STUDY OF OZONOLYSIS OF ULTRASONICALLY LEVITATED DROPLETS CONTAINING UNSATURATED FATTY ACIDS

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Carboxylic acids are present in the atmosphere as key components of secondary organic aerosol (SOA). It is known that meat cooking is an important source of atmospheric organic aerosols emission. For example, oleic acid (OA) is a C18 mono-unsaturated fatty acid that contributes considerably to the aerosol fraction due to the reactions that it undergoes, such as ozonolysis, which yields a series of products that have a notable impact on climate and health. It is one of the most abundant unsaturated fatty acids found in the troposphere, and also is associated with emissions from meat cooking. The reaction of gas-phase ozone with OA has been extensively benchmarked as a model system for heterogeneous atmospheric reactions of organic compounds and also to establish gas-particle interactions as well as the interfacial transport that influences chemical oxidation of aerosols (compare Zahardis and Petrucci, 2007).

Similarly, linoleic acid (LA) and palmitoleic acid (PA) are long chained unsaturated fatty acids found at lower concentrations in the atmosphere, from similar sources as oleic acid. Palmitoleic acid is a long chained mono-unsaturated fatty acid, but unlike OA, its chain is 16 carbons long. The reaction of ozonolysis of this fatty acid has not been as extensively studied as its 18C counterpart. Despite this, Spencer and Kleiman (1978) reported that the ozonolysis of palmitoleic acid yielded a seven-carbon aldehyde and a nine-carbon aldehyde-ester. In the case of linoleic acid, a C18 di-unsaturated fatty acid, it was found that the reaction of ozonolysis can proceed via different routes depending on the concentration of ozone. For example, Lee and Chan (2007) stated that linoleic acid can experience the formation of four conjugated diene hydroperoxides as a result of the auto-oxidation reaction at low ozone concentrations.

In the present work, the ozonolysis of acoustically levitated droplets of these three fatty acids has been studied at ozone concentrations ranging from 2 to 40 ppm, and has been analysed by Raman microscopy. The analysis of products of the ozonolysis has been carried out by means of gas chromatography mass spectrometry (GC–MS) and solid phase micro-extraction (SPME). A Matlab model (compare Pfrang et al., 2011) was used in order to evaluate how changes in kinetic parameters affect the fatty acid-ozone systems. The results indicate that ozonolysis of mono-unsaturated fatty acids, oleic and palmitoleic acids show a very similar decay behaviour, and apparently the size of droplet does not have a strong influence on the reaction. Unlike mono-unsaturated fatty acids, linoleic acid ozonolysis seemed to be influenced by the formation of peroxides, mainly at low ozone concentrations. It is known that the formation of products of ozonolysis of unsaturated fatty acids involves the formation of Criegee intermediates in secondary reactions of the mechanism. Figure 1 shows the ozonolysis of the three fatty acids at 2 and 40 ppm. At very high concentration, all acids show a gradual decay, which indicates the rupture of carbon-carbon double bonds as expected according to the Criegee mechanism. Nevertheless, at lower ozone concentrations, LA shows a slight increase, this may be a consequence of the formation of C=C peroxidation products.

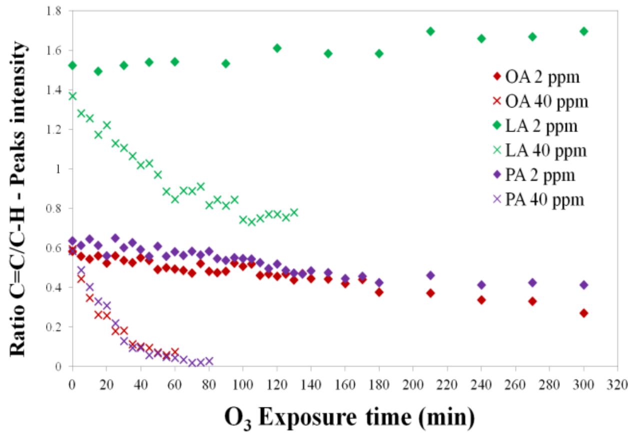

Figure 1. Changes in the peak intensity at 1664 (C=C bond) and 1453 cm^{-1} (C=C-H bond) of the unsaturated fatty acid levitated droplets at 2 ppm (◆) and 40 ppm (✕). Red: Oleic acid (OA); green: Linoleic acid (LA); purple: Palmitoleic acid (PA).

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