

Chapter 8. Online field-induced droplet ionization mass spectrometry probes heterogeneous reaction chemistry at the air – droplet interface: soft-sampling the products of the oleic acid – ozone reaction from single droplets

8.1. Abstract

Mechanically suspended droplets undergo chemical reactions and field-induced droplet ionization – mass spectrometry (FIDI-MS) characterizes the reaction products. Droplets containing either 10 μM oleic acid or 100 μM oleoyl-L- α -lysophosphatidic acid, LPA (18:1), react with gas-phase ozone for a specified reaction time up to one minute. At the droplet surface, ozone reacts with the double bonds generating intermediate ozonides before forming aldehydes and organic acids. Following a specified reaction time, a high electric field is rapidly applied to induce FIDI, generating jets of highly charged progeny that are characterized by mass spectrometry. When sampled at multiple reaction times, the spectra show a successively increasing ratio between the products and reactants. Reactions between ozone and LPA produce species that unambiguously localize the position of the double bond along the hydrocarbon chain. These studies indicate that FIDI-MS is a viable technique for kinetic studies of heterogeneous reactions on microdroplets.

8.2. Letter

Single droplet mass spectrometry represents an ideal solution to the challenges presented by the analysis of microliters of sample and the on-line characterization of heterogeneous reaction chemistry occurring on individual droplets. Researchers consider the reaction of gas-phase ozone with oleic acid as a model system for heterogeneous reaction chemistry and its implications for atmospheric chemistry.¹⁻⁵ Scheme 8.1 summarizes the reaction and expected products from the ozonolysis of oleic acid droplets. Briefly, ozone adds across the oleic acid (**1**) double bond forming a primary ozonide (**2**). This ozonide dissociates to an aldehyde and an energetic Crigee intermediate. In the presence of inert solvents, the intermediate may transfer energy and recombine with the aldehyde forming a secondary ozonide (**3**).^{6,7} The secondary ozonide subsequently dissociates forming 9-oxononanoic acid (**4**), 1-nonanoic acid (**5**), azelaic acid (**6**), and nonanal (**7**).¹ The short (~10 nm) characteristic diffusion distance of ozone into oleic acid before reaction supports the model of a heterogeneous reaction at the air-droplet interface.^{4,5} This reaction is well-studied but questions remain regarding the partitioning of products and the relative yields from the ozonolysis in Scheme 8.1.¹

Recently our laboratory pioneered field-induced droplet ionization – mass spectrometry (FIDI-MS).⁸ In a critically high electric field, E_c^0 , given by eq (8.1), neutral droplets elongate parallel to the field, developing two opposing conical tips that emit jets of oppositely charged progeny droplets.⁹⁻¹¹

$$E_c^0 \approx \left(\frac{5.28\sigma}{8\pi\epsilon_0 r} \right)^{1/2} \quad (8.1)$$

This critical field is known as the Taylor limit, named for G. I. Taylor, where ϵ_0 is the permittivity of free space while r and σ are the droplet radius and surface tension, respectively. Using a constant stream of droplets generated by a vibrating orifice aerosol generator, we demonstrated that the charged progeny droplets are a viable source of gas-phase ions for mass analysis.⁸ Rapidly switched electric fields and synchronized visualization allowed us to characterize the dynamics of the FIDI process. The timescale of droplet elongation, tip formation, and progeny droplet generation slightly above E_c^0 is related to the timescale of the natural harmonic oscillations slightly below E_c^0 . Equation (8.2) approximates the timescale for FIDI, τ_{FIDI} , and is a function of bulk solution parameters including the density, ρ .¹²

$$\tau_{\text{FIDI}} = 2.3 \left(\frac{r^3 \rho}{\sigma} \right)^{1/2} \quad (8.2)$$

Understanding the critical field and the timescale for FIDI enables new applications of mass analysis to chemical reactions. For instance, droplets can serve as miniature reaction cells prior to FIDI-MS. During this time, suspended droplets may undergo heterogeneous reactions in an electric field-free environment whose products are mass analyzed when the electric field is rapidly applied. Such applications motivate the present study where gas-phase ozone reacts with unsaturated analyte molecules within the droplets.

Individual droplets are mechanically suspended between a switched high voltage electrode and the capillary inlet to a Finnigan LCQ Deca ion trap mass spectrometer as shown in Figure 8.1. Under the initial conditions, the capillary, tubing, and electrode are maintained at electrical ground. Reactant solutions manually fed through the tubing

establish a ~1 mm diameter droplet in an electric field-free environment. A UV pen-ray lamp generates ~30 ppm ozone in air that continually washes through the FIDI region. Heterogeneous reactions between ozone and solution-phase analytes occur for a time 0-60 s between the point the droplet is established and sampled by FIDI-MS. A high voltage pulse on the electrode applies a strong electric field to the droplet resulting in the ejection of jets of small, highly charged progeny droplets. The high voltage pulse establishes a $1.5 \times 10^6 \text{ V m}^{-1}$, ~5 ms field to achieve jetting and FIDI as required by eqs (8.1) and (8.2). After FIDI-MS, pushing additional solvent through the tubing causes the existing droplet to fall off and establishes a fresh droplet for reaction.

Figure 8.2 shows the negative ion FIDI-MS spectra for the reaction between 10 μm oleic acid in 90% DMF and 10% methanol with 30 ppm ozone delivered by 500 mL min^{-1} air. The singly deprotonated dimer at 563 m/z dominates the FIDI-MS spectrum of oleic acid in the absence of ozone (frame A). Upon exposure to ozone, the droplets react with the ozone for a variable length of time before FIDI-MS samples the contents of the droplets. Frames (B)-(E) show varying relative concentrations of the reactants (563 m/z) and the products after instantaneous (< 1 s), 5 s, 20 s, and 60 s, respectively. Reaction products include deprotonated azelaic acid (**6**), at 187 m/z, doubly hydrated azelaic acid at 223 m/z and an unknown cluster containing azelaic acid at 250 m/z. Collision-induced dissociation (CID) reactions of the 187 m/z ion are identical to the CID spectra from pure azelaic acid purchased from Sigma Aldrich. Low energy CID spectra of the 223 m/z and 250 m/z ions principally produce singly deprotonated azelaic acid indicating cluster parent ions. Deprotonated 9-oxononanoic acid (**4**), is principally observed at 453 m/z complexed to oleic acid. After 60 s, spectra show a small quantity of deprotonated 9-

oxononanoic acid at 171 m/z. Deprotonated nonanoic acid (**5**), is not observed as expected at 157 m/z. Peaks due to nonanal are not expected because negative ion soft-sampling produces poor signal from aldehydes and previous research shows nonanal partially partitioning into the vapor phase.⁵ Figure 8.2 demonstrates that mass sampling the droplet by FIDI-MS is a viable route to the kinetics of heterogeneous chemistry with a soft-sampling analysis. Ongoing studies seek to quantify rate constants for reactions sampled by FIDI-MS.

In addition to heterogeneous reaction kinetics, the reaction between ozone and solution-phase analytes and FIDI-MS characterization localizes carbon-carbon double bonds within a molecule. We verify this with the reaction between ozone and 100 μm oleoyl-L- α -lysophosphatidic acid, or LPA (18:1), in methanol. Scheme 8.2 shows LPA (18:1) (**8**), and the expected aldehyde (**9**), and acid (**10**), reaction products based on the FIDI-MS results for the oleic acid / ozone reaction. Figure 8.3A shows the negative ion FIDI-MS spectrum of LPA (18:1) in the absence of ozone. Primary peaks are due to deprotonated LPA (18:1) at 453 m/z, a deprotonated dimer at 871 m/z, a doubly deprotonated sodium-bound adduct at 893 m/z, and a deprotonated ester cleavage product at 153 m/z. Figure 8.3B shows the FIDI-MS spectrum for droplets exposed to ozone for 5 s. The strong peak at 325 m/z confirms the deprotonated aldehyde reaction product (**9**). Additionally, the deprotonated acid product (**10**), appears as a weak signal at 341 m/z in addition to a strong, unknown peak at 373 m/z.

Deprotonated reaction products at 325 m/z and 341 m/z respectively correspond to the formation of an aldehyde and an organic acid at the 9th carbon atom in the ester. This is indeed the location of the double bond in LPA (18:1) indicating that FIDI-MS

successfully localizes double bonds and characterizes the reaction products with a soft-sampling ionization method.

FIDI-MS allows for real-time monitoring of the reaction chemistry in single droplets. Such reactions may include environmental studies involving online characterization of the kinetics of heterogeneous reactions between gas-phase and solution-phase species, and solution-phase photoinitiated reactions whose products are sampled by FIDI-MS after a predetermined reaction time. The applications may also be extended to include the examination of free droplets suspended in an electrodynamic balance or acoustically levitated.

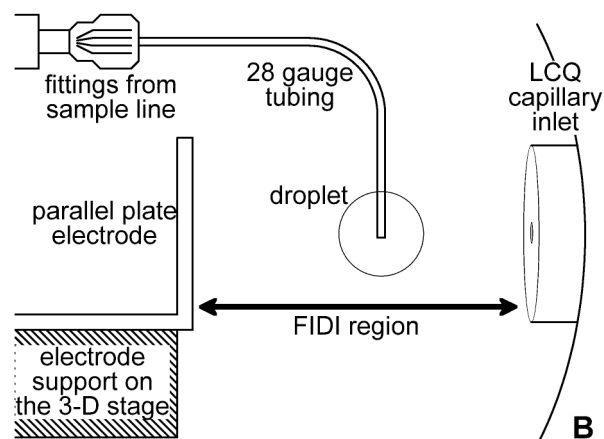
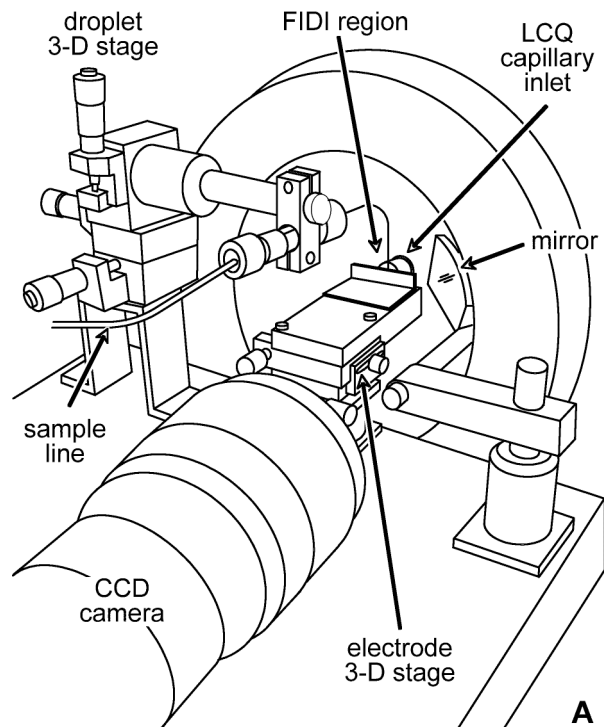


Figure 8.1. Schematic of the single droplet FIDI-MS apparatus (A) and the FIDI region (B). A droplet is mechanically suspended in the high field FIDI region defined by a parallel plate electrode and the LCQ capillary inlet. Independent three-dimensional translation stages align the droplet and the electrode. A CCD camera visualizes the FIDI region and the droplet is oriented such that the charged progeny jets are directed into the MS capillary for mass analysis.

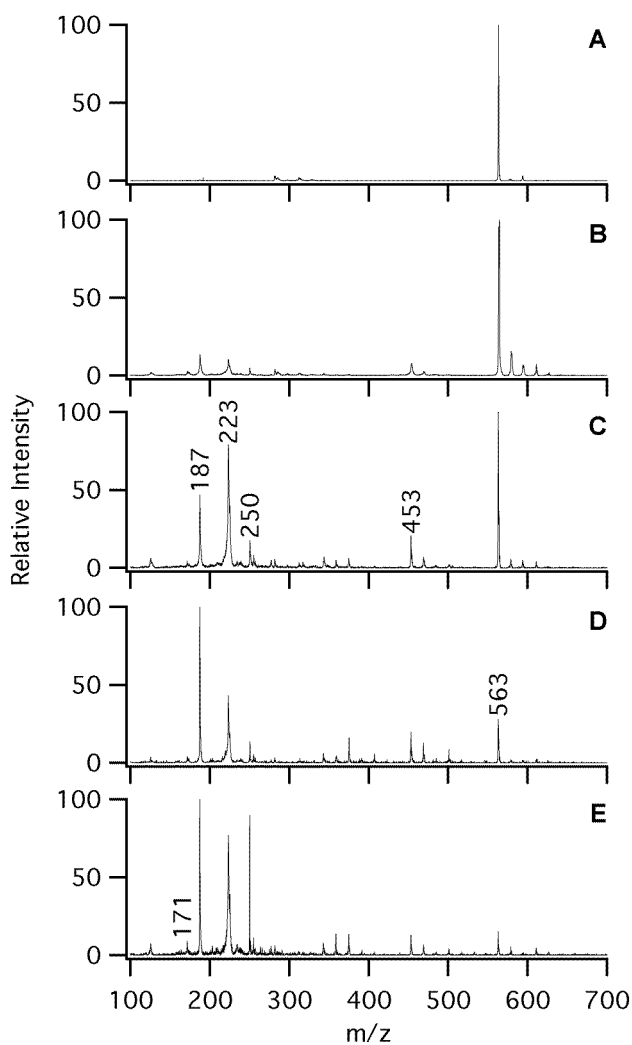


Figure 8.2. Oxidation of oleic acid by ozone as a function of time. In the absence of ozone, the negative ion FIDI-MS spectrum of oleic acid is dominated by the singly-deprotonated dimer peak at 563 m/z. Successive frames show reaction with (B) <1 s, (C) 5 s, (D) 20 s, (E) 60 s, exposures. Oxidation products are dominated by deprotonated azelaic acid at 187 m/z, doubly hydrated deprotonated azelaic acid at 223 m/z, an unknown cluster containing azelaic acid at 250 m/z, and a deprotonated oleic acid / azelaic acid cluster at 453 m/z.

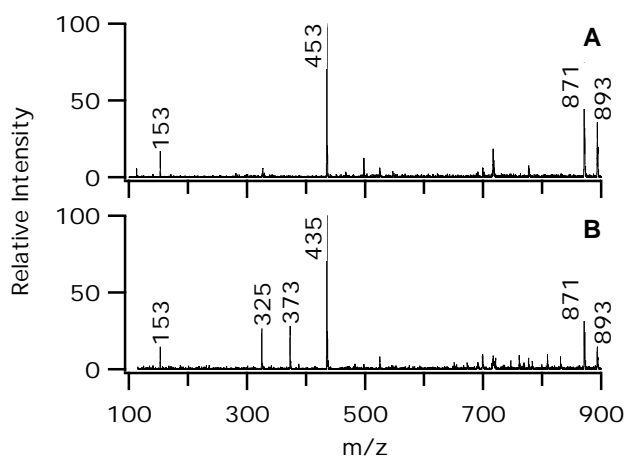
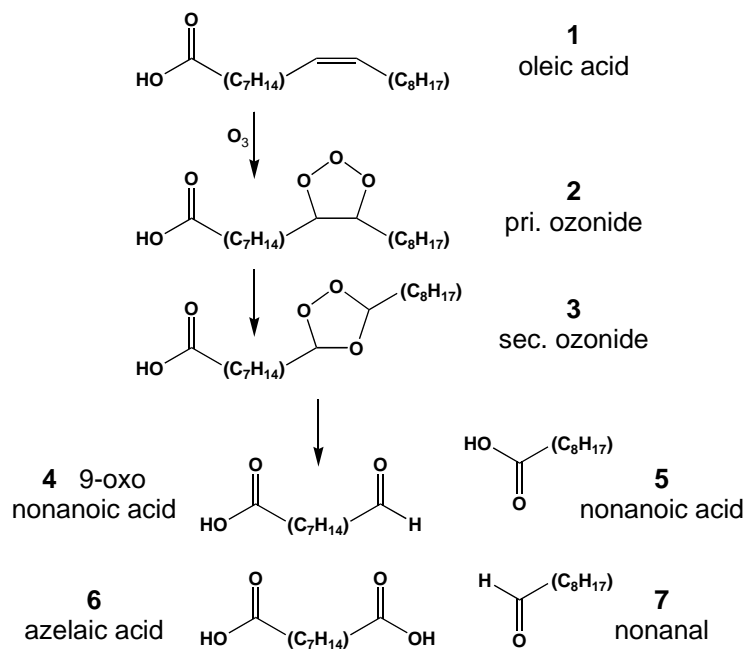
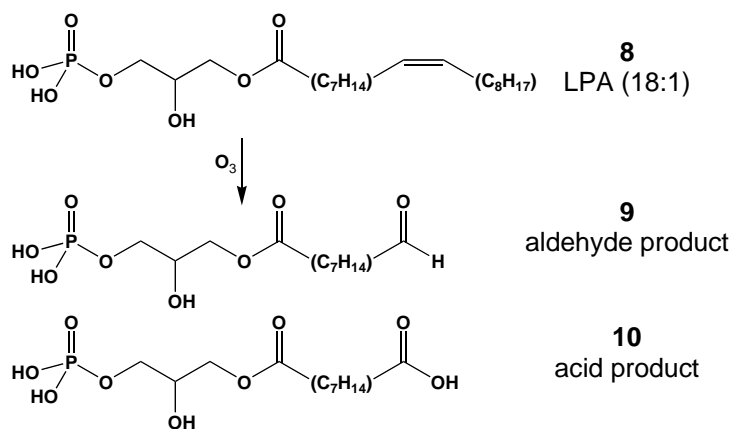


Figure 8.3. Oxidation of LPA (18:1) by ozone unambiguously demonstrates the location of the double bond along the hydrocarbon tail. In the absence of ozone (A), the singly-deprotonated monomer at 453, the singly deprotonated dimer at 871, and the sodium-bound dianion peak at 893 m/z dominate the negative ion FIDI-MS spectrum of LPA (18:1). Frame (B) shows the FIDI-MS spectrum containing the reaction products following 5 second exposures to ozone including the aldehyde product peak at 325 m/z, a weak signal at 341 m/z from the acid product, and an unknown peak at 373 m/z.

Scheme 8.1. Oxidation of oleic acid (1) by ozone on surfaces proceeds through primary (2) and secondary (3) ozonides before forming 9-oxononanoic acid (4), nonanoic acid (5), azelaic acid (6), and nonanal (7).



Scheme 8.2. Expected products in the ozonolysis of LPA (18:1) (**8**) are the aldehyde reaction product (**9**) and the acid reaction product (**10**).



8.3. References

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