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Lakey, PSJ, George, IJ, Baeza-Romero, MT et al. (2 more authors) (2016) Organics Substantially Reduce HO2 Uptake Onto Aerosols Containing Transition Metal ions. Journal of Physical Chemistry A, 120 (9). pp. 1421-1430. ISSN 1089-5639

https://doi.org/10.1021/acs.jpca.5b06316

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Organics Substantially Reduce HO_2 Uptake Onto Aerosols Containing Transition Metal ions

Pascale S. J. Lakey[1+], Ingrid J. George[2], Maria T. Baeza-Romero[3], Lisa K. Whalley[1,4] and Dwayne E. Heard[1,4,*]

[1] *School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK*

[2] *Now at National Risk Management Research Laboratory, U.S. Environmental Protection Agency, T.W. Alexander Drive, Research Triangle Park, NC 27711, USA*

[3] *Escuela de Ingeniería Industrial de Toledo, Universidad de Castilla la Mancha, Avenida Carlos III s/n Real Fábrica de Armas, Toledo, 45071, Spain*

[4] *National Centre for Atmospheric Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK*

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

+ 44 (0) 113 343 6471 (tel)

+44 (0) 113 343 6401 (fax)

+ née Matthews, now at Max-Planck-Institut für Chemie, Hahn-Meitner-Weg 1, 55128 Mainz, Germany

Abstract

A HO_2 mass accommodation coefficient of $\alpha = 0.23 \pm 0.07$ was measured onto sub-micron copper (II) doped ammonium sulphate aerosols at a relative humidity of 60 ± 3 %, at 293 ± 2 K and at an initial HO_2 concentration of ~ 1×10^9 molecule cm^{-3} using an aerosol flow tube coupled to a sensitive Fluorescence Assay by Gas Expansion (FAGE) HO_2 detection system. The effect upon the HO_2 uptake coefficient γ of adding different organic species (malonic acid, citric acid, 1,2 diaminoethane, tartronic acid, ethylenediaminetetraacetic acid (EDTA) and oxalic acid) into the copper (II) doped aerosols was investigated. The HO_2 uptake coefficient decreased steadily from the mass accommodation value to $\gamma = 0.008 \pm 0.009$ when EDTA was added in a one-to-one molar ratio with the copper (II) ions, and to $\gamma = 0.003 \pm 0.004$ when oxalic acid was added into the aerosol in a ten-to-one molar ratio with the copper (II). EDTA binds strongly to copper (II) ions potentially making them unavailable for catalytic destruction of HO_2, and could also be acting as a surfactant or changing the viscosity of the aerosol. The addition of oxalic acid to the aerosol potentially forms low-volatility copper-oxalate complexes that reduce the uptake of HO_2 either by changing the viscosity of the aerosol or causing precipitation out of the aerosol forming a coating. It is likely that there is a high enough oxalate to copper (II) ion ratio in many types of atmospheric aerosols to decrease the HO_2 uptake coefficient. No observable change in the HO_2 uptake coefficient was measured when the other organic species (malonic acid, citric acid, 1,2 diaminoethane and tartronic acid) were added in a ten-to-one molar ratio with the copper (II) ions.

Introduction

OH and HO_2 radicals play vital roles in atmospheric chemistry by controlling the oxidative capacity of the troposphere, with HO_2 acting as a short-lived reservoir for OH and a source of ozone in more polluted environments via its reaction with NO. Several field studies have observed significantly lower concentrations of HO_2 radicals than predicted using box models, and HO_2 loss onto aerosols was suggested as a possible missing sink [1-17]. For many of these field measurements, for example during the ARCTAS campaign in the Arctic and the Rishiri Island field campaign, the HO_2 uptake coefficient was estimated as 1, which is the maximum possible [7, 9]. However, of the relatively few laboratory studies measuring HO_2 uptake coefficients onto aerosols, it has been shown that the HO_2 uptake coefficient is only equal to the mass accommodation for aerosols containing elevated copper ion concentrations (~ 0.3 – 0.4 M) [18-21]. The mechanism for the catalytic destruction of HO_2 in the presence of copper ions is shown below [22].

$HO_{2(g)} \rightleftharpoons HO_{2(aq)}$	H_{eff}	(R1)
$HO_{2(aq)} \rightleftharpoons H^+_{(aq)} + O_2^-{}_{(aq)}$	(K_{eq})	(R2)
$Cu^{2+}_{(aq)} + HO_{2(aq)} \rightarrow O_{2(aq)} + Cu^+_{(aq)} + H^+_{(aq)}$	($k_3 = 1 \times 10^8$ M^{-1} s^{-1})	(R3)
$Cu^+_{(aq)} + HO_{2(aq)} + H_2O_{(l)} \rightarrow H_2O_{2(aq)} + Cu^{2+}_{(aq)} + OH^-_{(aq)}$	($k_4 = 1.2 \times 10^9$ M^{-1} s^{-1})	(R4)
$Cu^{2+}_{(aq)} + O_2^-{}_{(aq)} \rightarrow O_{2(aq)} + Cu^+_{(aq)}$	($k_5 = 8.0 \times 10^9$ M^{-1} s^{-1})	(R5)
$Cu^+_{(aq)} + O_2^-{}_{(aq)} + 2H_2O_{(l)} \rightarrow H_2O_{2(aq)} + Cu^{2+}_{(aq)} + 2OH^-_{(aq)}$	($k_6 = 9.4 \times 10^9$ M^{-1} s^{-1})	(R6)

It has previously been calculated that a typical copper ion concentration within aerosols in rural regions was ~2.9×10^{-3} M [23, 24]. This estimation was based upon the measured aerosol size distributions in rural areas and a soluble copper concentration of 3.1 ng m^{-3} measured at a site in central Sweden [24]. Thornton et al. [25] developed an expression that allowed the HO_2 uptake coefficient to be predicted based upon the copper ion concentration within the aerosol, as shown below:

$$\frac{1}{\gamma^{HO_2}} = \frac{1}{\alpha^{HO_2}} + \frac{w}{H_{eff} RT \sqrt{k^I D_{aq} \mathrm{Q}}} \qquad \text{(E1)}$$

where γ^{HO2} is the uptake coefficient of HO_2, α_{HO2} is the mass accommodation coefficient, w is the molecular thermal speed of HO_2, H_{eff} is the effective Henry's law constant, R is the universal gas constant, T is the temperature, k^I is the pseudo-first order rate constant that depends on copper ion concentration ($k^I = k^{II}$[Cu]), D_{aq} is the HO_2 diffusion constant in the aerosol and Q accounts for aqueous-phase diffusion limitations within the aerosol. k^{II} is calculated using the following equation [25]:

$$k^{II} = \frac{k_3 + \left(\frac{K_{eq}}{[H^+]_{aq}}\right) k_5}{\left(1 + \frac{K_{eq}}{[H^+]_{aq}}\right)^2} \qquad \text{(E2)}$$

where K_{eq}, k_3 and k_5 are defined above, and $[H^+]$ is obtained from the pH within the aerosol. By inputting the rate constants in Reactions 3 and 5 to obtain k^{II} into Equation 1 using the method described by Thornton et al. [25], it can be predicted that for non-viscous aqueous aerosols the HO_2 uptake coefficient would become equal to the mass accommodation at a copper concentration of 2.9×10^{-3} M. Mozurkewich et al.[19] performed laboratory measurements of changes in the HO_2 signal as a function of aerosol copper ion concentration. In that study, it was found that the HO_2 uptake coefficient started to increase at a concentration of ~ 10^{-4} M and reached the mass accommodation at a copper concentration of ~ 10^{-2} M, suggesting that the concentration of copper ions found within tropospheric aerosols may indeed be high enough to influence HO_2 uptake. However, 20 – 90 % of submicron particulate mass is attributable to organics [26, 27], and it is known that organics can act as surfactants, bind with metal ions and increase the viscosity of the aerosols [22, 25, 28-30]. All of these effects would be likely to cause a decrease in the HO_2 uptake coefficient, even if high copper ion concentrations were present within the aerosol. Therefore, in this work, the effect of adding organic species, which were chosen for their likelihood of strongly binding to copper ions within the aerosols, was investigated.

Experimental

The experimental setup used in this work is only briefly outlined below with a detailed description given in George et al.[18] The experiment consisted of an aerosol flow tube coupled

to a sensitive Fluorescence Assay by Gas Expansion (FAGE) instrument that measured HO_2 indirectly. Experiments were performed by moving an injector backwards and forwards along the flow tube to release HO_2 in the absence and presence of different concentrations of aerosols and measuring both the HO_2 signal and the total aerosol surface area. The relative humidity was controlled by mixing a flow which had passed through a bubbler with a dry flow to form a humidified flow (3.0 ± 0.2 lpm), this was mixed with an aerosol flow (1.0 ± 0.2 lpm) in a conditioning flow tube before entering the aerosol flow tube. The relative humidity was measured using a relative humidity probe (Rotronic Hygroclip 2) after the reaction flow tube and was stable within ± 3 %.

HO_2 radicals were formed by the photolysis of water vapour using a mercury lamp (L.O.T. Oriel, model 6035) followed by reaction with oxygen, found in trace amounts (normally specified as 20 – 30 ppm) in the nitrogen supply used, via the following reactions:

$$H_2O + h\nu\ (185\ \text{nm}) \rightarrow OH + H \qquad \text{(R7)}$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad \text{(R8)}$$

The HO_2 exited at the end of a moveable injector in a 1.3 ± 0.1 lpm flow where it mixed with the humidified aerosol flow. HO_2 radicals were sampled at the end of the flow tube by a FAGE cell which was kept at a pressure of ~ 0.85 Torr using a combination of a rotary pump (Edwards, model E1M80) and a roots blower (EH1200). The HO_2 radicals were detected following their conversion to OH by addition of NO, and detection of OH by laser-induced fluorescence spectroscopy at 308 nm [14, 31]. The detection limit towards HO_2, obtained by calibration, was ~ 10^7 molecule cm^{-3}.

Atomiser solutions were prepared by dissolving 1.32 g ammonium sulphate (Fisher scientific, > 99 %) and 0.125 g copper (II) sulphate pentahydrate (Fisher scientific, > 98 %) in 500 ml Milli-Q water. Therefore, the molar ratio of copper ions to ammonium sulphate was one to twenty and the copper molarity was estimated at a relative humidity of 60 % to be ~ 0.3 M using the Aerosol Inorganic Model (AIM) [32, 33]. Therefore, the lifetime of HO_2 within the aerosol is less than one nanosecond (based upon the reaction scheme shown by Reactions 1 –

6), and the HO_2 uptake coefficient would therefore equal the mass accommodation coefficient. Organic compounds were also added into the solution at different molar ratios to the copper ions. The organics were malonic acid (Acros organics, 99 %), citric acid (Fisher scientific, > 99.5 %), 1,2 diaminoethane (Fisher scientific, > 98 %), tartronic acid (Sigma-Aldrich, > 97 %), ethylenediaminetetraacetic acid (EDTA, Fisher scientific, 99 %) and oxalic acid (Fisher scientific, > 99 %). Aerosols were formed by using an atomiser (TSI, 3076) and the concentration of aerosols entering the flow tube was controlled using a high efficiency particulate air (HEPA) filter and a bypass. The proportion of flow passing through the bypass compared to the filter was regulated using a needle valve. Aerosols were analysed upon exiting the flow tube using a Scanning Mobility Particle Sizer (SMPS, TSI, 3080) to determine the overall surface area. Aerosols were passed through two neutralisers, one before the reaction flow tube (Grimm 5522) and one within the SMPS (TSI 3077) giving them a known charge distribution which could be accounted for by the SMPS software. An example of the size distribution obtained is shown in Figure 1.

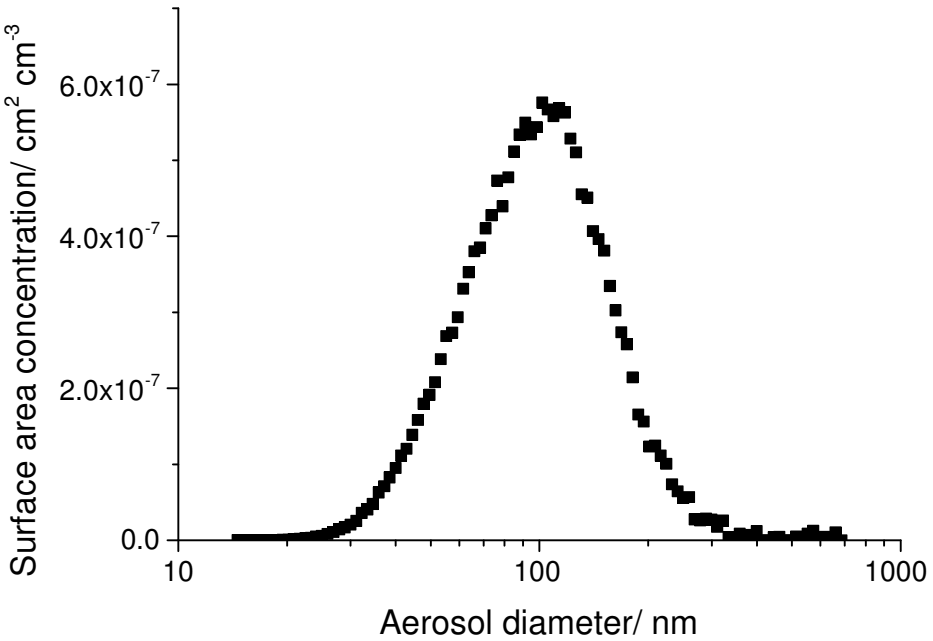

Figure 1. An example of the surface area concentration as a function of aerosol diameter for copper doped ammonium sulphate aerosols containing a 2:1 oxalic acid to copper (II) ion molar ratio at a relative humidity of 60 ± 3 % and at a temperature of 293 ± 2 K. The total surface area concentration in this example was 1.7×10^{-5} cm^2 cm^{-3}.

The data analysis has been previously described in detail by George et al.[18] and was performed assuming pseudo-first-order kinetics, such that the HO_2 loss rate is given by the following equation:

$$\ln[HO_2]_t = \ln[HO_2]_0 - k_{obs}t \qquad \text{(E3)}$$

where $[HO_2]_0$ is the initial concentration of HO_2, k_{obs} is the first order rate coefficient for the heterogeneous reaction of HO_2 with the aerosol particles and t is the reaction time. Examples of the background subtracted FAGE signal plotted against time in both the absence and presence of different aerosol concentrations are shown in Figure 2.

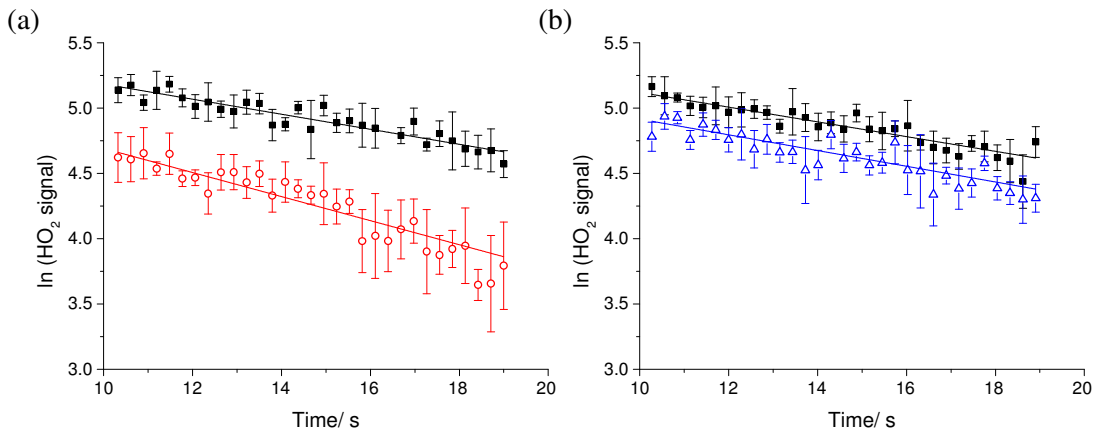

Figure 2. Pseudo-first order HO_2 temporal decays at RH = 60 ± 3 % in the absence of aerosols (black points) and with copper doped ammonium sulphate aerosols containing (a) a 2:1 oxalic acid to copper ion molar ratio at an aerosol surface area concentration of 1.7×10^{-5} cm^2 cm^{-3} (red points), and (b) a 10:1 oxalic acid to copper ion molar ratio at an aerosol surface area concentration of 1.4×10^{-4} cm^2 cm^{-3} (blue points). The error bars represent one standard deviation in the measured HO_2 signal measured at each point, which is averaged for 3 seconds. The gradient of these lines were used to determine k_{obs} from Equation 3. The lower initial signal in the presence of aerosols compared to the signal in the absence of aerosols is due to measurements starting after 10 seconds reaction time.

The observed pseudo-first order rate constants were then corrected for the non-plug flow within the flow tube using the iterative procedure outlined by Brown [34]. The Brown correction increased the pseudo-first-order rate constants on average by 34 %. The first order rate constant that had been corrected for the Brown correction (k') is related to the uptake coefficient (γ_{obs}) by the following equation:

$$k' = \frac{\gamma_{obs}\omega_{HO_2}}{4} S \quad \text{(E4)}$$

where ω_{HO2} is the molecular thermal speed of HO_2 (cm s^{-1}) and S is the total surface area of aerosols in a given volume (cm^2 cm^{-3}). Therefore, k' against S was plotted for all of the experiments and an example is shown in Figure 3.

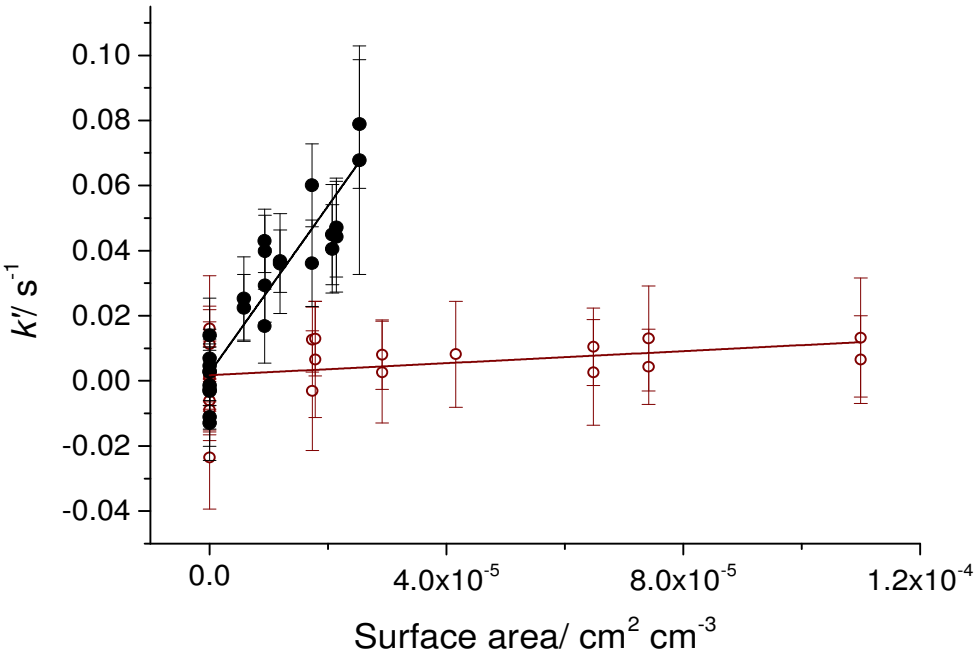

Figure 3. The pseudo-first order rate constants as a function of aerosol surface area for copper (II) doped ammonium sulfate aerosols (black) and with a 1:1 EDTA to copper molar ratio added to the aerosol. For pure copper (II) doped aerosols only a much smaller aerosol concentration range could be used as the HO_2 signal at ~ 11 - 19 seconds decreased to near background levels at higher aerosol concentrations.

The uptake coefficient was corrected in order to take into account gas phase diffusion. A correction for this gas phase diffusion effect was performed using the methodology described by Fuchs and Sutagin [35] and changed the uptake coefficient by less than 1 %.

Results and discussion

The HO_2 uptake coefficient was first measured onto copper (II) sulphate doped ammonium sulphate aerosols, with an example of k' plotted against aerosol surface area for this aerosol type shown in Figure 3. The average HO_2 uptake coefficient was measured as 0.23 ± 0.07 over the relative humidity range of 60 – 75 % and at an initial HO_2 concentration of 1×10^9 molecule cm^{-3}, a value that was expected to be equal to the HO_2 mass accommodation (α). The mass accommodation value is in agreement (within error) of the previous measurement of $\alpha = 0.4 \pm 0.3$ by George et al.[18] made with the same experimental setup and also agrees with the value of $\alpha > 0.2$ measured by Mozurkewich et al.[19] However, this value is lower than the mass accommodation values of $\alpha = 0.5 \pm 0.1$ and $\alpha = 0.53 \pm 0.12$ measured by Thornton and Abbatt [21] and Taletani et al.[20], respectively. Although the reason for this discrepancy remains unclear, George et al.[20] previously showed that the HO_2 mass accommodation coefficient is larger both for shorter interaction times between HO_2 and the aerosol, and for lower HO_2 concentrations. Therefore, the difference in the mass accommodation between the various studies may be due to varying experimental conditions, for example the longer reaction times utilised in this work of ~ 10 seconds at the start of the decay to ~19 seconds at the end of the decay compared to ~ 5 - 11 seconds used by Taketani et al.[20] and ~ 7 - 16 seconds used by Thornton and Abbatt.[21]

Several publications have suggested that organic species in aerosols could act as ligands for transition metal ions found in tropospheric aerosols [25, 29, 36-38]. If the organic species were acting as a ligand it could cause the copper ions to be unavailable for the catalytic destruction of HO_2 within the aerosol as shown in Reactions 1 - 6. Therefore, in order to test this hypothesis a very strongly binding hexadentate ligand (EDTA) with a binding constant of 18.8 [39] towards copper (II) ions was added into the copper doped ammonium sulphate aerosols in different molar ratios with the copper ion. As shown in Figure 3 the gradient of k' plotted against aerosol surface area reduced significantly when EDTA was added in a 1:1 molar ratio with copper. Figure 4 shows that the uptake coefficient started to reduce from the mass accommodation value of 0.23 ± 0.07 when the molar ratio of EDTA to copper was greater than 0.5.

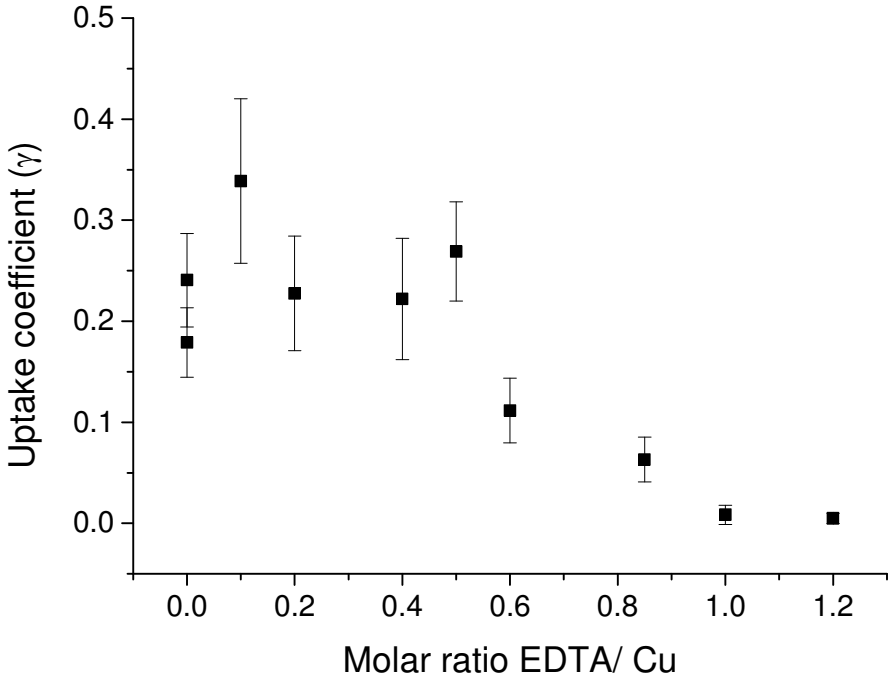

Figure 4. The HO_2 uptake coefficient for aerosols containing copper (II) doped ammonium sulphate aerosols as a function of the molar ratio of EDTA to copper in the aerosols. Experiments were performed at RH = 72 ± 4 % and at T = 293 ± 2 K. The error bars represent two standard deviations.

When the EDTA to copper (II) molar ratio was 1:1, the uptake coefficient was $\gamma = 0.009 \pm 0.009$ and at an EDTA to copper molar ratio of 6:5 the uptake coefficient was $\gamma = 0.005 \pm 0.005$ suggesting that the EDTA molecules binding to the copper ions make them unavailable for the catalytic destruction of HO_2 radicals.

To test whether the reduction in free (uncomplexed) Cu ion concentrations in the aerosol due to EDTA complexation with Cu alone could explain the decrease in the HO_2 uptake coefficient, HO_2 uptake coefficients were measured with aerosols containing different ammonium sulphate to copper (II) molar ratios, but in the absence of EDTA. The copper (II) concentration within the aerosols was estimated using the AIM model by assuming that both the ammonium sulphate molarity and the copper ion molarity would change by the same percentage between the atomiser solution and the aerosols. The results of this experiment are shown in Figure 5 and show that the HO_2 uptake coefficient starts to increase at an aerosol copper ion molarity of ~ 10^{-4} M and is fully limited by mass accommodation at an aerosol copper molarity of ~ 10^{-2} M

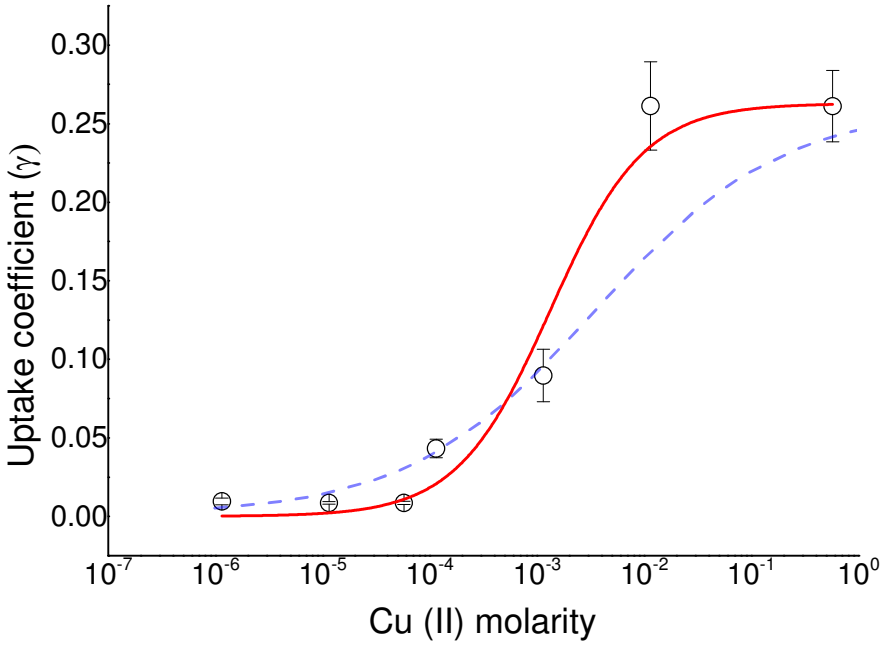

Figure 5. The HO_2 uptake coefficient as a function of the estimated Cu(II) molarity in the ammonium sulphate aerosols (estimated using the AIM model) at RH = 65 % and T = 293 ± 2 K. The error bars are 2 standard deviations. The red line represents a non-linear least-squares fitting of $1/\gamma = 1/\alpha + 1/(A \times [Cu])$ to the data (Equation 5). From the fit $\alpha = 0.26$ and $A = 197\ M^{-1}$. The dashed blue line represents the uptake coefficient derived from Equation 1 and assuming a pH of 5 but decreasing k' by approximately 4 orders of magnitude. See text for details.

The HO_2 uptake coefficient (γ) dependence upon the copper concentration within ammonium sulphate aerosols was well described by the following equation at aerosol copper molarities > 10^{-5} M:

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{1}{A[Cu]} \qquad \text{(E5)}$$

where A was determined from the best-fit to the data to be 197 M^{-1} and α =0.26. Equation 5 is loosely based upon the resistor model [40] with the first term being due to the mass accommodation of HO_2 and the second term due to reaction of HO_2 with Cu^{II} in the aerosol. A saturation term was not required meaning that the reaction was fast and would occur near the surface of the aerosol. The HO_2 uptake coefficient dependence upon aerosol copper molarities measured in this work is in agreement with the measurements made by Mozurkewich et al.[19],

who observed a changing HO_2 signal with a similar functional form with aerosol copper molarity. However, the measured dependence does not necessarily agree with the rate constants for the known aqueous chemistry shown in Reactions 1 – 6, as discussed previously by Thornton et al.[25]. If the literature rate constants for Reactions 1 - 6 are entered into Equation 1, using the methodology described by Thornton et al.[25], it would be expected that the HO_2 uptake coefficient would be fully limited by the mass accommodation at a copper molarity of ~ 10^{-4} M, rather than the experimental value of ~ 10^{-2} M. The dashed blue line in Figure 5 shows the best fit that could be obtained to the data using Equation 1. However, in order to achieve this best-fit, the product $k^I = k^{II}$[Cu] had to be reduced by approximately 4 orders of magnitude, requiring a reduction in the copper ion concentration and/or the rate constants R3 and R5 used to determine k^I as given by Equation 2.

There are several factors that may account for such a large change being required in order to fit Equation 1 to the data in Figure 5. On the one hand, the Cu^{II} concentrations in the aerosols have been calculated by a model that has not been specifically developed for Cu^{II}. It has been assumed that copper sulphate behaves like ammonium sulphate, which may introduce large errors in concentration determination. On the other hand, for a supersaturated microenvironment like aerosols, it may be more appropriate to use activities instead of concentrations in Equation 1, owing to the strong ionic interactions that are present. However, for a similar type of aerosol, Mao et al. [23] calculated that the Cu reactivity could decrease at most by about 1 order of magnitude owing to a reduction of its activity, meaning that a significant change in k^I is still needed in order to adequately fit the data in Figure 5.

Moreover, the reduction in reactivity is likely to be due, at least in part, to the microenvironment of the copper ions within the aerosols where the concentration of 'free' copper and/or the reactivity of copper could decrease. Following uptake of HO_2 radicals and diffusion, the reactions occur within supersaturated aerosols containing relatively high concentrations of dissolved ions. In contrast, the rate constants used in the calculations to obtain k^{II} were measured from kinetics experiments undertaken in more dilute solutions. Using Raman spectroscopy and an electrodynamic balance, Zhang et al. [41] found that at high concentrations, chemical interactions between sulfate ions with the metallic counter-cations were significant and led to the formation of contact ion pairs that modified the hygroscopic properties of the

aerosol. Zhang et al. [41] showed that contact ion pair mixtures shared sulphate ions and water molecules and those empirical mixing rules of water activity of atmospheric aerosols became invalid. Such effects and changes in molecular structures in a concentrated aerosol may reduce the reactivity or availability of Cu ions and hence k^I and explain, in part, why a significant reduction to the rate constants is required. In addition, Zhang et al. [41] also state that similar effects may occur in metal-organic ion systems.

Finally, there are other parameters which would influence the right-hand term of Equation 1 which controls the functional form of the Thornton et al. (2008) expression for the uptake coefficient versus copper molarity. We have already considered changes to k_3, k_5, [Cu] and above. The value of α^{HO2}, used in the first term of Equation 1 is constrained to the measured value and only impacts the value at high [Cu]. Assuming w, the molecular thermal speed of HO_2, R and T are accurate, then this leaves H_{eff}, the Henry's laws constant, D_{aq} the HO_2 diffusion constant in the aerosol and Q, which allows for aqueous-phase diffusion limitations within the aerosol. Also, in order to calculate k^{II}, the values of K_{eq} and $[H^+]$ are required. H_{eff} could be reduced owing to the microenvironment, although the mechanism for this is unclear (we discuss H_{eff} further below when organic-complexation can occur). D_{aq} for HO_2 has not been measured directly in aerosols themselves and so would be subject to uncertainty. As the aerosols are aqueous, diffusion limitations would not be expected, and so Q is likely to be very close to 1 (this may not be true for more viscous aerosols such as secondary organic aerosols). K_{eq} is very well established, but there is some uncertainty in the pH of the aerosol. 0.1 M – 2 M ammonium sulfate (a weak acid) solutions have a pH of between 5.5 and 6, and as the copper sulfate is also a weak acid and could also slightly acidify the aerosol (although being present at a much lower concentration), a pH of 5 was estimated for the aerosol and used in Equation 1. However, the true pH is unknown and may be considerably different to the pH 5 used.

In summary, there are several parameters in Equation 1 which have significant uncertainties, and when acting together could account for the four orders of magnitude change that are needed compared to the values in Thornton et al. (2008) to adequately fit the data shown in Figure 5.

Figure 6 shows the measured HO_2 uptake coefficients in the presence of EDTA as a function of free copper ions, and also a comparison with the HO_2 uptake coefficients calculated using Equation 5, using the best parameterised fit (A=197 M^{-1}) to the data shown in Figure 5.

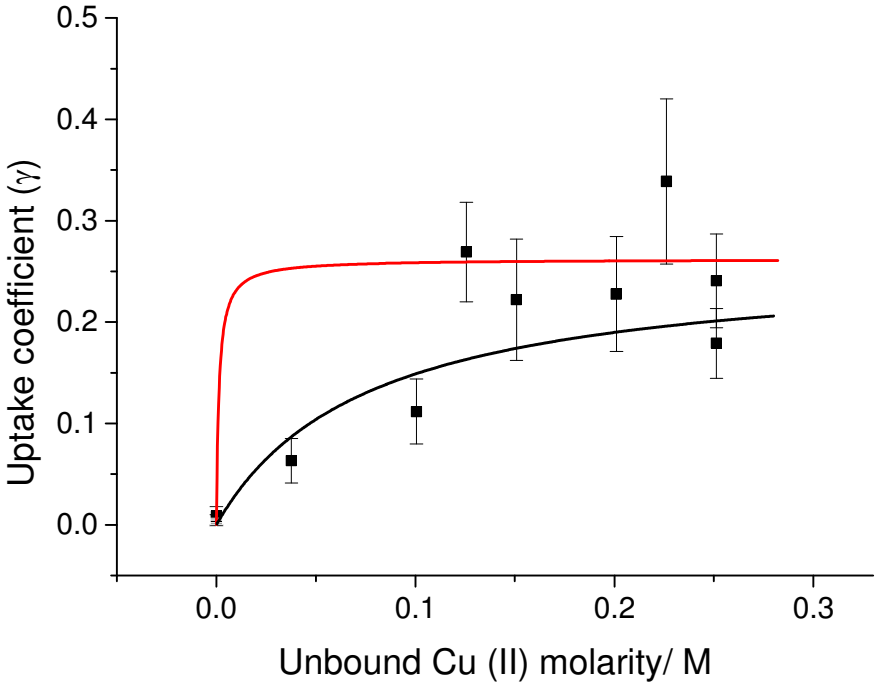

Figure 6. The HO_2 uptake coefficient for aerosols containing copper doped ammonium sulphate aerosols as a function of the concentration of the unbound Cu (II) ions assuming that EDTA binds to copper in a one to one ratio. The red line (R^2 = 0.72) represents the expected change in uptake coefficient controlled only by the changing copper (II) concentrations as given by Equation 5, and the black line (R^2 = 0.89) is the best fit of Equation 6 to the data, which assumes that an additional process is also controlling the change in the HO_2 uptake coefficient. Experiments were performed at RH = 72 ± 4 % and T = 293 ± 2 K. The error bars represent two standard deviations of the propagated error in the gradient of the k' against surface area graphs. See text for details.

It can be seen that the measured HO_2 uptake coefficient in the presence of EDTA increases considerably more slowly with [Cu(II)] compared with the uncomplexed case. Figures 5 and 6 can be directly compared due to the similar conditions under which these experiments were performed. A one-to-one binding ratio of copper ions to EDTA has been used to estimate the free copper ion molarity within the aerosols. For copper ion concentrations below 0.1 M the measured HO_2 uptake coefficients tend to fall below the calculated value from Equation 5, suggesting that the HO_2 uptake coefficient is not purely controlled by the binding of EDTA to the copper ions, which would make it unavailable for catalytic destruction of HO_2. A better fit

(R^2 = 0.89 versus 0.72) to the measurements was obtained using a modified form of Equation 5, which is also shown in Figure 6:

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{1}{197[Cu(II)]} + \frac{1}{B[Cu(II)]} \quad \text{(E6)}$$

where the parameter *B,* which reduces the uptake coefficient potentially as a result of the EDTA acting as a surfactant or causing a change in the viscosity of the aerosols, was found to be 3.5 M^{-1}. It has previously been shown that surfactants can reduce the uptake coefficient of a species by either forming a diffusion barrier, thereby reducing the mass accommodation coefficient, or by decreasing the Henry's law coefficient [41-43]. If EDTA was causing a change of viscosity within the aerosol it would also be expected that the HO_2 uptake coefficient would decrease due to slower diffusion of HO_2 into the bulk of the aerosol. The impact of viscosity upon uptake coefficients has previously been shown to be important and has been investigated on other systems such as the ozonolysis of oleic acid and the rate of heterogeneous reaction of particle-borne benzo[a]pyrene (BaP) with ozone within SOA particles [44, 45]. However, it is currently not possible to state with certainty which of these effects EDTA had upon the aerosol properties that caused the HO_2 uptake coefficient to decrease at a faster rate than expected when the EDTA concentrations within the aerosols were increased. More fundamental experiments would be required such as measuring the surface tension of the aerosols or measuring the diffusion of species through the aerosols in the presence and absence of EDTA. We return to the discussion regarding changes in viscosity or surface coatings after presenting the results for HO_2 uptake coefficients in the presence of other organic species.

However, as EDTA is not observed within tropospheric aerosols, other organic species were also investigated to determine whether these would similarly reduce the HO_2 uptake coefficient onto copper doped aerosols. Experiments were performed with malonic acid, citric acid, 1,2 diaminoethane, tartronic acid and oxalic acid. These species were chosen because of their likelihood to bind with metals in the aerosol based upon their Henry's law constant and their binding constant with copper (II) ions, and because of their presence in the atmosphere [29]. It should be noted that Okochi and Brimblecombe [29] predicted that based upon the Henry's law constant and their binding constants with copper (II), similar molarities (within 20 %) of oxalic

acid and tartronic acid would bind to a given copper (II) concentration, whereas the molarity of malonic acid would have to be at least an order of magnitude larger for it to bind to the same copper concentration.

Experiments were performed with either a 2:1 or a 10:1 organic to copper molar ratio within the atomiser solution and the relationships between the pseudo-first order rate constants and the aerosol surface areas are shown in Figure 7 and summarised in Table 1. However, it should be noted that for volatile organics the ratios may decrease within the aerosols.

Organic	**HO_2 uptake coefficient for a given organic : copper sulphate molar ratio**	
	2:1	**10:1**
Malonic acid	0.32 ± 0.09	0.28 ± 0.06
Citric acid	0.17 ± 0.05	0.31 ± 0.08
1,2 diaminoethane	0.32 ± 0.07	0.24 ± 0.05
Tartronic acid	0.24 ± 0.15	0.19 ± 0.07
Oxalic acid	0.17 ± 0.05	0.003 ± 0.004

Table 1. Uptake coefficients measured for copper (II) sulphate doped ammonium aerosols containing either a 2:1 or a 10:1 organic to copper (II) molar ratio. All experiments were performed at RH = 60 ± 3 % and T = 293 ± 2 K, and the estimated copper molarity within all of the aerosols was ~ 0.3 M. The error bars represent two standard deviations of the propagated error in gradients of the graphs of the pseudo-first order rate constant k' against aerosol surface area, S. The mass accommodation value obtained when no organics were present in the aerosols was $\alpha = 0.23 \pm 0.07$.

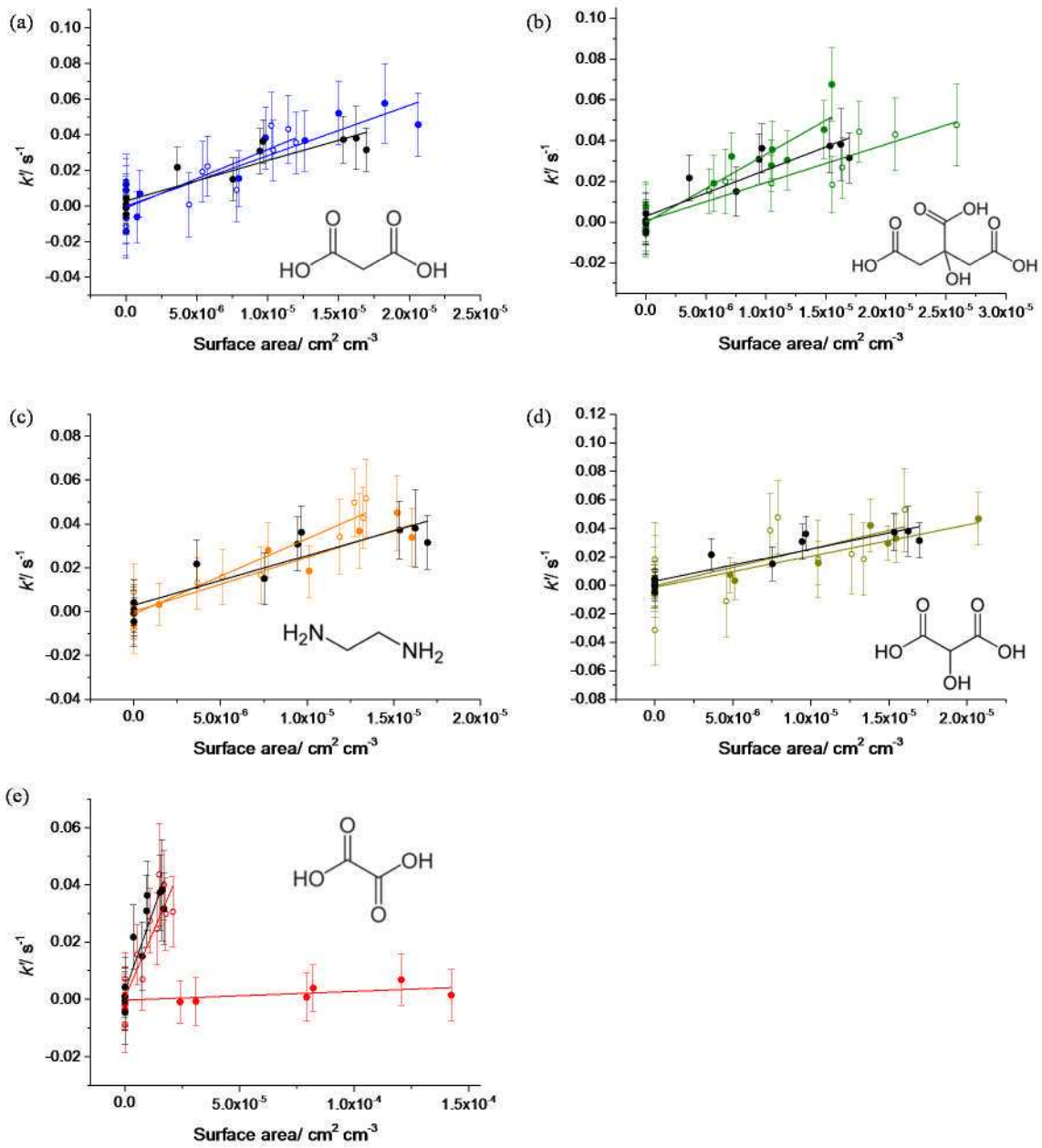

Figure 7. The pseudo-first order rate constants as a function of aerosol surface area for copper (II) doped ammonium sulfate aerosols (black, shown in all panels) and with (a) malonic acid (blue), (b) citric acid (green), (c) 1,2 diaminoethane (orange), (d) tartronic acid (dark yellow) and (e) oxalic acid (red) added. The open coloured symbols represent a 2:1 molar ratio of the organic to the copper and the closed coloured symbols represent a 10:1 molar ratio of the organic to the copper. All experiments were performed at RH = 60 ± 3 % and T = 293 ± 2 K. The error bars represent one standard deviation.

As shown in Table 1, when the organic species were present in the aerosols the HO_2 uptake coefficient was within error of the mass accommodation coefficient ($\alpha = 0.23 \pm 0.07$) with the exception of when oxalic acid was added into the aerosols in a 10:1 molar ratio with the copper.

Despite their similar chelating strengths, the difference in the effect of the addition of oxalic acid and tartronic acid on the HO_2 uptake suggests that the decrease in the HO_2 uptake coefficient in the presence of oxalic acid could not be purely due to copper-oxalate complexes forming. The presence of oxalic acid and/ or oxalate metal complexes must have either changed the properties of the aerosol (e.g. the viscosity) or the total concentration of copper within the aerosols (e.g. due to precipitation).

A recent study by Drozd et al. has shown that the addition of oxalic acid to aerosols containing inorganic salts (e.g $CaCl_2$, $MgCl_2$ and $ZnCl_2$) reduced both the volatility of the oxalic acid and the hygroscopicity of the aerosol [46]. The low hygrosopicities of the aerosols could either be due to a large increase in the viscosity of the aerosol or the formation of a strongly-bound insoluble metal-oxalate complexes (salts) forming a coating at the surface of the aerosol. An increase in the aerosol viscosity from the formation of the metal-complexes may have reduced the HO_2 uptake coefficient due to the slow diffusion of HO_2 in the aerosol. Alternatively, formation of a metal-oxalate complex precipitate in the aerosol may also have reduced the HO_2 uptake coefficient with increasing oxalic acid concentrations due to lower copper concentrations within the aerosol. A coating could potentially also have formed a diffusion barrier or affected the HO_2 Henry's law coefficient into the aerosols as shown by previous work [41-43]. However, other factors that may have decreased the HO_2 uptake coefficient cannot be ruled out. For example, Reactions 4 and 6 are dependent on the liquid water concentrations within the aerosols that would be expected to be lower when oxalate is present within the aerosol due to the lower hygroscopicity of the aerosol. However, the exact concentration of liquid water within the aerosols during the HO_2 experiments onto aerosols containing copper (II) ions and oxalic acid is unknown. Further experiments, such as measuring the surface tension or diffusion of species through aerosols in the presence and absence of oxalate may elucidate which mechanism is operating, or whether it is a combination of effects that decreases the HO_2 uptake coefficient in the presence of oxalate.

Organic-inorganic component interactions are typically not considered in atmospheric models, but as discussed by Drozd et al.[47] can greatly affect aerosol volatility and hygroscopicity. For example, Drozd et al.[47] reported a dramatic increase in the CCN (cloud condensation nuclei) activation diameter, up to 50 nm, for relatively small particle mass fractions of oxalic acid (10–20 %). In particular this was found for bi-dentate binding of di-carboxylic to soluble inorganic

ions, being particularly strong for di-valent metal ions (e.g. Ca^{2+}, Mg^{2+} and Zn^{2+}). Surface enrichment of insoluble metal-organic complexes (salts), giving a hard, insoluble coating which could result in particles that are hard enough to exhibit bounce on particle impactors and which could affect uptake onto those particles. Such a mechanism could operate for Cu(II) here in the presence of oxalate impacting the uptake coefficient for HO_2. The value of the effective Henry's law constant for HO_2 in the aerosols would be reduced, which as a denominator term in Equation 1, would result in a higher [Cu] needed to achieve a given uptake coefficient.

Atmospheric Implications

Dicarboxylic acids contribute ~15% of the total marine organic aerosol mass with oxalic acid contributing more than 50% of the total dicarbarboxylic acids [47-49]. During the Reactive Halogens in the Marine Boundary Layer (RHaMBLe) field campaign, which took place in Cape Verde, oxalate was measured as 78 – 151 ng m^{-3} in PM_{10} aerosols [50]. In this work, a 10:1 oxalic acid to copper molar ratio decreased the uptake coefficient by approximately three orders of magnitude. Therefore, if copper was the only metal ion that could bind with oxalate, a copper concentration in Cape Verde of 5.6 – 10.9 ng m^{-3} or less would be unable to catalytically destroy HO_2. The inability of the copper to catalytically destroy HO_2 would be likely to be due to the precipitation of copper-oxalate complexes or an increase in the aerosol viscosity. However, it should be noted that although the actual concentration of copper ions within the aerosols during the RHaMBLe field campaign remains unknown, Fomba, et al. [51] recently measured the copper concentration in Cape Verde as being in the range of 0.03 – 1.17 ng m^{-3}. In Cape Verde there were also other metals such as iron ions that could also potentially bind with oxalate and were measured in the range of 0.1 – 25.89 ng m^{-3} [51]. Therefore, further laboratory studies with different salts, metals, aerosol pHs, and oxalic acid to metal ratios would be required in order to definitively determine the effect of oxalate in aerosols and to relate this to tropospheric aerosols.

A box model which was constrained with gas-phase data taken during the RHaMBLe project [52] that took place in 2007 at the Cape Verde Atmospheric Observatory (CVAO) [53], which is situated on the island of Sao Vicente in the tropical Atlantic ocean (23.96° S, 46.39° W) was utilised to investigate the effect of the presence of oxalate within the aerosols during the RHaMBLe field campaign. The model, which utilises the Master Chemical Mechanism v3.2,

has been described previously and has formerly been used to calculate OH and HO_2 concentrations for comparison with those measured at CVAO (Whalley et al., 2010). The effect of mineral dust aerosols on HO_2 concentrations was also studied using this model [15, 54]. As stated in the Introduction, a typical copper ion concentration of 3.1 ng m^{-3} could lead to copper ion concentrations of ~ 2.9×10^{-3} M in aerosols in rural areas, which may be high enough for the HO_2 uptake coefficient to equal the HO_2 mass accommodation ($\alpha = 0.23 \pm 0.07$ in this work). However, based upon the measurements made by Fomba et al.[51], the copper molarity within the aerosols would be unlikely to be as elevated as this. With large concentrations of oxalate within the aerosols, as measured by Mueller et al.[50], the uptake coefficient would be reduced ($\gamma = 0.003 \pm 0.004$ in this work, Figure 7e). Therefore, these two uptake coefficients were inputted into the box model to determine the potential maximum impact upon gaseous HO_2 concentrations. For $\gamma = 0.003$ and 0.23 the HO_2 gaseous concentration decreased by 0.2 and 15 %, respectively, at solar noon.

In this work it has been shown that oxalate ions within aerosols, and potentially other organic species, may cause a significant change in the HO_2 uptake coefficient, and therefore, in the gaseous HO_2 concentrations within the troposphere if the aerosols contain substantial copper concentrations (> 10^{-4} M).

Conclusions

The addition of EDTA and oxalic acid to copper (II) doped ammonium sulphate aerosols decreased the HO_2 uptake coefficient significantly. For copper (II) doped ammonium sulphate aerosols a HO_2 uptake coefficient (or a mass accommodation value) of 0.23 ± 0.07 was measured which decreased to a value of 0.009 ± 0.009 when EDTA was added in a 1:1 molar ratio with the copper (II). The HO_2 uptake coefficient decreased from 0.23 ± 0.07 to a value of 0.003 ± 0.004 when a ten to one oxalic acid to copper molar ratio was present in the atomiser solution. However, no significant change was observed when malonic acid, citric acid or 1,2 diaminoethane were added to the atomiser solutions in a 10:1 molar ratio with the copper. It is postulated that the decrease in the HO_2 uptake coefficient from the presence of EDTA in the aerosols was due in part to EDTA binding to the copper (II) ions, reducing the free copper (II) concentration and making it unavailable to catalytically destroy the HO_2. Experiments

performed in the absence of any added organic species was used to measure the variation of γ as a function of concentration of the free copper (II). The uptake coefficient increased from a very low value towards the mass accommodation coefficient at a much higher concentration of Cu(II) than expected by the expression developed by Thornton et al.[25] using available kinetic data. This finding provides evidence that in the supersaturated ammonium sulphate aerosols contact ion pairs or complex structures are present which significantly reduces the reactivity of copper ions towards HO_2. There may also be uncertainties in the pH within the aerosol used to calculate the uptake coefficient.

In the presence of EDTA, the HO_2 uptake coefficient as a function of the free copper ion concentration calculated assuming a 1:1 complex was significantly different to that obtained in the absence of EDTA, suggesting that γ is not purely controlled by the binding of EDTA to the copper ions. EDTA may have acted as a surfactant or changed the viscosity of the aerosol, which would have reduced the diffusion coefficient of HO_2 within the aerosol resulting in a reduction in γ. It is hypothesized that the decrease in the HO_2 uptake coefficient when oxalic acid was added to the aerosols was due to either formation of a strongly-bound Cu-oxalate salt which is not soluble, forming a surface coating (preventing HO_2 reaching the bulk of the aerosol) or a precipitate which reduces further the concentration of free copper ions, or (b) there is a reduction in the bulk viscosity of the aerosol caused by the formation of strongly-bound metal-organic complexes, and hence reducing the diffusion constant of HO_2.

Overall, it has been shown that organic species within aerosols have the potential to decrease the HO_2 uptake coefficient significantly (from $\gamma = \alpha$ if there are sufficient transition metal ions within the aerosol), and thereby can have a significant impact on gaseous HO_2 concentrations within the troposphere. Although it is important to know the transition metal ion concentration within aerosols when predicting the HO_2 uptake coefficient, it is also extremely important to measure the organic content of the aerosol and to identify species that could affect the properties of the aerosol by binding to metals within the aerosol, by changing the viscosity of the aerosol or by acting as surfactants at the surface of the aerosol. However, in order to better understand the effect that organic species have upon the properties of the aerosol, and therefore on gaseous tropospheric HO_2 concentrations, more laboratory measurements are needed at different relative humidities, with different organic species at different concentrations and with

mixtures of transition metal ions within the aerosols. Experiments to measure the surface tension of the aerosols and measuring the diffusion of species through the aerosols in the presence and absence of organics is also highly desirable, in order to understand the mechanism by which these organics change the value of the HO_2 uptake coefficient.

Acknowledgements

This work was supported by the National Environment Research Council under grant NE/F020651/1. PSJL is grateful to NERC for the award of a studentship. LKW and DEH are also grateful to the National Centre for Atmospheric Science, which is funded by NERC, for ongoing support.

Tables

Table 1. Uptake coefficients measured for copper (II) sulphate doped ammonium aerosols containing either a 2:1 or a 10:1 organic to copper (II) molar ratio. All experiments were performed at RH = 60 ± 3 % and T = 293 ± 2 K, and the estimated copper molarity within all of the aerosols was ~ 0.3 M. The error bars represent two standard deviations of the propagated error in gradients of the graphs of the pseudo-first order rate constant k' against aerosol surface area, S. The mass accommodation value obtained when no organics were present in the aerosols was $\alpha = 0.23 \pm 0.07$.

Organic	**HO_2 uptake coefficient for a given organic : copper sulphate molar ratio**	
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Citric acid	0.17 ± 0.05	0.31 ± 0.08
1,2 diaminoethane	0.32 ± 0.07	0.24 ± 0.05
Tartronic acid	0.24 ± 0.15	0.19 ± 0.07
Oxalic acid	0.17 ± 0.05	0.003 ± 0.004

558 **Figures**

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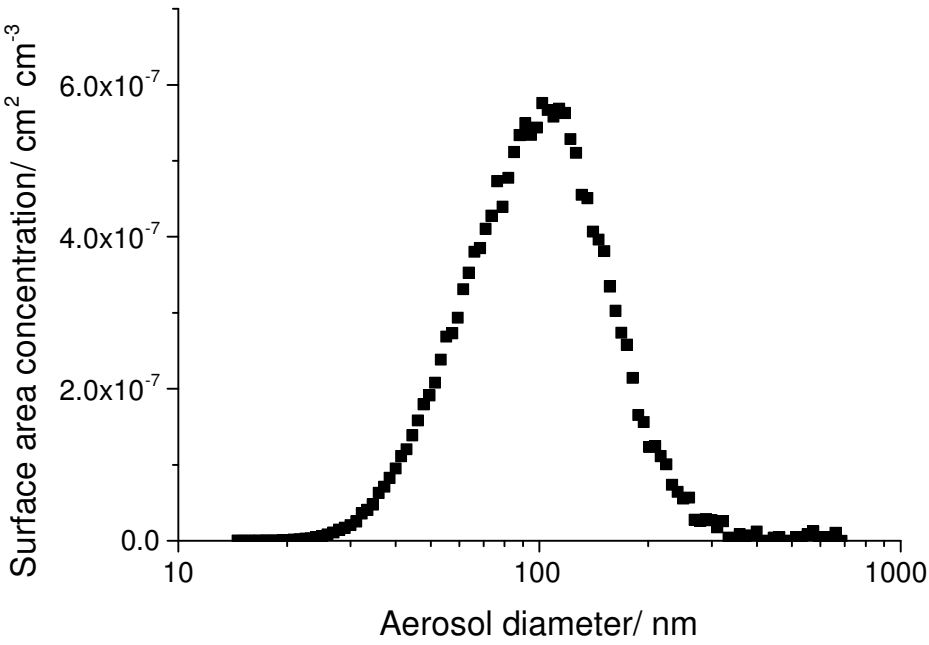

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565 **Figure 1.** An example of the surface area concentration as a function of aerosol diameter for
566 copper doped ammonium sulphate aerosols containing a 2:1 oxalic acid to copper (II) ion molar
567 ratio at a relative humidity of 60 ± 3 % and at a temperature of 293 ± 2 K. The total surface
568 area concentration in this example was 1.7×10^{-5} cm^2 cm^{-3}.
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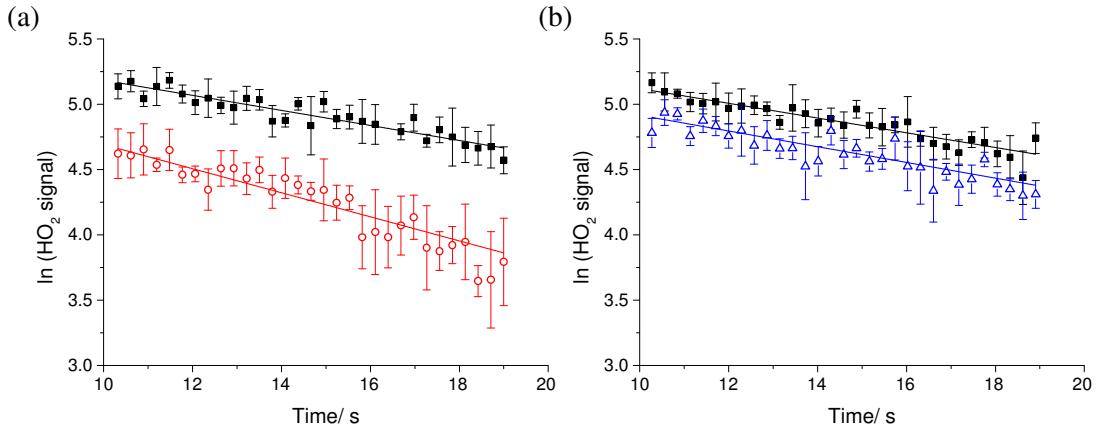

Figure 2. Pseudo-first order HO_2 temporal decays at RH = 60 ± 3 % in the absence of aerosols (black points) and with copper doped ammonium sulphate aerosols containing (a) a 2:1 oxalic acid to copper ion molar ratio at an aerosol surface area concentration of 1.7×10^{-5} cm^2 cm^{-3} (red points), and (b) a 10:1 oxalic acid to copper ion molar ratio at an aerosol surface area concentration of 1.4×10^{-4} cm^2 cm^{-3} (blue points). The error bars represent one standard deviation in the measured HO_2 signal measured at each point, which is averaged for 3 seconds. The gradient of these lines were used to determine k_{obs} from Equation 2. The lower initial signal in the presence of aerosols compared to the signal in the absence of aerosols is due to measurements starting after 10 seconds reaction time.

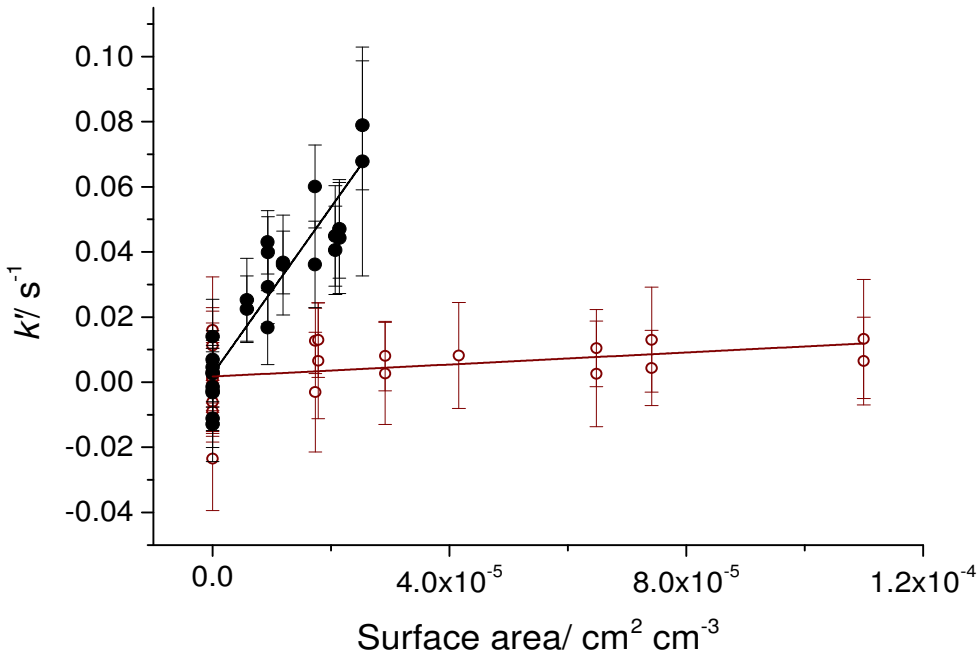

Figure 3. The pseudo-first order rate constants as a function of aerosol surface area for copper (II) doped ammonium sulfate aerosols (black) and with a 1:1 EDTA to copper molar ratio added to the aerosol. For pure copper (II) doped aerosols only a much smaller aerosol concentration range could be used as the HO_2 signal at ~ 11 - 19 seconds decreased to near background levels at higher aerosol concentrations.

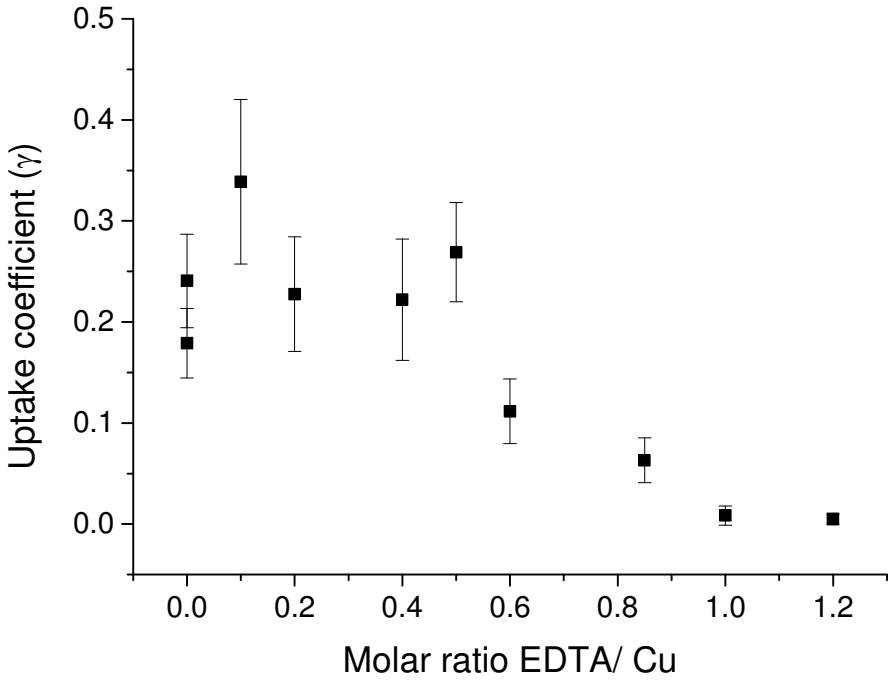

Figure 4. The HO_2 uptake coefficient for aerosols containing copper (II) doped ammonium sulphate aerosols as a function of the molar ratio of EDTA to copper in the aerosols. Experiments were performed at RH = 72 ± 4 % and at T = 293 ± 2 K. The error bars represent two standard deviations.

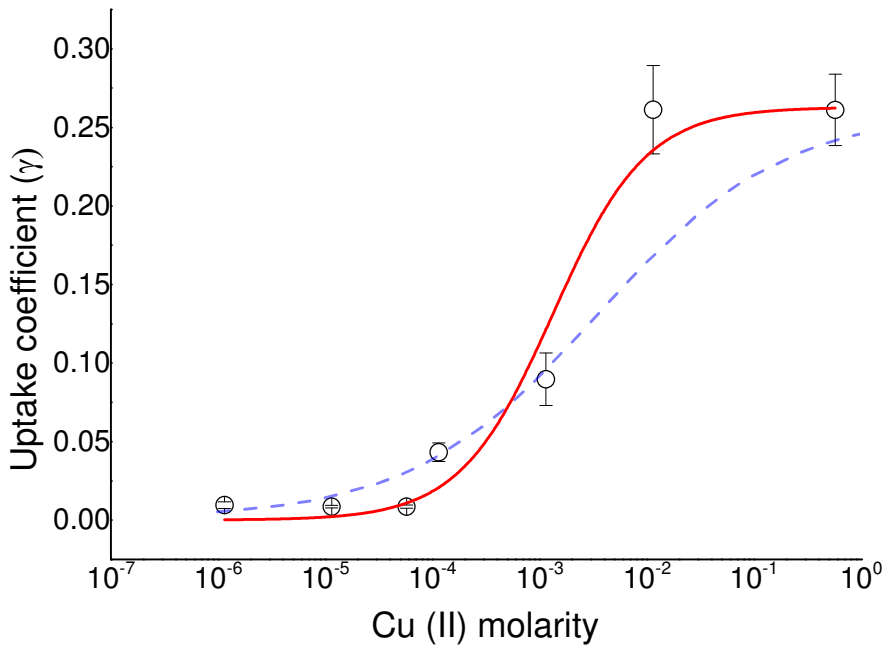

Figure 5. The HO_2 uptake coefficient as a function of the estimated Cu(II) molarity in the ammonium sulphate aerosols (estimated using the AIM model) at RH = 65 % and T = 293 ± 2 K. The error bars are 2 standard deviations. The red line represents a non-linear least-squares fitting of $1/\gamma = 1/\alpha + 1/(A \times [Cu])$ to the data (Equation 5). From the fit $\alpha = 0.26$ and $A = 197\ M^{-1}$. The dashed blue line represents the uptake coefficient derived from Equation 1 and assuming a pH of 5 but decreasing k' by approximately 4 orders of magnitude. (either due to a reduction of the rate constants for R3 and R5 or in the copper ion concentration, or a combination of both). See text for details.

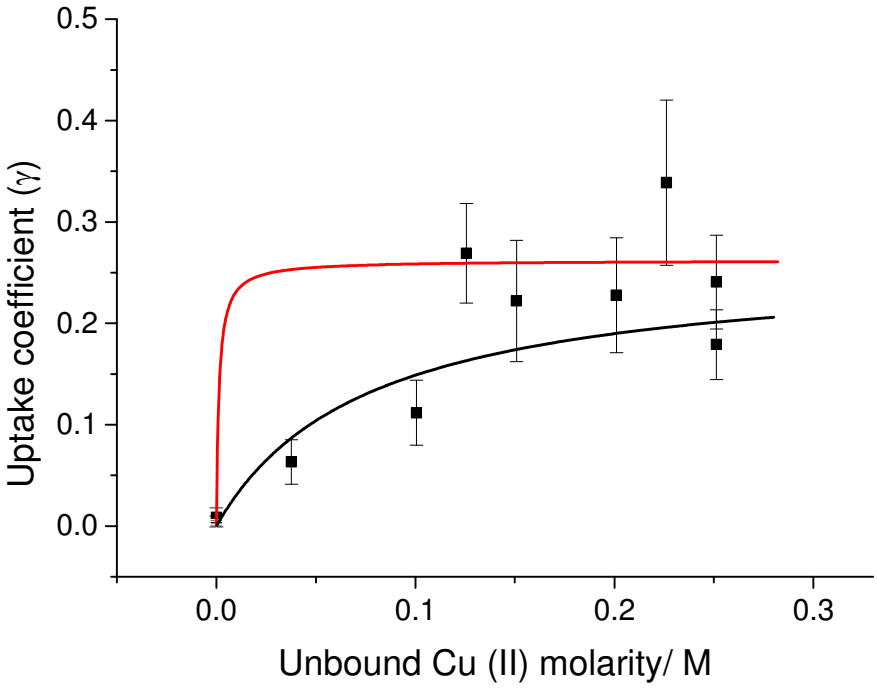

Figure 6. The HO_2 uptake coefficient for aerosols containing copper doped ammonium sulphate aerosols as a function of the concentration of the unbound Cu (II) ions assuming that EDTA binds to copper in a one to one ratio. The red line (R^2 = 0.72) represents the expected change in uptake coefficient controlled only by the changing copper (II) concentrations as given by Equation 5, and the black line (R^2 = 0.89) is the best fit of Equation 6 to the data, which assumes that an additional process is also controlling the change in the HO_2 uptake coefficient. Experiments were performed at RH = 72 ± 4 % and T = 293 ± 2 K. The error bars represent two standard deviations of the propagated error in the gradient of the k' against surface area graphs. See text for details.

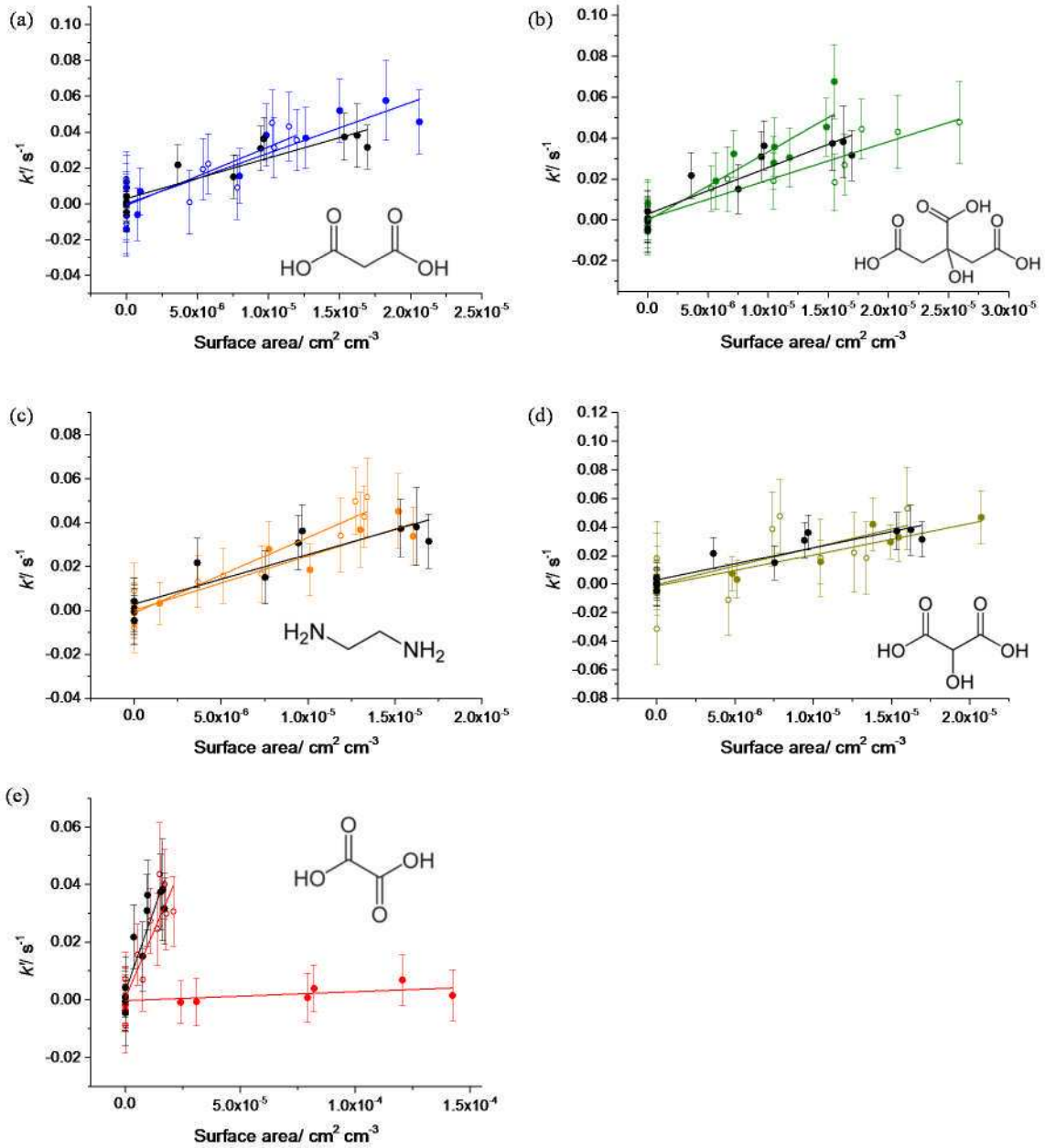

Figure 7. The pseudo-first order rate constants as a function of aerosol surface area for copper (II) doped ammonium sulfate aerosols (black, shown in all panels) and with (a) malonic acid (blue), (b) citric acid (green), (c) 1,2 diaminoethane (orange), (d) tartronic acid (dark yellow) and (e) oxalic acid (red) added. The open coloured symbols represent a 2:1 molar ratio of the organic to the copper and the closed coloured symbols represent a 10:1 molar ratio of the organic to the copper. All experiments were performed at RH = 60 ± 3 % and T = 293 ± 2 K. The error bars represent one standard deviation.

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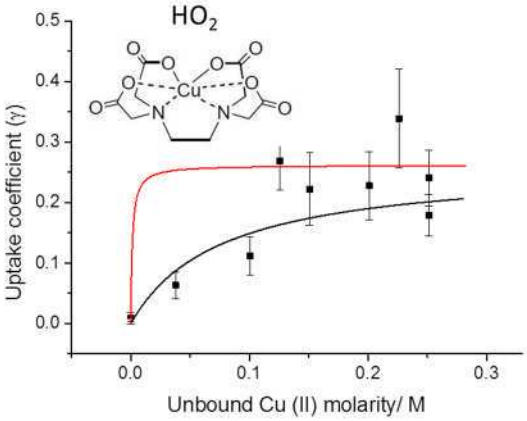
Table of Contents Image


HO2
Cu
N
N
O
Uptake coefficient (γ)
0.0
0.1
0.2
0.3
0.4
0.5
Unbound Cu (II) molarity/ M