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### **Supplementary Information**

#### **Materials & Methods**

#### Particle generation and size selection

Particles were generated by heating reservoirs of pure oleic acid and pure myristic acid to 100-150°C to generate vapors. The reservoirs are bends in  $\frac{1}{2}$ " o.d. glass tubing wrapped with heating rope, and they are joined to make a continuous glass piece in the shape of a "Y." The vapors were swept out with 100 standard cubic centimeters per minute (sccm) of N<sub>2</sub>, mixed together at ~350°C and allowed to cool to room temperature generating a polydisperse distribution of particle sizes. The polydisperse aerosol was then sent into an electrostatic classifier (TSI model 3080) where particles were selected by their mobility diameter. Particles can have one, two, or three charges on them leading to the possibility of three different sizes. However, the polydisperse size distribution going into the classifier was narrow enough that the contribution from double or triply charged particles was less than 1% of the mass weighted signal as determined by an aerodynamic particle sizer (TSI model 3321).

To ensure that internally mixed particles were generated, the mass spectrometer signal was measured as a function of particle size with the mixing region hot (~350°C) and cold (20°C). The same relative mass spectrometer signal was measured for oleic acid and myristic acid at all particle sizes when the mixing region was hot; when the mixing region was cold separate size distributions were measured for myristic acid and oleic acid signals indicating the presence of externally mixed particles. Additionally, myristic acid is not expected to react readily with ozone but does react with products from the ozonolysis of oleic acid (Criegee intermediates), and the decrease in myristic acid signal as a function of oleic acid ozonolysis indicates that the particles are internally mixed.

It is conceivable that the particles were created with a "core-shell," or coated particle, morphology. These particles would contain a solid alkanoic acid core surrounded by a liquid solution consisting of mostly oleic acid. Such a particle morphology could complicate the interpretation of the decay data, though we can rule out this possibility by monitoring the loss of the myristic acid, as well. The myristic acid does not react with ozone because it does not have a double bond, but it does react with

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the so-called Criegee intermediates formed from the reaction of ozone with oleic acid.<sup>1</sup> In a coated particle, these secondary reactions would take place in the liquid coating but not in the core where there is no oleic acid. Consequently, the extent of reaction of the myristic acid will be limited to the amount that is soluble in the oleic acid. For many of our mixed particles we observed a much larger reaction of the myristic acid than can be explained by this coated particle morphology. Such a large difference is inconsistent with a coated particle morphology but can be explained by a particle containing many small solid myristic acid domains surrounded by the OA/MA solution. In that case, the surface area / volume ratio for the solid is much larger, and the Criegee intermediates will be much more likely to react with the myristic acid.

### Flow tube reaction and particle detection

A nitrogen flow (2000 sccm) containing ozone ( $\sim 10^{-4}$  atm = 2.5 x  $10^{15}$  molecules/cm<sup>3</sup>) is introduced at the rear of a jacketed flowtube, and the monodisperse particle flow (200 sccm) is injected into the reactor through a meter-long <sup>1</sup>/<sub>4</sub> in. o.d. glass injector. The laminar flow (Re ~ 60) does not greatly disturb the particle flow, and particles remain on-axis for the length of the flow tube as determined by visual inspection of scattered laser light (532 nm) and the constant mass spectrometer signal as the injector is pulled back in the absence of a reaction. This setup allows a variable gas-particle reaction time of 0 to 6 seconds. The particles were then sampled through a heated glass capillary and the resulting vapor was chemically ionized by proton transfer from protonated water clusters ((H<sub>2</sub>O)<sub>2</sub>H<sup>+</sup>). Ion generation via a radioactive polonium source (Po, NRD, Inc.) and detection with a quadrupole mass spectrometer (ABB Extrel, location) were performed as described previously.<sup>2</sup>

### Mass spectrometer detection sensitivity

To measure the relative detection sensitivities of the components of the mixtures, internally mixed aerosols were generated by making a known mixture and nebulizing the heated mixture into a flask. Polydisperse particles were then swept out of the flask with a flow of nitrogen (10-20 sccm) and sampled into the Aerosol CIMS. The relative detection sensitivities measured in this way were used to determine the composition of

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the particles generated via homogenous nucleation. The relative sensitivities were routinely  $1.00 (\pm 0.15)$  indicating similar sensitivities to oleic acid and myristic acid.

## FTIR Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) measurements were made with a benchtop Bruker Vector 22 spectrometer. A polydisperse particle size distribution (mass-weighted geometric mean = 950 nm, geometric standard deviation = 1.40) was generated by nebulizing a heated solution of the pure organic liquids. Particles were then stored in the 10 cm path length absorption cell with NaCl windows. Scans were conducted with the maximum resolution ( $1 \text{ cm}^{-1}$ ), and 64 scans were averaged for each spectrum.

# Chemicals

Gases were purchased from National Welders with the following purities:  $N_2$  (99.99%) and  $O_2$  (99% through polonium, 99.99% for ozone generation). Ozone was generated and stored as described previously. Oleic acid (90%) and myristic acid (99%), were purchased from Sigma Aldrich and used without further purification. Control experiments with higher purity oleic acid (99+%) confirmed that use of the nominally less pure (90%) sample did not affect the supercooling or reactivity measurements.

# REFERENCES

1. P. S. Bailey, *Ozonation in Organic Chemistry*, Academic Press, New York, 1978, Vol. 1.

2. J. D. Hearn and G. D. Smith, *Anal. Chem.*, 2004, **76**, 2820.