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004 EPA STAR Graduate Fellowship Conference *Next Generation Scientists—Next Opportunities*

Photoelectron Resonance Capture Ionization Aerosol Mass Spectrometry: A New Method for the Study of Organic Aerosols

ERVIEW

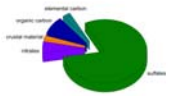
bonaceous Particles

heric particulate matter (including carbonaceous particles) responsible for poor visibility on humid days:

Comparison of low and high particulate days in Burlington, Vermont

Source: http://www.hazecam.net/burlington.html

Contribution to Particulate Composition



Source: http://www.hazecam.net/burlington.html

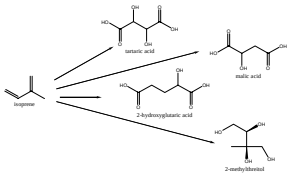
ant fraction of total atmospheric particulate matter contains carbon in Eastern U.S.

t of fossil fuel combustion

- Complex mixture of compounds
- Health hazard
- Undergo active heterogeneous chemistry in atmosphere

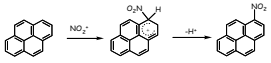
dary organic aerosol formation

- Photochemical oxidative products of (primarily) gaseous emissions from trees generally less volatile than emitted molecules
- Oxidized products condense to form ultrafine particles



heric Processing

- Particles undergo heterogeneous chemical reactions with atmospheric gas phase species
- Particles act as sink for reactive gases, such as OH and ozone, altering the oxidizing capacity of the atmosphere
- Physical and chemical properties of particles can be affected – possible climate change implications
  - Light scattering properties of particles can be affected
  - Can affect cloud formation
- Can have severe impact on human health, e.g. nitration of polycyclic aromatic hydrocarbons (PAHs):



nolysis of Oleic Acid Particles

come the model system for studying complex behavior of heterogeneous reactions involving multi-component aerosols

c fraction of total atmospheric particulate matter is significant and may:

- Impact radiative properties of particles
- Reactively take up atmospheric trace gases
- Pose severe human health hazards

nce of model system to atmospheric processes:

- Oleic acid is common fatty acid in troposphere (1 ng m^{-3} in remote marine environment)
- Ozonolysis of oleic acid particles may improve their ability to act as cloud condensation nuclei and may disrupt the balance of atmospheric oxidants.

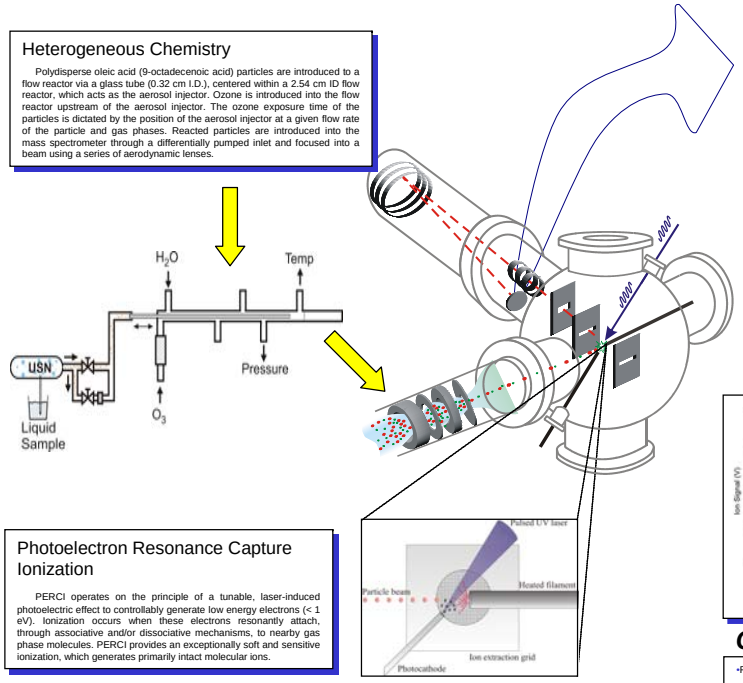
METHODS

Experimental Approach

- Methods are needed for the on-line, real-time analysis of atmospheric carbonaceous particles
- Aerosol Mass Spectrometry is the method of choice for analysis of atmospheric particles in real-time, however, difficulties are encountered with analysis of organics
- Soft ionization by photoelectron resonance capture ionization (PERCI) can minimize molecular fragmentation and simplify molecular identification
- Model heterogeneous reaction system, oleic acid particles and ozone gas, studied to evaluate PERCI
- PERCI allows for the identification of previously undetected particle-phase reaction products

Heterogeneous Chemistry

Polydisperse oleic acid (9-octadecenoic acid) particles are introduced to a flow reactor via a glass tube (0.32 cm I.D.), centered within a 2.54 cm ID flow reactor, which acts as the aerosol injector. Ozone is introduced into the flow reactor upstream of the aerosol injector. The ozone exposure time of the particles is dictated by the position of the aerosol injector at a given flow rate of the particle and gas phases. Reacted particles are introduced into the mass spectrometer through a differentially pumped inlet and focused into a beam using a series of aerodynamic lenses.



A close-up of the PERCI source, located adjacent to the ion extraction grid of the time-of-flight mass spectrometer. Since the analyte molecules must be in the gas phase for efficient ionization, a heated filament is placed in the particle beam to vaporize the particles.

Photoelectron Resonance Capture Ionization

PERCI operates on the principle of a tunable, laser-induced photoelectric effect to controllably generate low energy electrons (< 1 eV). Ionization occurs when these electrons resonantly attach, through associative and/or dissociative mechanisms, to nearby gas phase molecules. PERCI provides an exceptionally soft and sensitive ionization, which generates primarily intact molecular ions.

LaFranchi BW and Petrucci GA, J. Am. Soc. Mass Spectrom. 15:424-430, 2003

LaFranchi BW, Zahardis J, and Petrucci GA, Rapid Comm. Mass. Spectrom.: **in press**, 2004.

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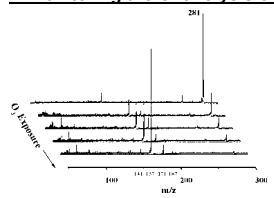
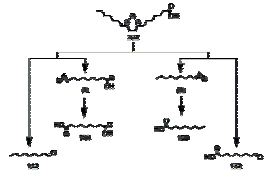
RESULTS

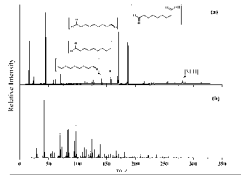
1. Monitoring the Ozonolysis of Oleic Acid



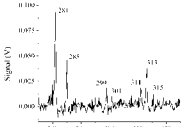
Generalized Reaction Scheme



Facilitated Product Identification

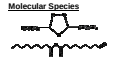
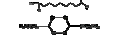
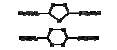
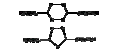
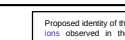
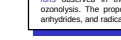


Higher Order Oxygenates Identified



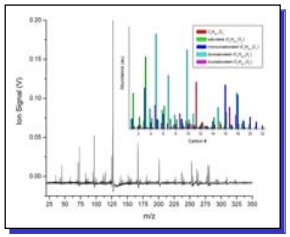
A closer look at the high mass region of the product mass spectrum shows the presence of additional minor products alluding to a complex series of reactions and intermediates involved in the ozonolysis of oleic acid.

Comparison of PERCI (a) with conventional electron impact (b) mass spectrometry of the ozonolysis products of oleic acid particles. The minimal fragmentation in the PERCI spectrum simplifies identification of the reaction products. The 4 major products shown in the generalized reaction scheme above, are detected as the $[M-H]^-$ ions.

Molecular Species	Molecular Weight	Ion Observed
	300 u	299 m/z $[M-H]^-$
	312 u	311 m/z $[M-H]^-$
	313 u	313 m/z M^-
	316 u	315 m/z $[M-H]^-$
	330 u	285 m/z $[M-H-CO_2]^-$
	346 u	301 m/z $[M-H-CO_2]^-$
	360 u	315 m/z $[M-H-CO_2]^-$

Proposed identity of the molecular species corresponding to the higher molecular weight ions observed in the PERCI mass spectrum of oleic acid particles undergoing ozonolysis. The proposed species include secondary ozonides, geminal diperoxides, anhydrides, and radical species.

2. Biodiesel Analysis



Analysis of a complex mixture of organics is possible using PERCI since molecular integrity of the analyte components is maintained. Here a liquid sample of biodiesel fuel is analyzed by PERCI. From the mass spectrum, a distribution of the carbon chain lengths of the molecular components in the fuel can be determined. The degree of saturation can also be determined.

CONCLUSIONS

- Four major products of ozonolysis of oleic acid particles observed *directly*
- Previously undetected higher order oxygenates observed as particle phase products
- Chemical and physical implications in the troposphere:
  - Potential source of OH radical
  - Increased hygroscopicity of oxygenated products enhances the propensity of these particles to act as cloud condensation nuclei
  - Intermediates may react with additional atmospheric gas and particle phase components such as formaldehyde or other environmentally relevant carbonyls
- PERCI can be applied to any type of analysis involving complex mixtures of organics, such as biodiesel fuel

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