

Exploring the Influence of Particle Phase in the Ozonolysis of Oleic and Elaidic Acid

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Abstract

Aerosol particles in the atmosphere undergo heterogeneous transformations due to interactions with various gas-phase oxidants such as ozone. While it is known that these reactions are significantly affected by the phase state of the particle, a direct comparison between the reaction kinetics and product distributions for the same reactive process occurring in the different phases remains elusive. This study uses single particle levitation and flow-tube methods to measure and compare the ozonolysis of particles containing oleic acid and its *trans* isomer elaidic acid in liquid, supercooled liquid, and solid states. We measure their evolving size, optical properties, phase, and chemical composition during reaction. Both primary reactions and secondary chemistry were explored, along with the influence of particle phase state on reaction kinetics and product formation. Notably, we directly compare the reaction kinetics of supercooled liquid elaidic acid particles with liquid oleic acid particles, revealing similar uptake coefficients indicative of similar inherent reactivity of the C=C moiety. We go on to compare the kinetics of solid elaidic acid particles, formed due to solidification at room temperature and freezing at low temperature. We found a significant slowing in reaction kinetics that may be attributed to the phase of the particle and the influence of slowed molecular diffusion, supported by qualitative agreement with a multilayer kinetic model (KM-SUB). We further explore differences in the product distributions between particles exhibiting different phase states. These results provide important insights into how the chemical aging of ambient aerosol particles may be influenced by their physicochemical characteristics.

Keywords: Ozone, phase state, reactivity, diffusion

Graphical Abstract

Introduction

Aerosol particles are an important component of the atmosphere that have a variety of effects on the climate, air quality, visibility, and human health (Rosenfeld et al. 2014; Menon et al. 2008; Pöschl 2005; Mauderly and Chow 2008; Shiraiwa et al. 2017; Jacobson et al. 2000). They influence global radiation balance by scattering and absorbing incoming solar radiation (Srivastava, Dey, and Tripathi 2012; Lohmann and Feichter 2005), reduce the air quality of a region as a source of fine particles that can penetrate deep into the lungs (Richards 1988; C. A. Pope, Ezzati, and Dockery 2013), contribute to various health problems such as asthma and other respiratory illness (Mauderly and Chow 2008; Shiraiwa et al. 2017), and act as nuclei for cloud droplets leading to the formation of clouds and precipitation (Rosenfeld et al. 2014; Easterling 2000; McFiggans et al. 2006; McNeill 2017; R. Zhang et al. 2012). The relative magnitude and importance of these effects is determined by the coupled effects of parameters such as the size distribution, chemical composition, and physical properties of the constituent aerosol particles (Calvo et al. 2013; Pöschl and Shiraiwa 2015; Prather, Hatch, and Grassian 2008). The chemical composition is primarily determined by the source of the aerosol (Rogge et al. 1991; Simoneit 1989; Kolb and Worsnop 2012), but chemical reactions in the atmosphere change the composition leading to changes in both the physical properties and size distributions of aerosol particles (Krieger, Marcolli, and Reid 2012; Lambe et al. 2013; Lanz et al. 2010; Carson, Johnston, and Wexler 1997). There are several dominant mechanisms for aerosol chemistry to occur in the atmosphere, including photochemical reactions, heterogeneous reactions, and aqueous phase reactions due to the uptake of water (Li et al. 2019; Kroll et al. 2009; Chapleski et al. 2016; C. George et al. 2015; Hu et al. 2021). In this work, we focus on heterogeneous reactions involving ozone, an oxidant that is responsible for the degradation of unsaturated organic compounds.

Oxidative aging of aerosol particles containing unsaturated organic compounds, such as fatty acids, is a major chemical transformation that has been studied for many years due to its implications to atmospheric chemistry (I. J. George and Abbatt 2010; Thornberry and Abbatt 2004). It is a heterogeneous process that occurs when aerosol particles are exposed to reactive oxygen species, namely ozone, which leads to the formation of new compounds with different chemical properties. This alteration of chemical composition further leads to changes in their physical properties, such as size, morphology, volatility, hygroscopicity and optical properties,

which affects their role in environmental processes as well as how they subsequently interact with reactive species (Freedman 2020; Tang et al. 2019). Further, heterogeneous aging of aerosol particles contributes to the formation of diverse chemical functionalities, including dicarboxylic acids, ketones, aldehydes, keto-aldehydes, and carboxylic acids (Chapleski et al. 2016; Zhao et al. 2019; Q. Zhang et al. 2007). Understanding the chemical fate of aerosols containing unsaturated compounds through reactions with ozone assists in predicting and mitigating their environmental and health impacts. To achieve this, laboratory-based techniques, including single particle levitation and ensemble measurements using chambers and flow-tubes, have been relied upon for exploring aerosol chemistry (King, Thompson, and Ward 2004; Hearn and Smith 2004; Arata et al. 2019; Rissanen et al. 2015; Steimer et al. 2015; Berkemeier et al. 2021a). Efforts to measure the composition of these aerosol particles undergoing ozonolysis in both measurement techniques have relied mainly on mass spectrometry (Lanz et al. 2010; Morris et al. 2002; Jayne et al. 2000; Gallimore et al. 2017). Recent studies have shown that single particle measurements, which allow for the study of the molecular composition of super-micron levitated particles for an extended reaction timescale at low oxidant concentrations, may be an effective means of probing aerosol chemistry. Several articles have discussed the application of electrodynamic balance-mass spectrometry measurements of single particles to explore the ozonolysis of unsaturated organic particles (Müller et al. 2022; Müller, Stefanetti, and Krieger 2023; Willis, Rovelli, and Wilson 2020). These studies provide an alternative approach to the more established flow-tube techniques, which focus on sub-micron particles and often use high oxidant concentrations to measure reaction parameters, such as the uptake coefficient, across atmospherically relevant exposures (conc. $\times$ time). Although the uptake coefficient is formulated to be independent of size and oxidant concentration, previous studies have shown inverse size dependences in uptake coefficient, which may be attributed to diffusion limitations (G. D. Smith et al. 2002). Further, oxidant concentration and particle size may play a role in the reaction mechanism due to the influence of secondary chemistry and the rate of vapor partitioning for semi-volatile products (Kroll et al. 2009). Exploring both particle size and oxidant concentration motivates combined studies that utilize both sub-micron and super-micron methods to gain a more complete picture of aerosol chemistry.

The heterogeneous oxidation of oleic acid (mono-saturated omega-9 fatty acid) by ozone has been the subject of many experimental studies. Initially explored as a benchmark case in the

development of new experiments to probe aerosol chemistry (Morris et al. 2002), it has been the focus of many studies exploring the kinetics, reaction mechanisms and product branching ratios (Zahardis and Petrucci 2007; G. D. Smith et al. 2002; Gallimore et al. 2017; Berkemeier et al. 2021b). It is a significant component of indoor particulate matter due to its production during cooking (Rogge et al. 1991), and is a useful proxy for unsaturated organic compounds found in secondary organic aerosol. Elaidic acid, the *trans*-stereoisomer of oleic acid, is not a major component of atmospheric aerosol, but presents an opportunity to explore the influence of different phase states on the oxidation of particles while retaining the same fundamental chemical reactivity. The double bond of alkane chain in EA is *trans*, allowing EA molecules to remain straight and pack efficiently, resulting in a high melting point and a solid state at room temperature. In case of OA, the *cis* double bond leads to a kink and bend of the alkyl chain, inducing steric hindrance that prevents efficient packing of the molecules, leading to a lower melting point and a liquid state at room temperature. Recent measurements in an urban environment have compared the ozonolysis of oleic acid with elaidic acid, showing that the latter decays at 62% the rate of the former in real-world conditions, although the phase of the particles is not determined (Wang and Yu 2021). Laboratory studies exploring the reaction kinetics in different phase states reported that particles in which crystallization was induced by cooling below room temperature demonstrated reactivity decreased by a factor of 12 compared to supercooled particles of the same composition (D. Hearn and D. Smith 2005). However, similar studies using temperature to control the phase of oleic acid have shown that oxidation leads to melting and no effect on kinetics was observed (Hung and Tang 2010). Interest in how the phase state affects heterogeneous reactivity goes back to the initial observations of highly viscous phase states of organic aerosol particles (Virtanen et al. 2010; F. D. Pope et al. 2010). Both experiments and modelling studies have shown that high viscosity leads to slow diffusion, impacting reaction kinetics and the chemical evolution of aerosol particles (Shiraiwa et al. 2011; Houle, Wiegel, and Wilson 2018; Davies and Wilson 2015; Hearn and Smith 2005). It is important to note, however, that the influence of viscosity and diffusion limitations depends on the timescales of the process (Berkemeier et al. 2021b; Xu et al. 2022). At high oxidant concentrations, diffusion limitations would be expected to be more significant, as the timescales are reduced giving the system less time to diffusively mix. This points towards a potential oxidant concentration dependence that may couple with a size-dependence in determining the influence of diffusivity on the chemical evolution. Although oleic acid particles are expected to remain liquid,

and thus not exhibit diffusion limitations under ambient conditions, diffusion may still play a role at high oxidant concentrations or with very large particles. Furthermore, recent work by Xu et al. using optical microscopy has shown that ozonolysis can lead to the formation of a new phase morphology, which is a result of liquid-liquid phase separation (Xu et al. 2022). In the work of Milsom et al., the self-organization of oleic acid into nanostructured lamellar structures was reported to influence oxidation kinetics (Milsom, Squires, et al. 2022). The influence of phase on the ozonolysis of oleic acid has been explored by mixing oleic acid with stearic acid and lauric acid (Katrib et al. 2005; Knopf, Anthony, and Bertram 2005). While these studies show that embedding oleic acid in a solid or viscous matrix will lead to slower reactions, they do not directly explore how phase influences chemistry, as the composition of the particles is modified in order to vary the phase state.

In this work, we study and compare reactive transformations of oleic acid (OA, *cis*-isomer) and elaidic acid (EA, *trans*-isomer) due to heterogeneous ozonolysis, with an emphasis on characterizing the phase of particles during the reaction. This chemical system provides a unique opportunity to explore reactivity based on phase state for molecules that are very similar with little chemical perturbation to the system. We use both single particle and flow-tube methods, allowing a wider range of sizes and conditions to be explored and compared than either method alone. We use a linear quadrupole electrodynamic balance (LQ-EDB) coupled with mass spectrometry (MS) to precisely analyze single levitated particles undergoing ozonolysis in real-time. Using broadband light scattering, we can determine the size and optical properties of spherical particles, and gain insight into the phase morphology following a phase transition. Sequential sampling of particles from the LQ-EDB to the open-port sampling interface (OPSI) coupled with an Orbitrap mass spectrometer reveals the chemical composition as a function of time during the reaction (Kaur Kohli and Davies 2021; Kaur Kohli, Van Berkel, and Davies 2022). We explore different reaction conditions, such as RH and ozone concentration, to determine their effect on the ozonolysis kinetics and product distributions. By identifying the phase of the particles, we can unambiguously compare the influence of phase on the observed chemical changes in the particles. Further, we compare single particle measurements on super-micron particles with flow-tube measurements on sub-micron particles. Flow-tube measurements were also performed across a range of temperatures to explore the influence of phase changes induced by freezing/melting on the rate of ozonolysis.

Materials and Methods

Single Particle Levitation

Chemicals and Sample Preparation

The chemicals in this study were used as supplied without further purification. Measurements were performed on sample particles containing oleic acid (OA, Sigma, analytical standard, $\geq 99\%$ (GC)) and elaidic acid (EA, Sigma, $\geq 99\%$ (GC)) respectively. Both OA and EA samples were prepared as organic solutions at known concentrations using ethanol (Koptec, 200 Proof Pure Ethanol) and 1-propanal (Acros Organics, 99.5%, for analysis) respectively. Solution concentrations were chosen to yield levitated particles with a radius of around 5 μm , usually 5 to 10 g/L, with a starting size determined by the microdroplet dispenser. The bulk solutions were transferred to a microdroplet dispenser (Microfab MJ-ABP-01, 30 μm orifice) to generate particles with an initial diameter of approximately 50 μm in a burst mode with a known total number of droplets. The droplet dispenser was powered by a pulse generator, delivering pulses with widths between 20 and 50 μs with a voltage peak of up to 50 V.

To initiate ozonolysis, ozone was generated by passing a low flow of oxygen (20 sccm) through a quartz flow tube illuminated with a Hg lamp (Analytik Jena US, UVP Ozone Generator SOG-2) generating broadband UV light. The resulting flow was diluted with nitrogen (180 sccm) to make up a total flow of 200 sccm that was introduced into the LQ-EDB setup. Ozone concentrations were varied by changing the exposure area of UV lamp. Concentrations in the nitrogen flow introduced into the LQ-EDB were measured in a separate calibration process using an ozone monitor (2B Technologies, model 106-L). Dilution factors during the calibration process were determined and the reported ozone concentrations represent those exposed to levitated particles.

Particle Levitation and Environmental Control

A linear quadrupole electrodynamic balance (LQ-EDB) was used to levitate a stack of micrometer-sized particles for extended periods of time under controlled environmental conditions. Details on the principle and operation of LQ-EDB have been previously described (Kaur Kohli and Davies 2021; Price et al. 2022; Davies 2019). In brief, droplets were generated from organic solutions of the sample using a piezoelectric droplet dispenser and charged due to the presence of an induction

electrode (± 200 to 500 V) at the inlet to the LQ-EDB. The droplets become confined axially by the electrodynamic forces established within a vertically oriented quadrupole supplied with AC voltages (500 to 1000 V at 300 to 1000 Hz). A 532 nm laser (Thorlabs CPS532, 5 mW) was used to illuminate the levitated particles for their visual verification upon initial trapping and for positioning of the particles, and was disabled during measurements.

Solvent evaporation during the initial trapping step yielded sample particles confined in the electric fields. A counterbalance DC plate electrode with an applied voltage generated an electrostatic force to balance the forces on particles, including gravitational force and drag force due to gas flow. A continuous dry or humidified gas flow was introduced into the chamber to control the environmental conditions inside the LQ-EDB setup. The relative humidity (RH) inside the LQ-EDB was maintained by varying the ratio of dry and humidified nitrogen gas and a total flow of 200 sccm was typically used. A CMOS camera (Thorlabs DCC1545) was used to image and stabilize the position of the lowermost particle by varying DC voltage through a PID feedback loop, programmed using LabVIEW software. The LQ-EDB setup was coupled with Mie resonance spectroscopy allowing the lowermost particle to be probed in real-time to determine its size and real part of the complex refractive index. Compositional measurements of the particles were carried out by Orbitrap mass spectrometry (MS) that was coupled to the LQ-EDB using an open port sampling interface (OPSI) (Kaur Kohli, Van Berkel, and Davies 2022; Swanson, Worth, and Glish 2018; Van Berkel and Kertesz 2015). An overview of the whole experimental configuration is given in Figure 1.

Figure 1

Mie Resonance Spectroscopy

The lowermost particle in the stack was illuminated with a broadband red LED centered at 660 nm with a spectral width (FWHM) of 20 nm. Backscattered light from the particle was collected by optical fiber and delivered to a spectrophotometer (Ocean Insight HR4000). For spherical particles, a spectrum is obtained that is characterized by sharp resonance peaks associated with wavelengths that form morphology dependent resonances (MDRs) in the particle. The wavelength position of the MDRs is indicative of the size and refractive index of the particle. Using algorithms developed

by Preston and Reid, the experimental wavelength positions are compared to positions predicted by Mie theory for a dynamic library of size and refractive index combinations (Preston and Reid 2015; Price et al. 2020). A least-squares error minimization is performed, and the size is determined with an accuracy and precision of 5 nm and the RI is determined to within 0.001 to 0.005. Changes in the Mie resonance spectra, such as broadening and disappearance of peaks, is indicative of phase transitions, as discussed further in the results. Additionally, non-spherical particles cannot support MDR's, and backscattered spectra show only light reflected from the particle surface.

Compositional Analysis Using Mass Spectrometry

Compositional measurements were carried out by individually ejecting levitated particles from LQ-EDB into the open port sampling interface (OPSI) of a Q Exactive Focus Orbitrap Mass Spectrometer (Thermo Scientific). The OPSI acts as a sampling platform which connects LQ-EDB to the Heated Electrospray Ionization (H-ESI) probe of the mass spectrometer (MS). A detailed description of the operating principle, measurement method and data analysis for this procedure is discussed in our earlier works (Kaur Kohli, Van Berkel, and Davies 2022). In brief, the OPSI is continuously fed with a solvent mixture of methanol, doped with trace amounts trans-3-(3-pyridyl)acrylic acid (TPAA, Aldrich, 99% pure) to act as a standard, by a syringe pump (Chemxyx Inc., model Fusion 100T). The signal from the standard is analyzed to ensure ESI stability and account for any variations in the MS signal intensity over time. During a measurement, the lowermost particle is ejected from LQ-EDB, by pulsing the DC balancing voltage to zero for tens of milliseconds, prompting one particle to fall below the balancing electrode and out of the trap into the solvent reservoir at the top of OPSI. The particle dissolves in the solvent, and the analyte solution is drawn into the ESI probe due to the Venturi effect caused by reduced pressure region at probe tip. An electrospray is established at the spray tip and ions are generated according to standard ESI processes (Banerjee and Mazumdar 2012). The ESI nebulizing gas was nitrogen (technical grade, 99.97% pure) and a solvent flow (50 to 70 $\mu\text{L}/\text{min}$) was achieved based on nebulizer gas pressure at a set point of 30 psi. The MS was operated in negative ion mode with a typical scan range of 50 to 1000 m/z , a resolution of 35000 and maximum ion injection time of 100 ms. The resulting mass spectra were initially analyzed using Xcalibur 4.1 software (ThermoFisher Scientific) and extracted ion chronograms for the peaks of interest were exported

to data analysis software (MagicPlot Pro 2.8.2) for processing. The compositional abundance of species in each particle was determined in terms of the relative peak area of the respective ions with respect to its starting composition. Calibration measurements using OA, EA, and azelaic acid (AA) were performed to explore the relative ionization efficiencies of typical product compounds relative to the starting reactant.

Flow-Tube Measurements

Particle Generation and Characterization

A Pyrex tube was charged with small amounts of either liquid oleic acid (OA, Sigma-Aldrich Co., 99%) or solid elaidic acid (EA, Tokyo Chemical Industry Co., Ltd., >97%). For both samples, the tube was inserted into a furnace and heated to 105-110 °C, at which temperature the solid white elaidic acid crystals melted to a clear liquid and both EA and OA were partially vaporized. Dry nitrogen at a flow rate of 0.3 standard liters per minute (SLM) at room temperature was passed through the heated Pyrex tube and polydisperse particles were formed in the resulting flow by homogeneous nucleation. The flow was then passed through an annular charcoal denuder to remove residual organic from the gas phase and, as part of a precooling step, entered a loop of copper tubing submerged in the reservoir of the recirculating pump (Figure 2) to bring the particles to the desired temperature before passing on to the flow tube. Measurements are reported with and without this precooling step. Particle distributions were measured at the exit of the flow tube using a Scanning Mobility Particle Spectrometer (SMPS) consisting of a Differential Mobility Analyzer (3080, TSI Inc.) and a Condensation Particle Counter (3025A, TSI Inc.).

Flow Tube Reactor and Temperature Control

Particles and ozone were mixed in a cylindrical quartz flow tube reactor of fixed volume which at a typical total flow of 1.03 SLM results in a residence time of approximately 23 seconds. In addition to the particle-laden 0.3 SLM flow of N₂ from the nucleator oven, 0.5 SLM of pure N₂ and 0.2 SLM of dry O₂ (99.993%, Praxair) were introduced at the inlet of the reactor. Ozone was generated using a 0.1 SLM flow of O₂ into a corona discharge source (Ozone Services, Yanco Industries), after which the flow was diluted with 5 SLM of N₂ in a glass mixing cell. The concentration of O₃ in the flow was measured with a commercial ozone monitor (106M, 2B Technologies) at the exit of the mixing cell. The voltage on the corona discharge source was adjusted to achieve O₃ concentrations in the range 8 – 640 ppm. A rotameter (King Instruments) was used to deliver 30 sccm of the diluted O₃/O₂/N₂ flow into the flow tube reactor, where resulting O₃ concentrations range from 0.2 – 20 ppm. At the exit of the flow tube, the flow passed through an annular ozone scrubber packed with Carulite 200 catalyst, which terminated the ozonolysis reaction. The

temperature during the reaction was controlled by a chilled 50/50 ethylene glycol and water mixture fed through the outer jacket of the flow tube by a recirculating pump (VWR AD15R-30) with a thermostat setting between -20 and +20 °C.

Figure 2

APCI Mass Spectrometry

The reaction kinetics for ozonolysis measurements were monitored using a Velos Pro LTQ Mass Spectrometer (Thermo Scientific) fitted with an Atmospheric Pressure Chemical Ionization source, modified to take particle-laden gas flow through a ceramic inner bore, as described in Roveretto et. al (Roveretto et al. 2019). The outer ceramic inlet tube was heated to 180 °C to vaporize the aerosol particles prior to entering the ionization region. The flow into the inlet of the mass spectrometer included the N₂ sheath gas at a flow setting on the mass spectrometer of 1.8 (arbitrary units). The auxiliary gas flow was not used. Mass spectra were recorded with a typical scan range of 50 to 1000 m/z in negative ion mode. The discharge voltage was set to 1.5kV with a typical current of 8 µA. The analyzer region of the mass spectrometer was maintained with helium gas (99.998%, Airgas) at 40 psi. The decay of OA and EA were measured using the intensity of the $m/z = 281$ peak, corresponding to the [M-H]⁻ ion of each fatty acid. From the mass spectra, chronograms of the parent ions and product ions resulting from ozonolysis were extracted using XCalibur 4.1 and the Python-based “pymssfilereader” package (available at: github.com/frallain/pymssfilereader using Python 3.7.5).

Kinetic Analysis

To interpret and compare the ozonolysis kinetics across measurements, we apply a simple model to determine the effective rate constant and the uptake coefficient. The loss of OA or EA over time was fit to an exponential decay to give the rate constant according to:

$$\frac{[org]}{[org]_0} = e^{-k_{org}\langle O_3 \rangle_t t} \quad (1)$$

where k_{org} is the effective rate constant for the reaction of OA or EA (i.e. the organic), $\langle O_3 \rangle_t$ is the time-averaged ozone concentration, assumed to be equal to the measured ozone concentration, and t is time. Based on the analysis reported by Smith et al. (J. D. Smith et al. 2009), the uptake coefficient, defined as the ratio of the number of reactive decays of OA or EA molecules to the number of collisions with ozone molecules, may be formulated as:

$$\gamma_{O_3}^{org} = \frac{4k_{org}D\rho_{org}N_A}{6\bar{c}M_{org}} \quad (2)$$

where, $\gamma_{O_3}^{org}$ is the ozone uptake coefficient, k_{org} is the rate constant, D is the diameter of the particle, ρ_{org} is the density of reactant, N_A is Avogadro's number, $\bar{c}$ is the mean speed of ozone gas molecules and M_{org} is the molar mass of reactant molecules. This formulation allows for the surface-to-volume ratio effect on heterogeneous reactions to be normalized, however it does not account for size-dependent and time-dependent processes that may limit reactivity, such as diffusion limitations. It represents a useful tool for comparing across datasets, but care must be taken when interpreting absolute values. The uptake coefficients of super-micron particles using single particle measurements and sub-micron particles using flow-tube measurements are analyzed and compared in the subsequent sections.

Results and Discussion

A comparison between the ozonolysis of oleic acid (OA) and elaidic acid (EA) is presented to explore differences in their reactivity and phase behavior that arise from the different orientation of the carbon-carbon double bond. In bulk at room temperature, OA is a liquid while EA is a solid. Both species are soluble in organic solvents, such as ethanol and 1-propanol, which evaporates after levitation resulting in the formation of either liquid or solid particles. In general, levitated particles containing OA were observed to exist in liquid state, whereas EA attained both supercooled liquid and solid phase states on a pseudo-random basis. Ozonolysis measurements were performed to explore the influence of these phase states on reactivity and reaction mechanisms. Additional measurements using a temperature-controlled flow-tube were performed as a means of comparing phase states using temperature as a control.

In the following sections we break down the results into discussions of the size, refractive index, and phase morphology of OA and EA super-micron particles undergoing ozonolysis, with information derived from Mie resonance spectroscopy. We go on to discuss the evolving chemical composition using information derived from mass spectrometry. We then discuss measurements of sub-micron particles performed using a flow-tube setup, and finally discuss the influence of factors such as RH and ozone concentrations.

Evolution of the Physical State of Single Levitated Particles

Oleic Acid

The size and RI of liquid oleic acid particles were determined using Mie resonance spectroscopy and are shown in Figure 3A. The radius decreases as the reaction progresses and semi-volatile products are evolved into the gas phase, discussed in more detail later. In most experiments, this led to a corresponding increase in the RI as the ozonolysis proceeds, indicating the chemical composition is changing and leading to changes in the optical properties of the particle. In many datasets with OA, an abrupt change was observed in the RI, as seen in Figure 3A at around 500 s. This occurs as the Mie resonance spectra begins to degrade, shown in Figure 3B. A similar effect was noted, with different extent of spectral breakdown, in the majority of experiments on OA particles.

Figure 3

A likely explanation for degradation of the Mie resonance spectra is the occurrence of phase separation following the formation of low solubility organic species as the ozonolysis proceeds. This leads the particle to deviate from a well-mixed homogeneous composition and as a result, the Mie resonance spectrum becomes distorted. Possible morphologies that may form due to phase separation include a fully engulfed core shell-type morphology, in which the spherical structure is retained, and Mie resonance spectra appear undisturbed, a partially engulfed morphology, in which the particle deviates from a spherical structure and the spectra break down, and an emulsion-type morphology, where aggregates for product species form and scatter light either at the surface or in the bulk, leading to some distortion of the spectra. While these morphologies are more generally described in the context of liquid-liquid phase separation (LLPS), the formation of solid phases is possible and is indistinguishable from our measurements alone. Prior work has shown LLPS in oleic acid ozonolysis reactions, and microscopy images reported by Xu et al. indicate the formation of liquid islands at the surface, a form of aggregation due to the low solubility of the products in oleic acid (Xu et al. 2022). This is consistent with our observations, as the Mie resonance spectra retain the overall structure of a spherical particle, but with disruptions and deviations caused by the scattering of light by these islands. This leads to a degraded ability to accurately determine the size and the RI following phase separation.

Elaidic Acid

Although solid at room temperature in the bulk, levitated particles of EA typically exhibited a spherical morphology, indicative of a supercooled liquid phase state. In some cases, solid particles were formed, identified by the lack of regular scattering structure in the Mie resonance spectra. The formation of supercooled or solid EA particles appeared to be random and no dependence on any experimental parameters could be identified. Similar stochastic phase behavior has been observed in measurements of diacids under dry conditions (Price et al. 2022). In cases where the EA particles were formed as a supercooled liquid, Mie resonance spectroscopy was used to measure the size and RI, as with OA, shown in Figure 3C. Contrary to the liquid OA, these particles do not show any sign of abrupt changes in the scattering pattern or derived properties during the ozonolysis, which indicates that the particles do not undergo phase separation and, hence, retain a spherical homogeneous structure throughout the reaction (Figure 3D). Compared to OA, the straight chain EA molecules may be able to solubilize the reaction products to a greater extent than the bent OA molecules. Furthermore, the supercooled elaidic acid is already in a thermodynamically metastable state, indicating that some kinetic barrier exists to the nucleation of the solid phase that may also be present for the nucleation of a phase separated state.

During a typical experiment, up to ten droplets of the starting solution were trapped to produce a linear array of particles that are exposed to ozone. In around 1 in 10 experiments with EA, all particles in the array were formed with a solid phase state. Due to irregular shape of the solid phase, there was no regular Mie resonance scattering pattern observed which results in a lack of information on size and RI. For these particles, we rely on the mass spectrometry data and the assumption that their effective radius is equal to the radius of spherical particles created from the same starting solution. Further discussion of solid EA particles is presented in subsequent sections.

Chemical Evolution of Single Levitated Particles of Oleic and Elaidic Acid

The chemical evolution of particles as they react with ozone was determined using mass spectrometry. A linear sequence of initially similar-sized particles was trapped in the LQ-EDB, and ozone of a known concentration was introduced. Particles were ejected sequentially, over the course of several hours, and each yielded a snapshot of the composition at that point in the reaction. An example mass spectrum for OA before and after ozonolysis is shown in Figure 4A while the chronogram of the parent peak and primary products are shown in Figure 4B. The integrated area

corresponding to the chronogram signal for each peak of interest was determined for all particles in the experiment and plot as a function of exposure in subsequent figures.

Figure 4

Both OA and supercooled EA particles exhibit similar heterogeneous reaction rates with ozone, as reflected in the similar decay rate of the parent compounds as a function of exposure. In both cases, integrated peak intensity at m/z 281 was used to determine the amount of reactant in the unreacted particle at the start of the experiment, and the signal associated with subsequent particles undergoing ozonolysis is shown as a fraction of this starting value. While the peak area and intensity decreases for m/z 281, the signals for primary products emerge as ozonolysis proceeds (Figure 5A for OA and Figure 5B for EA). First-generation products are formed along with Criegee intermediate (CI) in the beginning due to reaction between OA (or EA) and ozone, after which these products further combine with CI, and dissociate or dimerize to result in the formation of second-generation products. The data for 187 and 171 m/z signals in Figure 5 represent the relative peak areas for the first-generation products azelaic acid (AA) and 9-oxononanoic acid (ONA), respectively. The MS signals for AA and ONA first increase and, for ONA, subsequently decrease as evaporation and further chemistry occurs during ozonolysis. A simple multi-component evaporation model (Kaur Kohli and Davies 2021), assuming ideal mixing of reactants and products, isothermal evaporation, and using the vapor pressures reported by Müller et al. (Müller et al. 2022), predicts timescales of evaporation for 10 μm diameter particles to be on the order of 100's seconds for ONA and on the order of 1000's seconds for AA. Thus, AA will likely accumulate in the particle to a greater extent than ONA, and the subsequent decrease in signal for ONA may be due to evaporation. Nonanoic acid and nonanal are both volatile on the timescale of these measurements and are not observed as products. The ionization efficiencies of measured products with respect to the parent compound vary, accounting for the different product signal intensity seen in Figure 5A and Figure 5B. For AA, the ionization efficiency with respect to EA was double that for OA. Thus, we expect to measure approximately double the amount of product signal in the EA system for the same amount of material. Considering this, our data shows no clear difference in the product formation between the two isomers.

Figure 5

An exponential fit of the form described by Equation 1 was applied to the OA and EA data to yield the solid lines shown in Figure 5. The exponential rate constant was used along with Equation 2 to determine the uptake coefficients. In a comparison across all experiments, there is a slightly higher uptake coefficient determined for elaidic acid, with $\gamma_{EA} = 8.6 \pm 1.1 \times 10^{-4}$ and $\gamma_{OA} = 7.1 \pm 1.7 \times 10^{-4}$, although there is agreement within the uncertainty in the standard deviations based on repeated trials at similar experimental conditions. The value for OA falls close to the expected literature values considering the size of the particles (Zahardis and Petrucci 2007). We break down these values further in a later section to explore more closely the influence of ozone concentration and RH on the measured values. Interestingly, even though OA was observed to undergo phase separation in most cases, the reaction kinetics were unaltered. This is likely due to the surface of the particle being insufficiently covered by product species to reduce the uptake and reaction of ozone. We further applied an exponential fit to the signal showing the formation of first-generation products of the form:

$$\frac{[prod]}{[X]_0} = A \cdot \{1 - e^{-k_{org}\langle O_3 \rangle_{t,t}}\} \cdot e^{-k_2\langle O_3 \rangle_{t,t}}$$

where A is a scaling factor to account for the reaction branching ratio, and k_2 is a reaction rate constant describing the loss of material due to secondary chemistry and/or evaporation. k_{org} was fixed at the value determined from the decay of the parent ($X = \text{OA or EA}$), while A and k_2 were allowed to vary. From the ratio $\frac{A_{ONA}}{A_{AA}}$ for OA averaged across three datasets at each ozone concentration under 0% RH, we observe a trend towards more ONA as the ozone concentration is decreased. At the lowest ozone concentration of 1.1 ppm, $\frac{A_{ONA}}{A_{AA}} = 4.0 \pm 0.9$, which falls to $\frac{A_{ONA}}{A_{AA}} = 2.9 \pm 0.2$ at 2.3 ppm and $\frac{A_{ONA}}{A_{AA}} = 2.4 \pm 0.2$ at 4.5 ppm. This shift in branching ratio reflects the complexity of the mechanism and is consistent with the work of Müller et al. in noting an ozone concentration dependence to the reaction pathways, owing to the importance of a variety of coupled factors such as evaporation and secondary chemistry (Müller et al. 2022). It should be noted, however, that the particle size range explored in the Müller work was $\sim 5 \times$ larger, thus the particles contained $\sim 125 \times$ more mass. A direct comparison between these results, and a full interpretation of our results, is not feasible without applying detailed kinetic models, as discussed

in the Conclusions, and goes beyond the intended scope of this work. Analysis of the EA product data reveals similar trends further confirming the similarity in product evolution between these two systems.

It should be noted that higher molecular mass products were observed in both OA and EA measurements (Figure 5C and 5D). Peaks at m/z 345, 359 and 375 were clearly associated with the particles and arise due to the formation of α -acyloxyalkyl hydroperoxides (AAHP). The peak at m/z 345 is ascribed to $C_{18}H_{34}O_6$ and is likely formed due to the reaction between CI and azelaic acid and/or nonanoic acid. The peak at m/z 359 is ascribed to $C_{18}H_{32}O_7$ and is formed by reaction between CI and ONA. Finally, the peak at m/z 375 is $C_{18}H_{32}O_8$ formed by reaction between CI and AA. The structures of these products are shown in Scheme 1 along with a simplified ozonolysis mechanism of ozonolysis. Detailed mechanisms are reported by Gallimore et al. (Gallimore et al. 2017). The relative abundance of these products is small compared to the first-generation products and a quantitative comparison is not possible due to the unknown ionization efficiencies.

Scheme 1

In the case of solid EA particles, much slower reaction kinetics were observed compared with the supercooled counterpart. Figure 6A shows the decay curves for a representative example of a solid particle compared to a supercooled liquid particle. The reaction between solid EA and ozone is drastically slower than ozonolysis of supercooled EA or liquid OA. An exponential decay curve was fit to the data to derive a rate constant, and the estimated particle size was used to determine the uptake coefficient. For measurements on solid elaidic acid particles in the LQ-EDB, we found $\gamma_{EA,s} = 3.2 \pm 1.6 \times 10^{-4}$, just under three times smaller than for the supercooled equivalent. The measured standard deviation in these measurements is greater due to the more limited number of observations. The quantitative analysis of the MS data for solid EA particles revealed that there were signals for the product ONA, while AA and other products were absent (Figure 6A inset). This may indicate that the reaction pathways for the solid particles may differ due to the limited mobility of products within the particle, prohibiting secondary chemistry. Furthermore, because first-generation products are formed at the surface, they can evaporate more easily and are thus

less clearly observed. It should be noted, however, that the low reaction extent brings challenges in reliably detecting product signals, and we hesitate to draw any conclusions from these data.

Figure 6

Influence of Temperature on Phase and Kinetics

Temperature-controlled flow-tube measurements were also performed as a complement to single particle measurements. As described in the Experimental Setup section, polydisperse aerosol of OA and EA were generated by homogeneous nucleation. In OA experiments, the mass-weighted mean diameter of the log-normal distribution lay between 154 and 167 nm, with a geometric standard deviation (σ_g) of 1.35. For EA, the mass-weighted mean of the particle distribution lies between 167 and 204 nm, with a σ_g of 1.37. Negative ion APCI-MS was used to measure the decay of each acid and the formation of products over ozone exposures up to 300 ppm s. As was observed in single particle measurements, the abundance of 1st generation products was significantly reduced in measurements on the solid particles. The insets in Figure 6B shows the measured signals arising from AA and ONA. The abundance of these products in frozen EA particles is less than for the same reaction extent on liquid EA particles at 20 °C, further indicating the chemistry is modified relative to the well-mixed case.

To explore the reaction kinetics, the exponential decay curves were analyzed in the same way as described earlier and reactive uptake coefficients were determined as a function of temperature, shown in Figure 7.

Figure 7

Comparing Flow-Tube and Levitated Particle Chemical Kinetics

A comparison between the data from the smaller flow-tube particles and the larger EDB particles reveals some interesting observations. First, the magnitude of the uptake coefficient is larger at room temperature for both OA and EA, indicating that the influence of diffusion limitations are reduced due to the decreased size of the particles, and the reaction occurs faster, as predicted by Smith et al. (G. D. Smith et al. 2002). Second, the uptake coefficient for OA particles is invariant with temperature, while for EA there is a steep decrease at between 260 and 270 K. The temperature at which slowing is observed likely coincides with the homogeneous freezing

temperature of the supercooled EA, and the resulting solid EA particles exhibit much smaller uptake coefficients that agree more closely with the measurements on solid EA particles in the LQ-EDB. Interestingly, when measurements were performed without a precooling step, the uptake coefficients measured were greater, although kinetic traces were not well-described by a single exponential as the decay appears to accelerate. We surmise that particles may form with a core-shell morphology that has a frozen shell and a liquid interior (i.e. they do not fully freeze) that would lead to slow initial reaction with a faster reaction at longer exposures, as seen in Figure 6B. The kinetic trend in data with precooling shows a single exponential decay with increasing ozone exposure, indicating particles were fully frozen and solid. When comparing against the larger uptake coefficients measured in the LQ-EDB, the different extent of slowing between the two measurements may be rationalized through either differences in the phase state, such as if EDB particles did not fully freeze and instead formed a slurry, or due to the additional slowing of the rate of diffusion in the flow-tube due to the low temperature. The decay trends in Figure 6 for both the solid LQ-EDB particles and the low temperature flow-tube measurements (with precooling) reveal a similar plateauing effect of the data, which is consistent with previous work on oxidation in viscous particles (Davies and Wilson 2015) and attributed to diffusion limitations.

To explore if slow diffusion can lead to the observed decay trends, we applied the KM-SUB model (Shiraiwa, Pfrang, and Pöschl 2010), generated using the MultilayerPy framework (Milsom, Lees, et al. 2022), and using the parameters reported by Shiraiwa et al. The model has been described in detail in several earlier papers. Briefly, KM-SUB is a multi-layer model of chemistry occurring in the surface and bulk regions of particles, with diffusion between layers to account for molecular transport. Previously, this model has shown that the ozonolysis of oleic acid is not limited by bulk diffusion and the bulk remains well mixed. We ran the model using the parameters previously determined for oleic acid and applied them to the elaidic acid data. Our simulations used 50 layers and no significant difference in output was observed when using either 20 or 100 layers. For measurements in the EDB and flow-tube where the particles were in a liquid form, the model agrees reasonably well although the parameters are not optimized for this system. When applying the model to the solid data, we manually varied the diffusion rate of all components (ozone, reactants, and generic products) and were able to achieve good agreement to the experimental data. In the case of the EDB data, diffusion coefficients were $10^2\times$ slower than for the liquid case, while

for the flow-tube, the diffusion coefficients were around $10^4 \times$ slower. The results of these simulations for solid EA particles in the LQ-EDB and frozen EA particles at -20°C (with-precooling) in the flowtube are included in Figure 6. While they demonstrate that slowed diffusion can qualitatively lead to the effects observed, we refrain from presenting quantitative data for the expected rates of diffusion due to the large uncertainties in other parameters, such as sticking coefficients and reaction rate constants, that might vary significantly with particle phase and temperature. A much more comprehensive study would be required to unambiguously identify the change in physical properties and chemistry that occur during the transition from liquid to solid particles.

Influence of Ozone Concentration and Relative Humidity

Over the course of these measurements, we explored the influence of varying ozone concentrations and relative humidity on the properties of liquid OA and supercooled EA particles. As previously discussed, the loss of liquid OA and supercooled EA over time was characterized with an exponential to give the rate constant, and an uptake coefficient was calculated. The values of uptake coefficients for varying ozone concentrations at 0% RH and varying RH at 2.3 ppm of ozone, respectively, are reported in Figure 8. Overall, we observe a higher value of the uptake coefficient for supercooled EA as compared to liquid OA, but neither system shows any measurable dependence on ozone concentration or RH. The latter observation is not surprising given the hydrophobic nature of the reactants and, while the products are expected to be more hydrophilic, the additional water present has no role in the decay of OA or EA. The influence of ozone concentration might be expected in systems that showed diffusion limitations, as the renewal of reactants at the interface cannot compete with the loss due to reaction when ozone concentrations are high. Due to the low concentrations of ozone and the slow rate of reaction, we expect minimal diffusion limitations, consistent with the constant uptake coefficient. Secondary reactions have been previously reported to vary with ozone concentration, however our measurements do not span a sufficiently large range to identify such trends (Müller et al. 2022).

Figure 8

Concluding Remarks

Single particle and flow-tube measurements were performed in this study to compare the ozonolysis kinetics and product distributions of two geometric isomers, oleic acid and elaidic acid, under a variety of laboratory conditions. The different physical states of oleic and elaidic acid under ambient conditions yield interesting experimental observations that are the focus of this work. The existence of elaidic acid in supercooled liquid state as single levitated particles resulted in similar ozonolysis kinetics as liquid oleic acid, which are significantly faster than the kinetics of solid elaidic acid particles. While it is known that high viscosity can lead to diffusion limitations that impede the rate of chemical reactions, experiments that show this impose other changes that may also influence reactivity, such as changes in the amount of water or the inclusion of additional compounds inside the particles. These results directly demonstrate the differences in reaction kinetics for the heterogeneous transformation of the same chemical system under different phase states. Furthermore, we confirm that liquid oleic acid particles react with ozone gas leading to the onset of phase separation. No changes in the ozonolysis kinetics were observed following phase separation, and the newly formed phase is likely a mixture of high-molecular weight products that are insoluble in liquid oleic acid, resulting in liquid-liquid phase separation, probably as inclusions, as observed by Mie resonance spectroscopy. There is no discernable difference in composition at the point of phase separation in oleic acid particles as compared to supercooled elaidic acid particles.

Flow-tube measurements using a temperature-controlled reactor were also performed, allowing for supercooled elaidic acid particles to be frozen to the solid state. These measurements agree with the single particle measurements, showing uptake coefficients for supercooled elaidic acid to be slightly higher than oleic acid, with a marked decrease at the temperature where homogeneous freezing occurs. Interestingly, the uptake coefficient was reduced to a lower value in the flow-tube measurements where pre-cooling was applied, with larger values observed without pre-cooling in the flow-tube and in the LQ-EDB measurements. We surmise this is due to the formation of a slurry in which the extent of solidification depends on the temperature and time. Additionally, the size dependence owing to diffusion rates in solid particles and those of intermediate viscosity may explain these differences (G. D. Smith et al. 2002; J. D. Smith et al. 2009).

Using an electrodynamic balance coupled with mass spectrometry, chemical transformations on super-micron single particles may be explored with extended timescales of levitation under reaction conditions that approach atmospherically relevant low-oxidant concentrations. Flow-tube measurements focus on sub-micron aerosol particles, in which the reaction timescales are shortened by utilizing higher concentrations of oxidants. Exposure of particles to ozone in both these techniques led to the formation of primary generation products which further undergo reactions with Criegee intermediates, resulting in the formation of second-generation products. A direct comparison reveals that the uptake coefficient is dependent on size, with sub-micron particles generated in flow tube have higher uptake coefficient value than single levitated super-micron particles. While the dependence we observe here differs from earlier work (G. D. Smith et al. 2002), this likely arises due to the different ozone concentrations, as reaction-diffusion effects will depend on both length and timescales. This work provides a comparison between these two common aerosol methods applied to the same chemical systems, demonstrating complementary information that may be obtained. Further, while oleic acid has been extensively studied in the literature, far fewer have investigated the impact of phase on its chemistry.

This work demonstrates that solid elaidic acid may be an effective proxy for oleic acid embedded in high viscosity media, allowing further study of the role of diffusion-limitations on chemical transformations. The uptake coefficient for elaidic acid reported by Wang and Yu (Wang and Yu 2021) in ambient particles fall in between those reported in this work for solid and liquid elaidic acid particles. This indicates that the phase state of ambient particles containing elaidic acid, and by extrapolation other high melting point organic compounds, may exist in a continuum between liquid and solid, complicating our understanding of heterogeneous reaction kinetics and raising the importance of developing *in-situ* probes of phase morphology when exploring heterogeneous reactions. Kinetic models that account for condensed phase diffusion have been applied to similar datasets. For example, the works of Berkemeier, Shiraiwa, Houle and co-workers have used a range of inductive and deductive methods to explore reaction-diffusion problems (Wiegel et al. 2015; Houle, Wiegel, and Wilson 2018; Berkemeier et al. 2021b; 2016; Shiraiwa, Pfrang, and Pöschl 2010). The application of such models to the present data, comparing oleic acid and elaidic acid, may allow a more rigorous exploration of the role of diffusion and particle morphology on the rate of ozonolysis. Qualitatively, using the KM-SUB model, we showed that slowed diffusion

can account for the observed differences between liquid and solid particles. However, owing to the large number of physical constants describing the processes controlling heterogeneous reactions, it is non-trivial to apply such models in the absence of additional physicochemical information, such as estimated changes in the rate of diffusion, sticking coefficients, and reaction rate constants (Berkemeier et al. 2023). Thus, while our data is shown to be consistent with slow diffusion influencing heterogeneous reactivity, a more comprehensive study would be required to quantitatively determine the effects.

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Figure 1: Schematic configuration of the ozonolysis setup including the linear quadrupole electrodynamic balance (LQ-EDB) coupled with mass spectrometer (MS) using open port sampling interface (OPSI) for studying ozonolysis on single levitated particles. A dry or humid flow of nitrogen with ozone generated from a photochemical ozone generator was introduced into the LQ-EDB for initiating heterogeneous transformation. A stack of 5 to 10 particles underwent ozonolysis at the same time, and the lowermost particle was probed in real-time using broadband spectroscopy and then ejected to the OPSI platform for sampling by mass spectrometry.

Figure 2: Flow-tube experimental apparatus showing the particle generation, ozone generation, temperature control using a recirculating pump and thermostatic bath, a DMA and CPC for characterizing particle size distributions, and the atmospheric pressure chemical ionization (APCI) source on the mass spectrometer. A full description of the apparatus is provided in the text.

Figure 3: (A) Size and RI evolution of liquid OA particles exposed to 2.3 ppm of O_3 under dry conditions. The circles correspond to the sequentially measured radius of all particles in the stack, and the crosses correspond to the RI of the particles. The accuracy of size is determined to be within 5 nm and the RI is within 0.001 to 0.005 for homogeneous and spherical particles. The shaded region indicates where phase separation occurs, with the spectra degrading and leading to much larger scatter in the size and RI. (B) Mie resonance spectra before and after ozonolysis of OA shows clear peaks indicative of a homogeneous spherical particle initially that becomes distorted following phase separation, consistent with the formation of surface islands due to product formation that interrupt the spherical cavity. (C) Size and RI evolution of supercooled liquid EA particles exposed to 2.3 ppm of O_3 under dry conditions. (D) Mie resonance spectra before and after ozonolysis of EA particles, showing a spherical homogeneous morphology is retained.

Figure 4: (A) Mass spectra of oleic acid particles with a diameter of $\sim 10 \mu m$ before and after ozonolysis (at an exposure of $\sim 3000 \text{ ppm.s}$) in the LQ-EDB. The black data represents the mass spectrum before the start of ozonolysis reaction whereas the gray data represents the mass spectrum after ozonolysis. Note that the y-axis is truncated for clarity and the full signal at $m/z = 281$ is on the order of 10^7 . (B) Mass chronograms show the time-dependent ion intensity of $[M-H]^+$ signals for a decrease in oleic acid reactant peaks (281 m/z) with simultaneous increase of first-generation product peaks, 9-oxononanoic acid ($m/z 171$) and azelaic acid ($m/z 187 \text{ m/z}$), on exposure to 2.3 ppm of ozone.

Figure 5: Normalized intensity of reactant and 1st generation products in OA (A) and supercooled EA (B) for particles with a starting diameter of $\sim 10 \mu m$ exposed to 4.1 ppm of ozone. The time evolution of high molecular weight products (see description in text) are shown in (C) and (D) for OA and EA, respectively. Note the x-axis reflects the ozone exposure in units of concentration (ppm) $\times$ time (s). The lines reflect exponential decay and product formations fits to the data as discussed in the text.

Figure 6: (A) A comparison of the decay of supercooled liquid EA particles compared to solid EA particles under the same reaction conditions in the LQ-EDB. The solid lines represent exponential fits while the dashed line represents model simulation using KM-SUB, as described in the text. The inset figure shows the signal for products AA (m/z

187) and ONA (m/z 171) for the solid particle. (B) A comparison of the decay of homogeneously frozen EA particles at $-20\text{ }^{\circ}\text{C}$ (with and without precooling) and supercooled liquid EA at $20\text{ }^{\circ}\text{C}$ in the flow-tube reactor. Inset plots show the signal for AA and ONA for $20\text{ }^{\circ}\text{C}$ and pre-cooled $-20\text{ }^{\circ}\text{C}$.

Figure 7: Uptake coefficients from temperature-controlled flow tube reactor studies. Solid circles correspond to measurements of oleic acid, and open shapes correspond to measurements of elaidic acid with (diamond) and without (circles) the precooling step described in the experimental section. Shaded horizontal regions show the LQ-EDB measurements for comparison, the vertical size of the bar indicating the uncertainty. We use the term “solid” here, although care should be taken with this description as discussed in the text.

Figure 8: (a) Comparison of uptake coefficients for liquid OA and supercooled EA undergoing ozonolysis as a measure of varying ozone concentrations under dry conditions. **(b)** Comparison of uptake coefficients for liquid OA and supercooled EA undergoing ozonolysis as a measure of varying relative humidity at 2.3 ppm of ozone. For both sets of measurements, liquid OA data is represented as red open circles and supercooled EA data is represented as green open diamonds. The error bars represent the standard deviations based on repeated trials at similar experimental conditions.

Scheme 1: Simplified ozonolysis mechanism, shown here for oleic acid, leading to the observed products.