in the injector alongside HO_2 following the photolysis of water vapour were removed within the injector.

Aerosol production and detection

Aerosols were produced using two different methodologies. For soluble organics (glutaric acid (Aldrich, 99%), glyoxal (Acros organics, 99%), malonic acid (Acros organics, 99%) and humic acid (Acros organics, 50 – 60%, sodium salt and Leonardite) 5 grams were dissolved into 500 ml milli-Q (mQ) water (only 1 gram in 500 ml for Leonardite humic acid, 1S104H). The solutions containing the humic acid were then filtered to remove insoluble particles, and an atomiser (TSI, 3076) was then used to produce aerosols. For experiments with mono ethanol amine sulphate-H_2SO_4 (MEA-H_2SO_4) and mono-methyl amine sulphate (MMS) aerosols, the amine MEA (Sigma Aldrich, > 99.5 %) and methyl amine (Sigma Aldrich, 40 % w/v) were added into 500 ml mQ water which had been acidified with sulphuric acid. The pH measured to be 8.1 and 8.5 for MEA-H_2SO_4 and MMS solutions, respectively. However, for insoluble organics (stearic acid (Sigma Aldrich, 99%), oleic acid (Sigma Aldrich, 99%) and squalene (Aldrich, 99%)) the aerosols were generated by homogeneous nucleation. Homogeneous nucleation involved placing the organic compound into a steel tube (21 cm length, 1.2 cm outer diameter, 1.0 cm inner diameter) and passing a 0.5 lpm flow over the organic whilst heating the tube to 106 - 111°C for stearic acid, 137 - 143°C for oleic acid and 139 - 140°C for squalene. For all experiments the aerosol concentration was varied using a HEPA filter and a bypass. The aerosol surface area was then measured using a Scanning Mobility Particle Sizer, which assumed a spherical geometry, (SMPS, TSI, 3080) at the end of the flow tube. Checks were made to ensure that the aerosol concentration did not change along the flow tube during the HO_2 decays for both experiments using the atomiser and during homogeneous nucleation experiments. and that the aqueous aerosols (glutaric acid, glyoxal, malonic acid, humic acid, MEA-H_2SO_4 and MMS) were never exposed to relative humidities below their efflorescence points.[52-55] The diameters of the aerosols contributing to the surface area weighted size distribution were measured as being between ~ 30 nm - ~ 400 nm. By decreasing the relative humidity (RH) in the flow tube a downwards shift in the aerosol size distribution was also observed for deliquesced aerosols but no change in the size distribution was observed for the effloresced aerosols. For example, with an Leonardite humic acid aerosol number concentration of 5.7×10^5 cm^{-3} the total aerosol surface area was measured as 9.5×10^{-5} cm^2 cm^{-3} at 75 % RH but decreased to 8.6×10^{-5} cm^2 cm^{-3} at 33 % RH. Information about the aerosol size distributions and the aerosol concentrations used is summarised in the Supplementary Information.

Data analysis

The observed decays followed pseudo first-order kinetics as given in Equation 1 when the injector was moved along the flow tube in both the presence and absence of aerosols:

$$ln\frac{[HO_2]_t}{[HO_2]_0} = -k_{obs}t \qquad \text{(E1)}$$

where $[HO_2]_t$ is the HO_2 concentration at time t, $[HO_2]_0$ is the initial HO_2 concentration and k_{obs} is the observed pseudo-first order rate constant. Therefore, as shown in Figure 1, the natural log of the background-subtracted signal was plotted against the reaction time (calculated from the dimensions of the flow tube, the flow rate and the injector position) in the flow tube. Measurements were made between ~ 11 and 20 seconds in order to ensure well mixed flows, with a mixing time of ~ 7 seconds having been previously calculated.[26] The k_{obs} values were then corrected (to k') for the non-plug flow conditions within the flow tube using the method described by Brown [56] which also subtracted the wall loss and increased the rate constants on average by 15 % compared to k_{obs} - k_{wall}. On average wall losses were measured as 0.04 s^{-1} with slightly higher wall losses measured at higher relative humidities (indicating a reaction limited wall loss). There was no change in the wall loss when the atomiser solution was swapped from pure water to the solutions containing organics suggesting negligible gas phase reactions between HO_2 and volatile or semi-volatile organics. The k' rate constants are related to γ_{obs}, the observed uptake coefficient, by Equation 2:

$$k' = \frac{\gamma_{obs} w_{HO2} S}{4} \qquad \text{(E2)}$$

where w_{HO2} is the molecular thermal speed of HO_2, and S is the total aerosol surface area. Therefore, k' was plotted against the total aerosol surface area, as shown in Figure 2, which enabled γ_{obs} to be obtained. A correction was made to correct for gas phase diffusion using the methodology described by Fuchs and Sutagin. [57] The change in the uptake coefficient due to this diffusion correction was less than 1 %. Initial HO_2 concentrations were determined by propagating back the wall loss decay back to time (t = 0 seconds) equaling 1×10^9 molecule cm^{-3}.

Results and discussion

The HO_2 uptake coefficients measured onto the different organic aerosols in this work are summarised in Table 1, and displayed in Figure 3. The measured HO_2 uptake coefficients were small ($\gamma < 0.004$ to $\gamma = 0.008 \pm 0.004$) for all of the organic aerosols (including the amine species) apart from the two brands of humic acid, where the uptake coefficient ranged from $\gamma = 0.007 \pm 0.002$ to $\gamma = 0.06 \pm 0.01$

for the Acros organics humic acid, and from $\gamma = 0.043 \pm 0.009$ to $\gamma = 0.09 \pm 0.03$ for the Leonardite humic acid over a range of humidities. Due to the much higher HO_2 uptake coefficients measured for the humic acids, the atomiser solutions were tested for the presence of metal ions using Inductively-coupled Plasma Mass Spectrometry (ICP-MS, Perkin Elmer Elan DRCe, sensitivity 1 ppt) to test for copper and iron ions. The HO_2 radical is catalytically destroyed in the presence of copper and iron forming either hydrogen peroxide or water.[58, 59] The results of the ICP-MS analysis for the atomiser solutions is shown in Table 2. The copper and iron ion concentrations in the Acros organics humic acid aerosols at 50% RH were estimated as $(5.5 \pm 0.3) \times 10^{-4}$ M and $(8.3 \pm 0.5) \times 10^{-2}$ M, respectively, whereas the copper and iron ion concentrations of Leonardite humic acid were estimated as $(1.2 \pm 0.1) \times 10^{-4}$ M and $(4.8 \pm 0.3) \times 10^{-3}$ M respectively. These estimations were based upon the change in the humic acid mass fraction within the atomiser solution (assuming no filtration had occurred) and the mass fraction of humic acid within the aerosols based upon the growth factors of humic acid measured by Badger et al.[60] However, it should be noted that Badger et al. [60] used a different humic acid to that used in this work and so the growth factors may be slightly different. Also, as the humic acid solutions were filtered there would have been less than one gram of Leonardite humic acid and less than 5 grams of Acros organics humic acid in the 500 ml of water and hence the mass fractions of humic acid within the atomiser solutions were overestimated. Therefore, it is likely that the molarity of iron and copper ions in the aerosols would be much higher than the concentrations calculated above. Mozurkewich et al. [31] showed that at copper (II) ion concentrations greater than 10^{-4} M, the HO_2 uptake coefficient starts to increase until it reaches the mass accommodation value at a copper ion concentration of 10^{-2} M. Therefore, it seems likely that the high HO_2 uptake coefficients observed for the two humic acids was due to the presence of elevated copper ion concentrations, and perhaps also the elevated iron ion concentrations, within the aerosols. However, it should be noted that aerosols containing humic like substances in the troposphere do not necessarily contain elevated transition metal ion concentrations and that therefore the HO_2 uptake coefficients onto those aerosols may deviate from the measurements in this work.[48]

In the absence of metals, the HO_2 uptake coefficients measured onto organic aerosols were similar to the uptake coefficients that have previously been measured onto effloresced and deliquesced salt aerosols using the same experimental setup,[26] suggesting that the rate of the HO_2 self-reaction within the aerosols determines the HO_2 uptake coefficient rather than the aerosol composition and hence the reaction of HO_2 with an organic. Another trend that can be observed in Table 1 is that the HO_2 uptake coefficients for the deliquesced aerosols tend to be larger than for the effloresced aerosols. For solid organic aerosols only an upper limit could be calculated ($\gamma < 0.004$), however, as these particles are non-spherical the HO_2 uptake coefficients are likely to be significantly lower than this upper limit. Larger HO_2 uptake coefficients have previously been measured onto deliquesced salts than onto effloresced salts and this trend has also been observed by Taketani et al. [35] for deliquesced dicarboxylic acid particles compared to effloresced dicarboxylic acid particles. The impact of organic aerosols on atmospheric HO_2 concentrations is likely to be small (a few % maximum) unless aerosols contain a concentration of copper ions of at least 10^{-4} M. A similar effect was observed with inorganic salt aerosols.[26] The exact effect upon tropospheric HO_2 concentrations would depend on the total aerosol surface concentration as well as the aerosol phase, the relative humidity and the aerosol liquid water content. However, given the magnitude of the uptake coefficients measured in this work, it seems unlikely that uptake of HO_2 to organic aerosols can explain the discrepancy that has sometimes been seen between measurements made in the field and predictions made by box models. In previous work the uptake coefficient measured onto salt ($\gamma = 0.01$) and dust ($\gamma = 0.031$) aerosols have been included into a box model but the impact on gaseous HO_2 concentrations has been small, ~ 2% and 0.3 - 6.5% (depending on the aerosol surface area), respectively.[26,30] The first HO_2 uptake coefficient measurements onto aerosols containing MEA-H_2SO_4 and MMS which have been suggested for carbon capture were made. It was shown that these would also not have a large impact upon the HO_2 uptake coefficient if these amines were to partition to the aerosol phase.

Although HO_2 uptake coefficients have not previously been measured and published in the literature for most of the organic aerosols chosen in this work, Taketani et al.[35] measured the HO_2 uptake coefficient onto aqueous glutaric acid aerosols. In this work, as shown in Table 1, the HO_2 uptake coefficient onto aqueous glutaric acid aerosols was measured as ranging from $\gamma < 0.004$ to $\gamma = 0.006 \pm 0.002$ in the relative humidity range of 23 – 76 %. In contrast, Taketani et al.[35] measured a HO_2 uptake coefficient of 0.15 ± 0.04 onto glutaric acid aerosols at a relative humidity of 68 % RH. In general Taketani et al. (2013) also measured high HO_2 uptake coefficients onto deliquesced aerosols ($\gamma = 0.13 \pm 0.04$ to $\gamma = 0.18 \pm 0.07$) and effloresced aerosols ($\gamma = 0.02 \pm 0.01$ to 0.07 ± 0.03) compared to lower HO_2 uptake coefficients measured in this work onto deliquesced aerosols containing low transition metal ion concentrations ($\gamma < 0.004$ to $\gamma = 0.008 \pm 0.004$) and effloresced aerosols ($\gamma < 0.004$). The discrepancy between the uptake coefficients measured with the experimental setup used in this work and measured by Taketani et al.[33] has previously been discussed by George et al.[26] for aqueous sodium chloride and ammonium sulphate aerosols, where Taketani et al.[33] measured uptake coefficients that were also at least an order of magnitude larger than with the experimental setup used in this work. Possible reasons for the difference between this work and literature values [33, 35] include differences in the reaction time, the HO_2 concentration that was used, and the trace metal ion content of the aerosols. Taketani et al. [35] measured HO_2 uptake with reaction times of approximately five to eleven seconds, whereas in this work the reaction times were between approximately eleven and twenty seconds. Taketani et al.[35] also worked at initial HO_2 concentrations of ~ 10^8 molecule cm^{-3} compared to an initial HO_2 concentration of 1×10^9 molecule cm^{-3} in this work. George et al.[26]

measured larger uptake coefficients at shorter reaction times and at smaller HO_2 concentrations for aqueous inorganic salt aerosols, consistent with the observed difference for organics in the two studies. Potential explanations given by George et al. for the time and HO_2 concentration dependence included a saturation mechanism or a trace reactant being used up over time. Future work will likely include the interpretation time and HO_2 concentration dependences for γ observed by George et al. (2013) [26] within the framework of the kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB), described by Shiraiwa et al.[61].

The humidity dependence of the HO_2 uptake coefficient onto humic acid aerosols

In this work a large humidity dependence was observed for HO_2 uptake onto humic acid aerosols. The HO_2 uptake coefficient increased from 0.007 ± 0.002 to 0.06 ± 0.01 between 32 and 76 % RH for the Acros organics humic acid, and from 0.043 ± 0.009 to 0.09 ± 0.03 between 33 and 75 % RH for the Leonardite humic acid. If the HO_2 uptake coefficient was solely controlled by the copper and iron ion concentrations within the aerosols, a decrease in the HO_2 uptake coefficient would have been expected with increasing humidity as the aerosols absorb more water, and become more dilute in metal ions at higher humidities. Therefore, although the presence of copper and iron ions within the aerosol has the potential to explain the magnitude of the uptake coefficients, it cannot explain the humidity trend.

Badger et al.[62] observed a similar uptake trend onto humic acid aerosols for N_2O_5, with the N_2O_5 uptake coefficient increasing from 2×10^{-4} to 9×10^{-4} between 25 and 75 % RH. The mechanism that was suggested for N_2O_5 uptake within aerosols involved the presence of water. However, at relative humidities of less than 40 % the uptake coefficient was limited by the liquid water content of the aerosols. Similarly, it is expected that the HO_2 uptake mechanism would be dependent upon the liquid water content of the aerosols. The mechanism in the aerosols with the low concentrations of copper ion present in the aerosols is expected to be given by:[58]

$$HO_{2(g)} \rightleftharpoons HO_{2(aq)} \tag{R3}$$

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

$$HO_{2(aq)} + HO_{2(aq)} \rightarrow H_2O_{2(aq)} + O_{2(aq)} \tag{R5}$$

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

$Cu^{2+}_{(aq)} + HO_{2(aq)} \rightarrow O_{2(aq)} + Cu^{+}_{(aq)} + H^{+}_{(aq)}$ (R7)

$Cu^{+}_{(aq)} + HO_{2(aq)} + H_2O_{(l)} \rightarrow H_2O_{2(aq)} + Cu^{2+}_{(aq)} + OH^{-}_{(aq)}$ (R8)

$Cu^{2+}_{(aq)} + O_2^{-}{}_{(aq)} \rightarrow O_{2(aq)} + Cu^{+}_{(aq)}$ (R9)

$Cu^{+}_{(aq)} + O_2^{-}{}_{(aq)} + 2H_2O_{(l)} \rightarrow H_2O_{2(aq)} + Cu^{2+}_{(aq)} + 2OH^{-}_{(aq)}$ (R10)

Therefore, as can be seen from the reaction scheme above, Reactions 6, 8 and 10 are dependent upon the liquid water content within the aerosols that may limit the HO_2 uptake coefficient at low relative humidities. The liquid water content of the aerosols could also explain the slightly lower HO_2 uptake coefficient measured for glyoxal aerosols at 33 % RH compared to 80 % RH and for humic acid aerosols over a range of humidities, although the viscosity of these aerosols could affect the uptake if the aerosols were much more viscous at lower humidity.[63, 64] The same mechanism would be expected to occur in the presence of iron ions although the rate constants between HO_2/ O_2^- and iron ions are significantly lower (~ 2 orders of magnitude) than with copper ions.[58]

However, there are other possible explanations for the relative humidity dependence of the HO_2 uptake coefficient at higher humidities. Humic acid is known to have surfactant properties and several studies have shown that it can form micelles at the surface of aqueous solutions.[65, 66] Badger et al.[62] suggested that the humic acid surfactant could cause a diffusion barrier to an incoming species thereby reducing the mass accommodation coefficient. As the humidity increases there would be a greater probability of water being present at the surface of the aerosol and therefore the mass accommodation would increase. Alternatively, the humic acid at the surface of the aerosol could cause a decrease in the Henry's law coefficient for HO_2 leading to a slower initial solvation of the HO_2 into the aerosol. However, in this work, accurate concentrations of copper and iron ions within the humic acid aerosols are not known with only a lower limit having been calculated in the first paragraph of the 'Results and discussion' section, so that it is currently difficult to determine whether it is a change in the mass accommodation or the Henry's law coefficient that is causing the HO_2 uptake coefficient dependence upon relative humidity. Finally, it should be noted that if atmospheric aerosols were to contain high concentrations of copper (> 10^{-2} M), the uptake coefficient would not necessarily be equal to the mass accommodation coefficient if humic acid was also present within the aerosol. However, more investigation is required to determine at what humic acid concentration the uptake coefficient deviates from the mass accommodation.

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Tables

Table 1: Summary of the HO_2 uptake coefficients measured in this work for organic aerosols at 293 ± 2 K and at an initial HO_2 concentration of 1×10^9 molecule cm^{-3}. The error represents two standard deviations.

* Determined by the efflorescence and deliquescence points of the organics.

$^+$ The magnitude of these uptake coefficients was influenced by the presence of copper and iron ions within the aerosol.

Compound	**RH/ %**	**Aqueous or Solid** *	**Uptake coefficient (γ)**
Stearic acid	32 - 75	Solid	< 0.004
Oleic acid	32	Solid	< 0.004
Squalene	32	Solid	< 0.004
Glutaric acid	32	Aqueous	< 0.004
	54	Aqueous	0.006 ± 0.002
	76	Aqueous	< 0.004
Glyoxal	33	Aqueous	0.003 ± 0.003
	80	Aqueous	0.008 ± 0.004
Malonic acid	55 - 76	Aqueous	< 0.004
Mono ethanol amine sulphate- H_2SO_4	32	Aqueous	< 0.004
Mono-methyl amine sulphate	36	Aqueous	0.005 ± 0.004
Humic acid (Acros organics)	32	Aqueous	0.007 ± 0.002$^+$
	54	Aqueous	0.017 ± 0.003$^+$
	65	Aqueous	0.031 ± 0.009$^+$
	76	Aqueous	0.06 ± 0.01$^+$
Humic acid (Leonardite)	33	Aqueous	0.043 ± 0.009$^+$
	51	Aqueous	0.07 ± 0.02$^+$
	75	Aqueous	0.09 ± 0.03$^+$

Table 2: The copper and iron ion concentrations measured by ICP-MS within the atomiser solutions and the estimated copper and iron ion molarities within the aerosols. Atomiser solutions were made by dissolving 5.0 grams of an organic into 500 ml of milliQ water with the exception of Leonardite humic acid where 1.0 gram was dissolved into 500 ml of mQ water. Both of the humic acid solutions were then filtered before being used for experiments. The range of molarities given for the glyoxal, glutaric acid and malonic acid aerosols is due to the range of humidities to which the aerosols were exposed. For humic acid aerosols only a lower limit of the molarity could be calculated as the ratio of humic acid to the transition metal ions was unknown due to the filtration of the atomiser solutions.

Compound	**Iron concentration in 500 ml mQ water / ppb**	**Estimated iron molarity within the aerosols/ M**	**Copper concentration in 500 ml mQ water / ppb**	**Estimated copper molarity within the aerosols/ M**
Humic acid (Acros organics)	51000 ± 3000	$> 8.3 \times 10^{-2}$	380 ± 20	$> 5.5 \times 10^{-4}$
Humic acid (Leonardite)	600 ± 30	$> 4.8 \times 10^{-3}$	16 ± 1	$> 1.2 \times 10^{-4}$
Glyoxal	12 ± 2	$\sim (1.1 - 2.5) \times 10^{-5}$	5 ± 1	$\sim (4.2 - 9.4) \times 10^{-6}$
Glutaric acid	1620 ±70	$\sim (1.7 - 3.4) \times 10^{-3}$	0.7 ± 0.1	$\sim (0.7 - 1.3) \times 10^{-7}$
Malonic acid	46 ± 3	$\sim (4.8 - 7.2) \times 10^{-5}$	5 ± 1	$\sim (4.7 - 7.0) \times 10^{-6}$

Figures

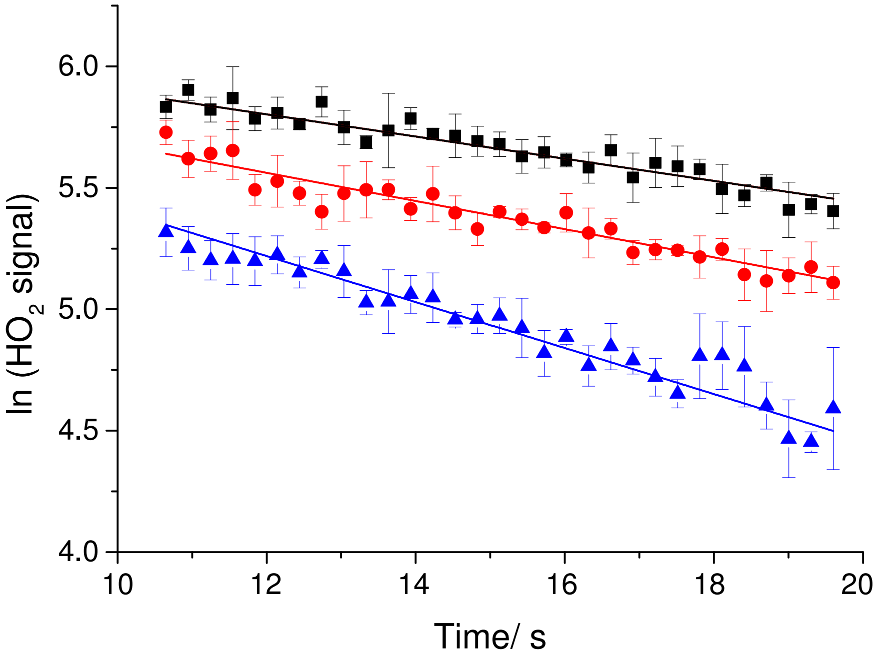

Figure 1: Examples of the HO_2 wall loss along the flow tube (black squares) and HO_2 loss in the presence of Leonardite humic acid aerosols with a surface area of 5.3×10^{-5} cm^2 cm^{-3} (red circles) and 8.9×10^{-5} cm^2 cm^{-3} (blue triangles) at a relative humidity of 33 %, an initial HO_2 concentration of 1×10^9 molecule cm^{-3} and a temperature of 293 ± 2 K. The gradient of the lines represent k_{obs} as given by Equation 1. The error bars represent one standard deviation.

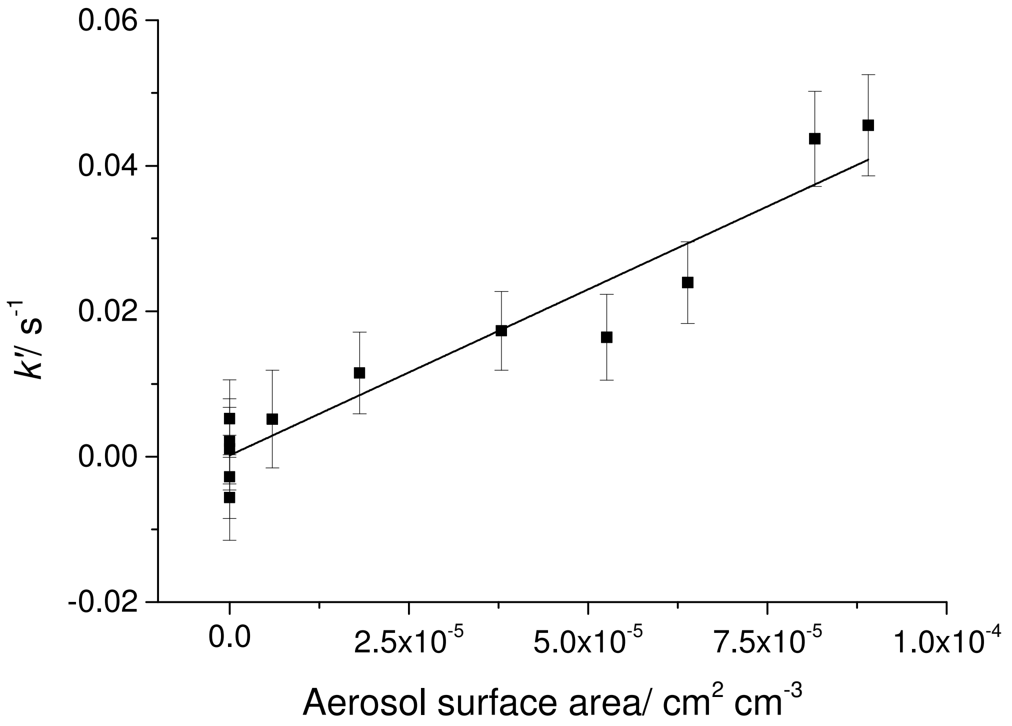

Figure 2: The pseudo-first order rate constant as a function of aerosol surface area for Leonardite humic acid at a relative humidity of 33 %, an initial HO_2 concentration of 1×10^9 molecule cm^{-3} and a temperature of 293 ± 2 K. The gradient of the line represents $(\gamma_{obs} w_{HO2})/4$ as given by Equation 2. The points at an aerosol surface area of 0 cm^{2}cm^{-3} are repeats of the wall loss decays taken throughout the experiment and show the natural variability of the measurements although they are within error of each other. The error bars represent one standard deviation.

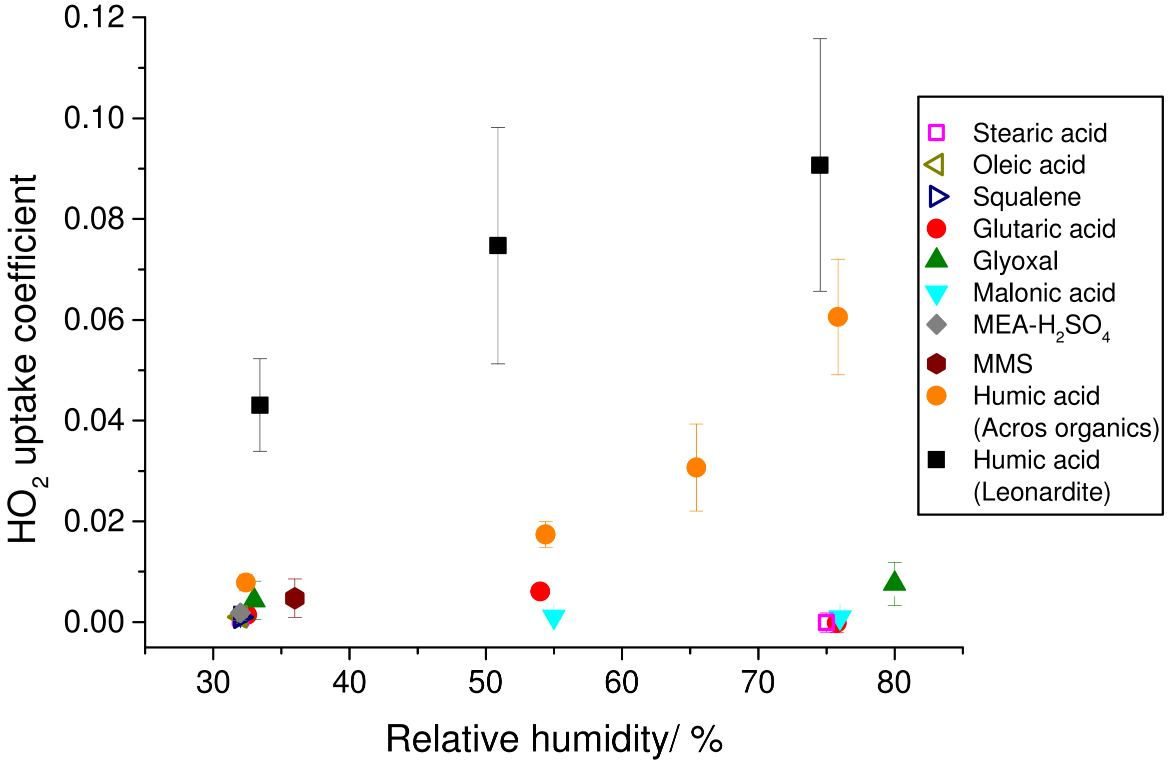

Figure 3: HO_2 uptake coefficients measured in this work for organic aerosols at 293 ± 2 K and at an initial HO_2 concentration of 1×10^9 molecule cm^{-3}. At 32 % relative humidity there are points for MEA-H_2SO_4, oleic acid, squalene, stearic acid and glutaric acid all plotted over each over. Open symbols represent solid phase aerosols. The error represents two standard deviations of the propagated error in the gradients of the *k′* against aerosol surface area graphs. The magnitude of the HO_2 uptake coefficients measured onto humic acid aerosols was influenced by the presence of copper and iron ions.