

Secondary Organic Aerosols Formed via Ozonolysis of Limonene Studied by Aerosol VUV Photoelectron Spectroscopy

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Abstract

Secondary organic aerosols (SOA) can be formed via ozonolysis of unsaturated hydrocarbons, such as terpenes, which can considerably alter the cloud formation microphysics and atmospheric chemistry. While terpenes are largely of biogenic origins, they can also be released via numerous anthropogenic activities. Recently, we applied the aerosol VUV photoelectron spectroscopy to study the valence electronic structures of two limonene isomers and their ozonolysis products. The observed photoelectron spectra show that the two limonene isomers, including S- and R-limonene exhibit distinct ionization energies and different formation yields of SOA. Moreover, we found that presence of water medium significantly enhanced the yields of SOA. The possible reaction mechanisms of ozonolysis of limonene and the role of water in affecting the SOA formation is discussed. This set of studies provides new insights into the crucial role of water in the SOA formation upon ozonolysis of limonenes and in the atmospheric aerosol chemistry.

Keywords – *Aerosol VUV photoelectron spectroscopy, Limonene, Ozonolysis, Water*

Introduction

Aerosol, broadly defined as particulate matters suspended in the air, exhibit diverse physical, chemical, optical and biological properties, crucially depending on their internal structure, chemical composition and external morphology.

Monoterpenes (C₁₀H₁₆) belong to a unique type of unsaturated hydrocarbons. They can react readily with atmospheric oxidants, such as ozone to form secondary organic aerosols (SOA), which in turn serve as cloud condensation nuclei (CCN) and play a crucial role in mediating the climate. Common monoterpenes include α -pinene, β -pinene and limonene. While α -pinene accounts for nearly half of global monoterpene emission, the ozonolysis of limonene has been suggested to be the most abundant source of SOA among monoterpenes, likely due to their double C=C bonds characteristics.

Despite the complex nature of limonene oxidation capacity, which is inherently governed by its electronic structure properties, the valence electronic structures of limonene in the aerosol phase and its ozonolysis products have not been studied. In this study, we investigate the ozonolysis of limonene by applying aerosol VUV photoelectron spectroscopy using the undulator-based VUV radiation as the ionization source. The valence electronic properties of two limonene enantiomers, including R-(+)-Limonene and S-(-)-limonene in the

aerosol phase have been measured. The ozonolysis products are systematically characterized by photoelectron spectroscopy at varying ozone concentrations for the first time. The role of water is also interrogated. By comparing the difference between the two enantiomers of limonenes, the steric structural effect in ozonolysis of terpenes is also interrogated.

Experiments

The new aerosol instrument includes three main parts, including a source chamber which houses the adjustable aerodynamic lens system, a differential pumping region and a main photoelectron investigation chamber where the photoionization takes place.

Due to the high intensity, wide tunable photon energy range and excellent coherence, undulator-generated VUV synchrotron radiation is an ideal light source for the valence photoelectron spectroscopic studies. The light source is provided by the 9 cm period undulator (U9) at BL21B2, NSRRC. The samples be formed from aerosol generator and ozone generator, and they are going to the aerosol instrument.

Results and Discussion

The partially vibrationally-resolved structures of limonene, including R-limonene and S-limonene in the aerosol phase were measured for the first time by the VUV photoelectron spectroscopy. (Fig 1.) From the photoelectron spectrum of pure limonene aerosols at 25 eV, the first electronic band of the photoelectron spectrum

corresponding to the removal of π electron from the carbon ring exhibits a vertical ionization energy of ~ 8.5 eV for R-limonene and 8.7 eV for S-limonene.

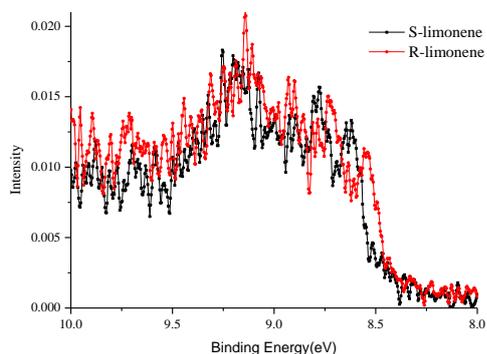


Fig 1. VUV Photoelectron Spectroscopy of Two Limonene Aerosols

With increasing levels of ozone exposure, the reaction products produced via ozonolysis of limonene spectrum structure exhibit significantly dose-dependent photoelectron spectra with ozone (Fig 2.).

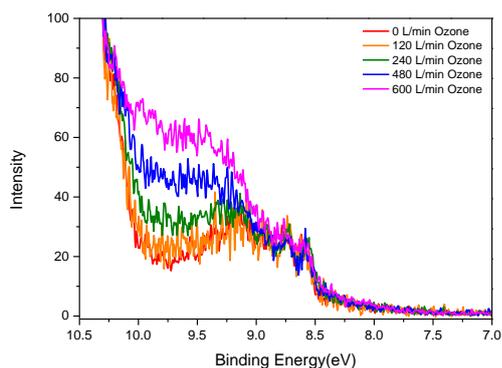


Fig 2. Dose dependence of ozone upon reacting with Limonene

It is also intriguing to note that upon reacting with ozone, the presence of water significantly affects the formation of the SOA. (Fig 3.)

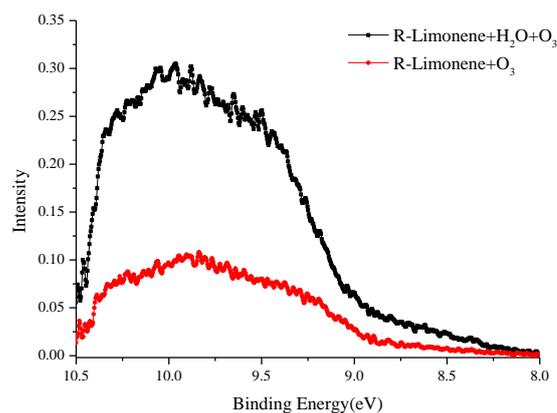


Fig 3. Water effect on ozonolysis of R-limonene

The possible cause underlying the role of water in enhancing the SOA formation have been interrogated. We anticipate that water medium not only provides a reaction site, but also likely directly participate in the ozonolysis processes, opening a new reaction channel to form SOA (Fig 4.). This finding exhibits profound implication. It implies that the formation of indoor SOA may be greatly increased under high relative humidity.

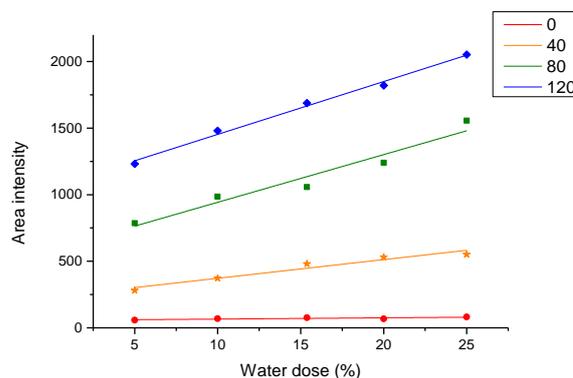


Fig 4. Dose dependence of water on the SOA formed via ozonolysis of limonene

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