Research paper

Time resolved study of hydroxyl radical oxidation of oleic acid at the air-water interface

Xinxing Zhang, Kevin M. Barraza, Kathleen T. Upton, J.L. Beauchamp *

Noyes Laboratory of Chemical Physics and the Beckman Institute, California Institute of Technology, Pasadena, CA 91125, United States

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ABSTRACT

The ubiquity of oleic acid (OA) renders it a poster child for laboratory investigations of environmental oxidation chemistry. In the current study, mechanistic details of the oxidation of OA by hydroxyl radicals at the air-water interface are investigated using field-induced droplet ionization mass spectrometry (FIDI-MS). Products from OH oxidation of both unsaturated and saturated carbon atoms are identified, and mechanisms for both types of oxidation processes are proposed. Uptake of oxygen in the interfacial layer increases linearly with time, consistent with Langmuir-Hinshelwood reaction kinetics. These results provide fundamental knowledge relating to OH initiated degradation of fatty acids in atmospheric aerosols.

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1. Introduction

Fatty acids are pervasive in nature. Being surfactants, they tend to exist at oil-water or air-water interfaces. They widely occur in many kinds of oils [1,2] and living organisms [3,4]. Due to this ubiquity, fatty acids such as oleic acid (OA) are found on the surfaces of atmospheric aerosols formed by sea spray [5–8] and result from anthropogenic activities like cooking [9,10]. In the atmosphere, interfacial reactions associated with the oxidation of organics are of major interest because resultant secondary organic aerosols (SOA) are known to have adverse impacts on climate, human health, atmospheric chemistry in general and organic aerosols in particular. Hence, the degradations of fatty acids due to interfacial chemistry, especially interfacial oxidation reactions, are very important environmental processes.

Differences in the oxidative behaviors between saturated and unsaturated fatty acids center around the C=C double bond. Oxidation of airborne organics are mainly initiated by reaction with ozone (O_3), nitrate radical (NO_3), and hydroxyl radical (OH) [11]. Ozone selectively reacts with unsaturated C=C bonds, but behaves inert towards saturated hydrocarbons. In contrast, NO_3 and OH react with both saturated and unsaturated hydrocarbons, with the rate coefficients for oxidation of unsaturated hydrocarbons being significantly larger than for oxidation of corresponding saturated molecules [11]. This is reasonable in the sense that the C=C double bond is considered to be electron-rich while oxidation is essentially an electron flow to the oxidizers. Among these three oxidizers, the OH radical is especially interesting because it is

responsible for initiating oxidative degradation of most trace species in the lower atmosphere [12], with the deserved reputation of being the "atmosphere's detergent". The OH oxidation of saturated hydrocarbons is initiated by abstraction of an H atom, resulting in an alkyl radical and a water molecule. Unsaturated hydrocarbons, on the other hand, can undergo addition of OH to the C=C bond, yielding a nascent β-hydroxylalkyl radical [11].

OA has become a model system used to study the atmospheric oxidation of fatty acids not only because it contains both saturated and unsaturated carbon atoms, but also because field studies have demonstrated that OA is the most prevalent unsaturated fatty acid observed in the amphiphilic coats of marine aerosols, and it is also highly abundant in tropospheric particulate matter [8,9]. Further, the oleoyl group of OA is one of the most prevalent unsaturated hydrophobic chains found in phospholipids. To date, the oxidation of OA by ozone at the air-water interface has been studied by field-induced droplet ionization mass spectrometry (FIDI-MS) [13], sum frequency generation vibrational spectroscopy [14], and by monitoring other surface properties such as surface tension and surface pressure [15,16]. The NO_3, OH and ozone oxidation studies of oleic acid particles were also performed using flow tube reactors [17–20], chamber studies [21], attenuated total reflectance infrared spectroscopy [22], as well as aerosol mass spectrometry [23]. In these studies, the products, mechanism, and kinetics of oleic acid oxidation by various oxidizers have been examined. However, to the best of our knowledge, no detailed studies of OH mediated oxidation of oleic acid at the air-water interface has been reported.

Recently, our group pioneered the technique field-induced droplet ionization mass spectrometry (FIDI-MS) [24–27]. This interface-sensitive technique employs a soft ionization method to sample ions from the surface of microliter liquid droplets using a

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* Corresponding author.
  E-mail address: jlbchamp@caltech.edu (J.L. Beauchamp).

pulsed critical electric field, for analysis by mass spectrometry. In the current study, we couple the FIDI-MS technique with a steady flow of OH radicals generated from a dielectric barrier discharge source (DBDS). By varying the exposure time of the hanging droplet to the DBDS, we obtain the time-dependence of product yield at the droplet surface. We observe that the C=C double bond of OA is always oxidized first, with further oxidation products of both the saturated and unsaturated carbon atoms containing five or more oxygen being identified by mass spectrometry. To clarify the mechanism of saturated hydrocarbon oxidation, similar experiments are performed with the saturated analog stearic acid to compare with the results for OA. By postulating the oxidation mechanisms, we aim to provide a model system to understand the OH oxidation of amphiphiles at the air-liquid interface.

2. Methods

2.1. Chemicals and reagents

Oleic acid (≥99%) and stearic acid (≥98.5%) were purchased from Sigma Aldrich (St. Louis, MO, USA) and used without further purification. All solvents (water and methanol) are HPLC grade and purchased from EMD Chemicals Inc. (Gibbstown, NJ, USA). A 2 mM solution is firstly obtained by dissolving oleic acid and stearic acid in methanol as the stock solution, and then diluted to 100 μM by water for experimental use.

2.2. Air-water interfacial oxidation by OH

The FIDI-MS instrument has been described in detail elsewhere [24]. Briefly, a hanging droplet of ∼2 mm o.d. (∼4 μL in volume) is suspended on the end of a stainless steel capillary between two parallel plate electrodes separated by 6.3 mm. Droplets are formed from liquid fed through the capillary using a motorized syringe pump. The parallel plates are mounted on a translation stage to allow alignment of an aperture in the electrically grounded plate with the atmospheric pressure inlet of an LTQ-XL mass spectrometer (Thermo-Fisher, Waltham, MA). The capillary is mounted on a separate translation stage to place the droplet exactly midway between the two plates and to align with the inlet of the LTQ-XL. Mass spectrometric sampling of the hanging droplet is accomplished by applying a pulsed high voltage (typically −3 to −5 kV, 100 ms duration) to the back parallel plate and to the capillary at half the magnitude applied to the back plate to maintain field homogeneity between the front and back plate. When a sufficiently high voltage is applied, the electrical forces overcome the surface tension of the droplet, resulting in the bipolar ejection of highly-charged progeny droplets less than 1 μm in diameter from the opposite ends of the suspended droplet [24,28]. Charged droplets of a specific polarity enter the transfer capillary of the mass spectrometer, resulting in the detection of gas-phase ions. In this case, we apply negative voltage on the back plate in order to detect the deprotonated oleic acid and stearic acid anions and their oxidation products. After each droplet is formed, we allow 60 s for the molecules to diffuse to the air-water interface before exposing the droplet to hydroxyl radicals for a variable reaction time typically up to 60 s. Amphiphile concentrations, kept below the critical micelle concentration (CMC) limit, are sufficient to insure formation of a monolayer with a subsurface excess. After the OH oxidation, we trigger the high voltage to sample both reactants and products. Sampling occurs on a millisecond time scale.

2.3. Dielectric barrier discharge source (DBDS)

Hydroxyl radicals are generated using a dielectric barrier discharge source (DBDS) composed of a borosilicate tube (1/4″ OD,

3/16″ ID) which acts as the dielectric material. A tungsten filament inner electrode is sealed within the tube, and a conductive silver epoxy coating (McMaster-Carr, Santa Fe Springs, CA, USA) acts as an outer electrode. A glass bubbler provides water saturated helium through the DBDS, with a flow of 1000 mL/min monitored by a Type πMFC Digital Mass Flow Controller (Model PFC-50, MKS Instruments). A high voltage AC power supply (Trek PM04015) biased the inner electrode during experiments at 12 kV (peak to peak) and 1000 Hz, while the outer electrode remained grounded. Between the power supply and the tungsten filament, there is a 1 MΩ resistor used as a current limiter. A low temperature plasma (dielectric barrier discharge) is generated inside the tube, producing hydroxyl radicals in the gas flow. Compared to the tropospheric OH radical concentration that was measured to be 1–3×10^6 molecules cm^{-3} [29], the DBDS can generate $\sim 1 \times 10^9$ molecules cm^{-3} OH radicals based on the time required to oxidize a monolayer of surfactant with an average of one oxygen per surfactant molecule. This significantly accelerates the oxidation process compared to ambient conditions.

3. Results and discussion

3.1. Oxidation product analysis by mass spectrometry

Fig. 1 presents the mass spectra of the OH oxidation products of OA at the air-water interface. The time periods each droplet was exposed to OH radicals are 0 s, 15 s, 30 s and 60 s. The deprotonated OA monomer and dimer are observed at m/z 281 and m/z 563, respectively. As oxidation proceeds, the intensity of the dimer relative to the monomer increases in the FIDI mass spectra. This
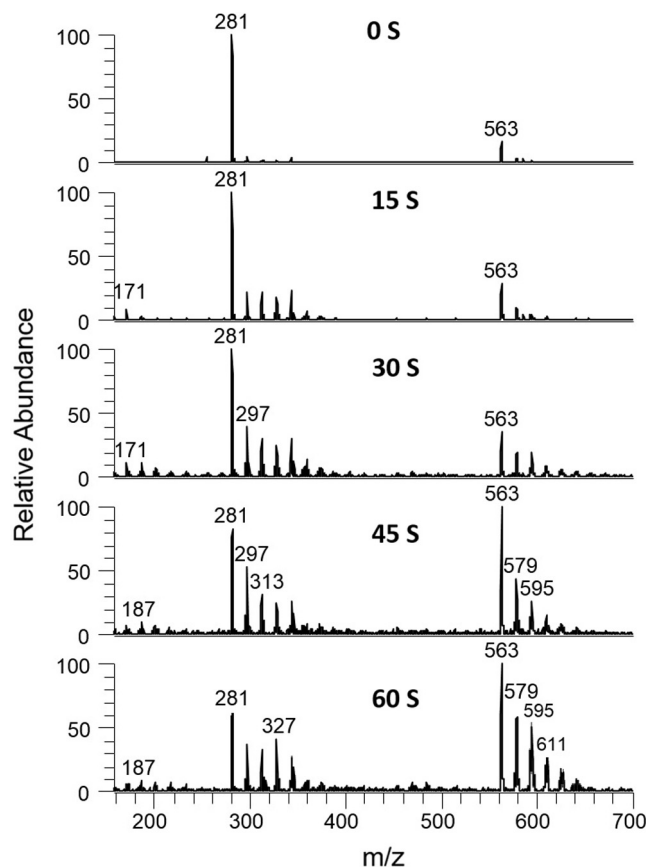

Fig. 1. Time-resolved FIDI-MS spectra including the reactant and products of the reaction between OA and OH radicals. The monomer and proton bound dimer of deprotonated OA appear at m/z 281 and 563. Low abundance bond cleavage products are observed starting at m/z 171.