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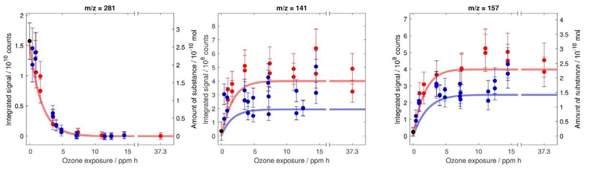

Electrodynamic balance–mass spectrometry reveals impact of oxidant concentration on product composition in the ozonolysis of oleic acid

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Often laboratory experiments studying aerosol aging are carried out in flow tubes or reaction chambers with limitations on the lifetime of the aerosol particles. Therefore, experimental conditions in these experiments deliberately deviate from atmospheric conditions in that short reaction times are compensated with high reactant concentrations. It is simply assumed that a constant reactant exposure (product of reactant concentration and time) leads to the same experimental outcome.

The application of electrodynamic balance–mass spectrometry of single particles allows the validity of this assumption to be investigated, since it provides information on the molecular composition of aerosol particles for a wide range of reaction durations under well-defined oxidation conditions. Here, we demonstrate the capabilities of a new setup on levitated oleic acid droplets reacting with ozone at mixing ratios of 0.2 and 15 ppm, i.e. spanning almost two orders of magnitude in ozone concentration,[Ox]. We show that the reactive removal of oleic acid can be accurately expressed as a function of ozone exposure [Ox] x time, whereas the product concentrations depend on [Ox] and time independently [1]. This can be seen in Fig. 1, which shows concentration versus ozone exposure of the mother ion of oleic acid at m/z=281 and two product ions (m/z=141 and m/z=157) for experiments with two substantially different ozone concentrations.

As the underlying reason for the breakdown of the exposure metric, we suggest a competition between evaporation of volatile first-generation products and their accretion reactions with reactive Criegee intermediates, converting them into low-volatility dimers and oligomers. Kinetic modeling using the aerosol process model KM-SUB supports this hypothesis. KM-SUB explicitly resolves the competition between evaporation and secondary chemistry as a function of the experimental timescale and ozone mixing ratio. The lines in Fig. 1 show the predictions of the model, reproducing the final product distributions successfully.

[1] Müller, Mishra, Berkemeier, Peter & Krieger (2023), *PCCP* 24, 27086-27104.