

**Journal: ACP**

**Title: Size Dependent Chemical Ageing of Oleic Acid Aerosol Under Dry and Humidified Conditions**

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Dear Editor,

Error bars have now been added to both figures 9 and 10. Whilst calculating the error bars on figure 9 it was noticed that the wrong data had been graphed in the previous response to reviewers and the quoted gamma was also wrong. We apologize for this mistake which has now been rectified.

The appropriate data set shows some difference in the derived gamma values between the humid and the dry runs. The calculated gammas are as follows:  $\gamma_{\text{dry}} = 3.86 \pm 0.54 \times 10^{-4}$ ,  $\gamma_{\text{wet}} = 2.40 \pm 0.36 \times 10^{-4}$ , and the value when both the dry and wet data are combined is  $\gamma_{\text{combined}} = 3.13 \pm 1.49 \times 10^{-4}$ , where the stated errors are  $2\times$  the standard error of the mean. Since only 3 measurements were made under both dry and wet conditions the confidence limits for the combined data set is low, so we choose to show the confidence prediction limits for the combined data set in Figure 9. The new results have not significantly changed our conclusions. The kinetics section has been amended to reflect these changes and is reproduced below. Changes have been highlighted by underlining.

We have also taken on the following editorial comments: “Please make sure to state somewhere in the manuscript that if the reaction occurs at or near the surface, the uptake coefficient remains the same, while the degradation rate of OL is size dependent. You could cite Steimer et al., ACP, 2014, where the math of this has been explicitly outlined. In turn, the size dependent degradation then also allows to draw the conclusion about the kinetic regime (surface reaction or reaction-diffusion limitation), you could cite Berkemeier et al., ACP, 2013, for the definitions and terminology.”

In the kinetics section we now state the following – “The observed kinetics are what we expect if the initial reaction between OL and O<sub>3</sub> occurs at or near the surface. Steimer et al. (2016) provide detailed mathematical analysis showing for this reaction scenario the degradation rate of OL is size dependent but the uptake coefficient remains the same. It follows that the kinetics of the ozonolysis of OL is surface limited rather than reaction diffusion limited, detailed discussion of different kinetic regimes are provided in Berkemeier et al (2013).”

### **3.11 Kinetics of Oleic acid ozonolysis and product formation**

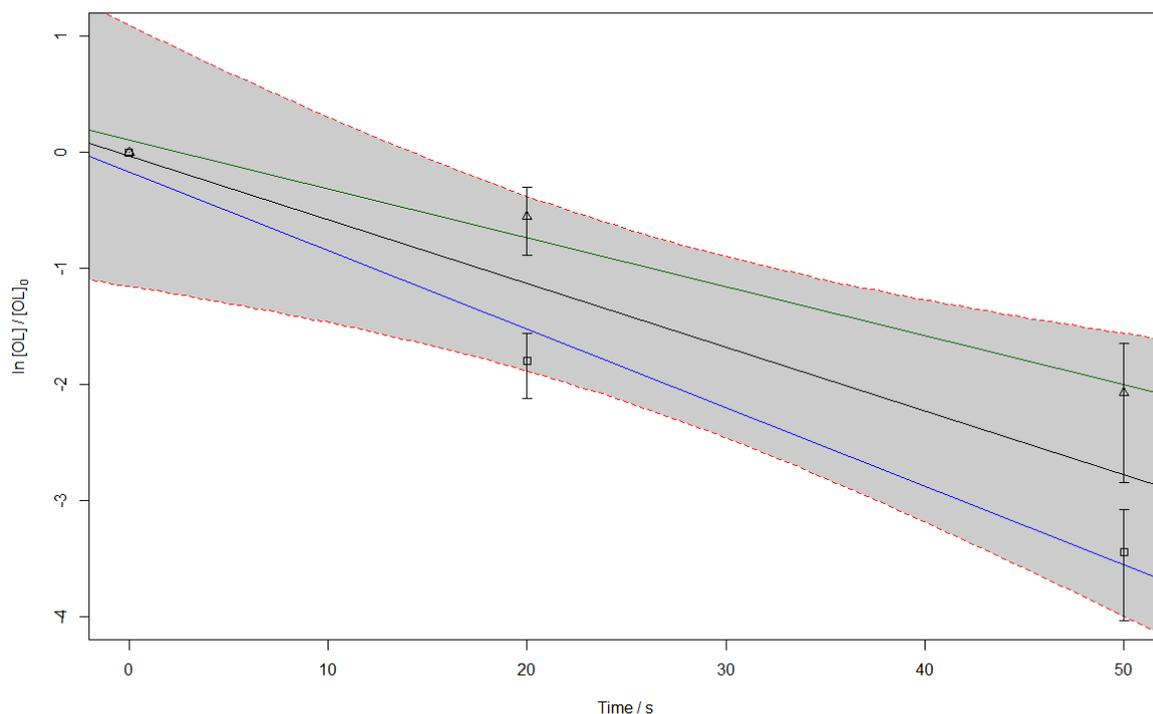
The kinetics of the ozonolysis of a near-monodisperse sized ensemble of oleic acid particles in the size range of 0.4-0.5  $\mu\text{m}$  with a mean diameter of 0.48  $\mu\text{m}$  was investigated. Through the use of 3 different sized aerosol flow tubes (AFT), but with otherwise identical conditions to the experimental setup detailed previously, the interaction time between ozone and oleic acid particles could be obtained at 20, 50 and 135 s. The longest time was the same as that used in the product distribution study shown in Figures 7 and 8. In the absence of O<sub>3</sub> the effective interaction time is zero. We observed that the concentration of oleic acid was negligible at the longest interaction time (135 s) and

hence the kinetics could only be followed in the time range of 0-50 s. The kinetics of the loss of OL was measured under both dry (0.5% RH) and humidified (65% RH) conditions. The kinetics of oleic acid loss appears to be a little faster under dry conditions compared to humid conditions. This is surprising since oleic acid is only marginally hygroscopic and any water that is available will likely partition to the hygroscopic region of the molecule around the carboxylic acid functional group and not the lipophilic C=C double bond where the ozonolysis occurs.

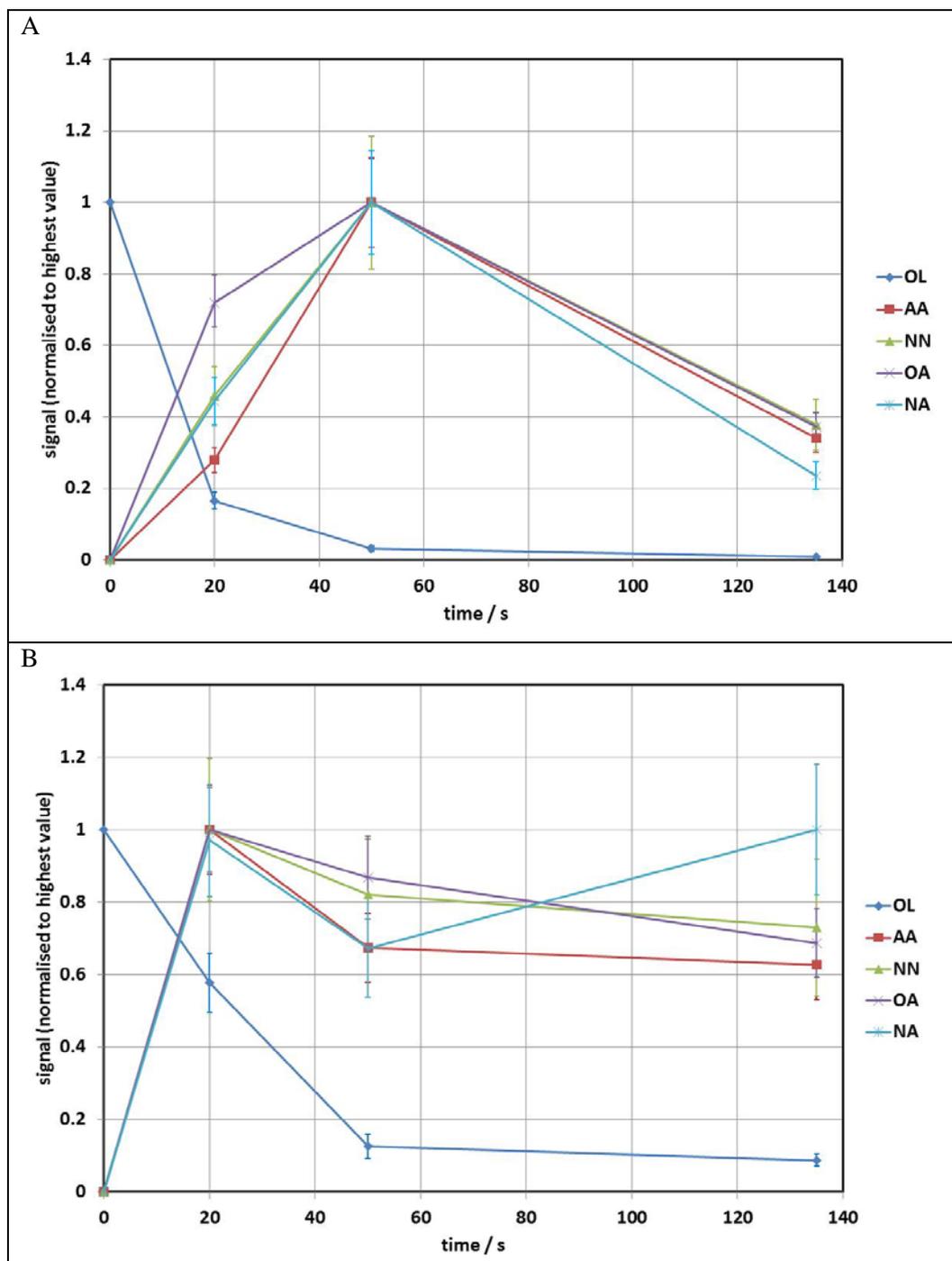
The measured data, for both the dry and humid runs, show a linear relationship between the plot of  $\ln\{S(\text{OL})/S(\text{OL}_0)\}$  versus interaction time, where  $S(\text{OL})$  is the oleic acid signal, as shown in figure 9 below. This is consistent with surface limited reaction, as described by Case 3 kinetics initially proposed by Hearn et al. (2005). Using the same approach as Hearn et al. (2005), using the Case 3 kinetics approach, to derive gamma uptake coefficients ( $\gamma$ ), we obtain  $\gamma_{\text{dry}} = 3.86 \pm 0.54 \times 10^{-4}$ ,  $\gamma_{\text{wet}} = 2.40 \pm 0.36 \times 10^{-4}$ , and the value when both the dry and wet data are combined is  $\gamma_{\text{combined}} = 3.13 \pm 1.49 \times 10^{-4}$ , where the stated errors are  $2\times$  the standard error of the mean. These values are similar to previous measurements of  $\gamma$ , e.g. Hearn and Smith (2004), Moise and Rudich (2002), Hearn et al (2005), Thornberry and Abbatt (2004), Ziemann (2005), Knopf et al. (2005). The observed kinetics is what we expect if the initial reaction between OL and  $\text{O}_3$  occurs at or near the surface. Steimer et al. (2016) provide detailed mathematical analysis showing, for this reaction scenario, the degradation rate of OL is size dependent but the uptake coefficient remains the same. It follows that the kinetics of the ozonolysis of OL is surface limited rather than reaction diffusion limited, detailed discussion of different kinetic regimes are provided in Berkemeier et al (2013).

In addition to the oleic acid reactive decay kinetics, we also observed the time dependent formation of the four major first generation reaction products nonanoic acid (NA), azelaic acid (AA), nonanal (NN) and oxononanoic acid (ON), see Figure 10. The high molecular weight (HMW) products were not observable in these experimental runs which are consistent with the low levels observed in figures 7 and 8 in the 0.3-0.5  $\mu\text{m}$  size bin. It is noted that low levels of HMW products were observed in the

product distribution study but longer averaging times were used. It is clear that whilst the kinetics of oleic acid loss is very similar under both dry and humidified conditions, there are obvious differences in the formation kinetics of the four major first generation reaction products. In particular, under dry conditions the reaction products form more promptly, and once formed stay at relatively similar concentrations. Under humidified conditions the formation of the peak concentration of the products is slower but also their subsequent loss is more substantial. The kinetic data does not provide any definitive mechanistic understanding. However, these results are consistent with the hypothesis that water can act as a reactant with the CI thereby reducing the amount of secondary chemistry observed between OL and the primary reaction products, hence the more stable product distribution after the initial ozonolysis step.



**Figure 9.** Reactive decay of oleic acid as a function of time for particles in the size range 0.4-0.5  $\mu\text{m}$  (mean diameter = 0.48  $\mu\text{m}$ ). Square symbols = measurements under dry conditions (RH = 0.5%), triangle symbols = measurements under humid conditions (RH = 65%), black line = linear fit of combined dry and humid data, blue line = linear fit of dry data set, green line = linear fit of humid data set, grey shading is the confidence limits for the linear fit to the combined data set at the 95% confidence limits for prediction. Error bars on the individual data points are  $2\times$  the standard error of the mean.



**Figure 10.** Time dependent signals of oleic acid and the four major first generation ozonolysis products. Graph A was obtained under dry conditions (RH = 0.5%) and B was obtained under wet conditions (RH = 65%). To aid ease of comparison of the different time series, the signals for all investigated species have been normalized relative to the peak signal achieved by the species investigated. Error bars are 1× the standard error of the mean.