

O₃-initiated heterogeneous oxidation of linoleic acid and its dependences on ambient temperature and relative humidity

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Atmospheric aerosols are a complex mixture of inorganic and organic components and have been widely recognized as key elements in environmental issues ranging from air pollution, sky visibility, public health, to climate change. They often have a characteristic core-shell structure. Such a feature is inherent considering the properties of individual aerosol components, the aerosol emission sources, and their continuous aging while entrained in the air. As the organic coating is more likely to interact with reactive gaseous species than the inorganic core, the physiochemical properties of the organic surface determine, to a large extent, the environmental role of the aerosols. Despite recent extensive studies towards heterogeneous oxidation of unsaturated organics (mostly oleic acid) initiated by ozone¹⁻², little is known about effects of ambient temperature and relative humidity on the chemical transformation of organic aerosols.

In this work, we used linoleic acid as a proxy for atmospheric unsaturated organics to investigate its heterogeneous oxidation by O₃ over a wide range of temperatures (257-313 K) and relative humidities (0-80% RH). Linoleic acid, which is found in lipids of cell membrane and plays important roles in various biologic processes, has been observed in atmospheric aerosols³. Our experiments were carried out using a flow reactor coupled to an attenuated total reflection infrared spectrometer (ATR-IR). Pseudo-first order rate constants and overall reactive uptake coefficients were acquired from absorbance changes in peaks located near 1743 cm⁻¹; 1710 cm⁻¹; 1172 cm⁻¹ and 1110 cm⁻¹, which can be assigned to C=O in ester; C=O in acid; C-C and C-O stretching modes, respectively. Experimental results showed that heterogeneous loss of O₃ onto linoleic acid was highly efficient with an uptake probability close to 3×10⁻² at 293K. It was found that the uptake coefficients increased with increasing temperature, and within the temperature range studied here the O₃ reactive uptake was enhanced by one order of magnitude. It was also noted such temperature enhancement effect on the reaction kinetics was much more effective at lower temperatures. For example, the Pseudo-first order rate constants increased nearly by 7-fold when temperature was changed from 257 K to 273 K. Such behavior can be explained by change in physical state of linoleic acid at lower temperatures which was confirmed by shifts of both CH₂ and C=O stretching modes. A decrease in absorbance ratio of (*A*₁₇₄₃/*A*₁₇₁₀) with decreasing temperature was also observed, an indicative of a smaller amount of α-acyloxyalkyl hydroperoxide-related products formed during oxidation of linoleic acid with O₃ at lower temperatures. In addition, RH study results showed that water vapor promoted heterogeneous reactive uptake of O₃ on linoleic acid surface. Furthermore, water uptake studies showed that O₃ initiated heterogeneous oxidation enhanced hydrophilicity of organic surface.

References

1. Carlton, A. G.; Wiedinmyer, C.; Kroll, J. H. A review of Secondary Organic Aerosol (SOA) formation from isoprene. *Atmospheric Chemistry and Physics* **2009**, 9 (14), 4987-5005.
2. Hildebrandt, L.; Donahue, N. M.; Pandis, S. N. High formation of secondary organic aerosol from the photo-oxidation of toluene. *Atmospheric Chemistry and Physics* **2009**, 9 (9), 2973-2986114.
3. Chebbi, A.; Carlier, A. Carboxylic acids in the troposphere, occurrence, sources, and sinks. *Atmospheric Environment* **1996**, 30 (24).