

Molecular-level measurement and modelling of heterogeneous chemistry in organic aerosols

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Organic compounds are a dominant component of particles in the lower atmosphere. It has become evident in recent years that aerosols and cloud droplets are not merely reservoirs for organic molecules but also the site of complex reactions¹. This study aims to better characterise particle-phase organic chemistry, which is currently poorly understood.

In particular, the following questions are addressed:

1. What are the timescales for different particle-phase reactions?
2. How does aerosol chemical composition influence reactivity?

We combine here novel mass spectrometry (MS) measurements and a detailed physical chemistry model:

- Extractive Electrospray Ionisation (EESI) MS, demonstrated by Gallimore and Kalberer², is used here to obtain highly time-resolved measurements of aerosol chemical composition. The technique involves directing particles into an electrospray which gently dissolves and ionises the aerosol analytes. A major advantage is that molecular ions are produced – this allows the monitoring of individual organic components.

- The time series of individual components are interpreted using an aerosol chemistry model based on Griffiths et al. (2009). The model includes explicit physically-based descriptions of accommodation, diffusion, reaction and evaporation for each species. By constraining the model using the MS data, parameters such as reaction rate constants and uptake coefficients can be derived.

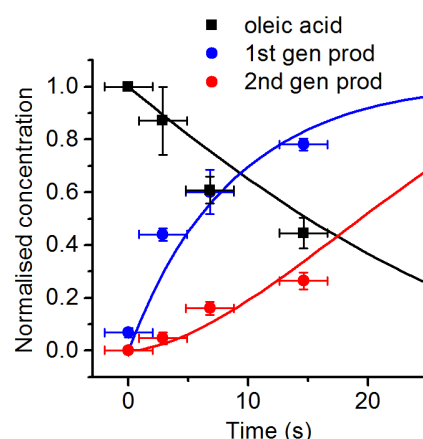


Figure 1: Measured (markers) and modelled (lines) concentrations of oleic acid and reactions products during the heterogeneous oxidation of oleic acid aerosol with ozone.

A proof-of-principle study involving the ozonolysis of oleic acid aerosol will be discussed (Figure 1) which provides insight into the relative rates of particle-phase reactions, centred around the fate of Criegee intermediates (CIs) formed from the initial cycloaddition of ozone. The evidence from online measurements and modelling suggest that a number of oligomeric products are relatively stable, and there is a particular preference for forming secondary ozonides via CI reactions with carbonyls. Preliminary results from a newly-commissioned atmospheric aerosol chamber will also be discussed.

References

- (1) Ziemann, P.J. and Atkinson, R., *Chem. Soc. Rev.*, 41, 6582-6605, 2012.
- (2) Gallimore, P.J. and Kalberer, M., *Environ. Sci. Technol.*, 47, 7324-31, 2013.
- (3) Griffiths, P.T. et al., *J. Phys. Chem. A*, 113, 5082-90, 2009.