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Characterization of Secondary Organic Aerosol (SOA) formed by the Reaction of β-caryophyllene, Soot and Ozone: Climate Impact

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Abstract

Diesel soot (black carbon, BC) is an important light absorbing aerosol component in atmosphere that can cause tropospheric heating. Laboratory studies have found it to be unreactive to ozone at ambient temperature. The low uptake coefficient i.e., $\gamma_{300 K}$ = 2×10^{-7}, of the soot-O_3 reaction indicates a low probability of irreversible O_3 loss from gas phase to surface-adsorbed product (Particle phase). This shows clearly that at low temperature soot is not reactive with atmospheric oxidants. In contrast, sesquiterpenes (SQT) such as β-caryophyllene ($C_{15}H_{24}$), which are produced primarily by plants, are extremely reactive with ozone. For example, the residence time of β-caryophyllene in the atmosphere is only 2 min in the presence of 60 ppb ozone. Thus, ozonolysis reaction of β-caryophyllene is expected to be a significant source of biogenic secondary organic aerosols. These oxidized products may condense onto soot particles, and a question arises as to how they will partition between the soot surface, vapor phase, and aqueous aerosol phases. Liquid chromatography- mass spectrometry (LC/MS), Fourier transform infrared (FTIR) and UV-Vis spectroscopies are being used to study the β-caryophyllene-dark ozonolysis reaction at low ozone levels (40-60 ppb). Products identified include low molecular weight highly volatile and water soluble products such as formaldehyde, acetaldehyde, acetone, and acetic acid. Also identified are high molecular weight components (~350 Dalton) with lower water solubility and vapor pressures. The SOA coatings of these SQTs on soot are being evaluated to determine their hygroscopicity. As these compounds absorb in the IR and UV-Vis they can add to radiative forcing by submicron aerosols and need to be better understood for climate modeling.

Introduction

Sesquiterpenes (SQT, $C_{15}H_{24}$) are one of the important sources of non-methane hydrocarbons in the atmosphere that are produced primarily by plants, mainly conifers and have been found to be precursors of secondary organic aerosols (SOA) (Baltensperger et al. 2005). SQT have very low vapor pressures and SOA are formed when these biogenic precursor species react with atmospheric oxidants at ambient temperature (298-300K). These biogenic hydrocarbons (SQT) have a very short lifetime and they are so reactive with atmospheric oxidants (e.g. O_3, OH, NO_3) that it is very difficult to measure them directly in the atmosphere. However, their oxidized products are highly volatile and they can influence radiative balance directly by absorbing and scattering radiation as coatings on carbonaceous aerosols. Primary carbonaceous aerosol, such as soot, has been found to be reactive towards ozone (O_3) at higher temperature in the range of 473-573K (Smith DM et al.1996). These "black carbon species" are important light absorbing aerosols and their surface oxidations at room temperature with ozone are thought to be very slow. This paper provides a summary of an examination of ozone reaction with soot and an upper limit for uptake on the surface of a standard diesel soot (NIST 2975), as well as preliminary chemical characterization of SOA particles generated from the biogenic precursor β-caryophyllene and the ubiquitous atmospheric oxidant O_3. A specific focus in our analysis has been on the evaluation of water soluble species from the ozone reaction with this model sesquiterpene.

Materials and Methods

Soot-O_3 reaction was carried out in a simplified reaction chamber (Fig. 1). NIST standard diesel soot 2975 (0.05-0.08 mg) was placed inside the reaction chamber. N_2 gas flowed continuously through the chamber at a rate of 275 cm^3 min^{-1} at 298-300 K and atmospheric pressure. O_3 gas was generated by passing atmospheric air through an O_3 generator,(Dasibi model 1009 CP) and the air flow was kept constant at 1.21 $Lmin^{-1}$. This instrument also monitors the ozone concentration continuously using long-path UV
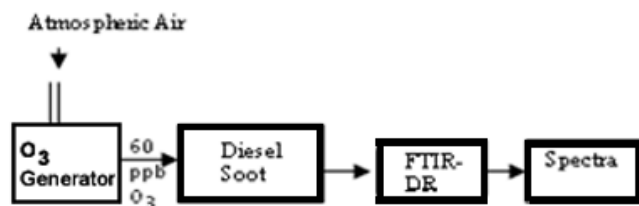
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Figure 1. Block diagram of reaction of Ozone with Diesel soot.

absorption to assure a specific ozone concentration is maintained during the soot exposure. At the end of every reaction FTIR spectra of ozonated soot were obtained on Nicolet 6700 Fourier transform infrared spectroscopy (FTIR)-diffuse reflectance infrared Fourier transform (DRIFTS) technique. All the individual parts of reaction setup were connected by using 1/8 inch Teflon® tubing connected with Teflon® Swagelok® fittings to assure a gas-tight system. The experimental setup was slightly modified for the β-caryophyllene-dark ozonolysis reaction. The same ozone generator was used and two impinger tubes of volume of 30 ml were fitted in parallel to allow the carrier gas to equilibrate with the organic vapor pressure and then allow ozone to react with the vapor. The ozone concentration for this reaction was maintained at 60 ppb ozone and the oxidized products, gases and aerosols were bubbled through 10 ml water in another impinger tube that allowed for water soluble products to be collected for analysis.
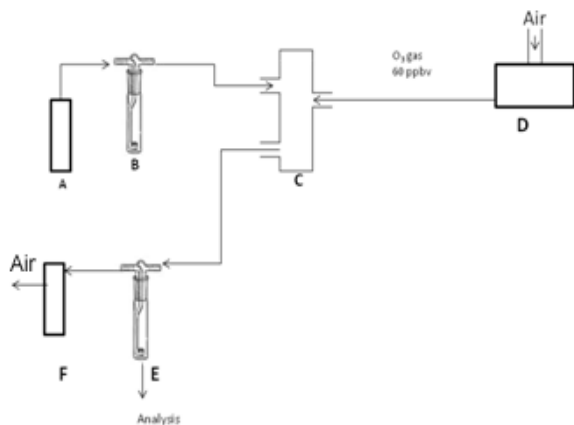

Figure 2. Block diagram of Ozonolysis reaction of β-caryophyllene. Where A=Carrier Gas Nitrogen (N_2); B=First impinger tube containing Beta Caryophyllene C=Reaction chamber where Beta caryophyllene vapor and O_3 were mixed; D=O_3 Generator (Dasibi model 1009 CP); E=Second impinger tube containing water; F=charcoal tube.

All the parts of this reaction setup were connected by using 1/8 inch Teflon® tubing connected with Teflon® Swagelok® fittings. Spectra of these oxidized products were obtained from FTIR-spectroscopy using attenuated total reflectance (ATR) technique using a Zn-Se crystal in spectral region of 650-4000 cm^{-1} at resolution 4 cm^{-1}. Spectra were averaged using 64 scans. UV-Vis absorption spectra of these oxidized products were obtained from 280-800 nm by using UV-Vis Beckman DU 600 instrument. LC-MS spectra were obtained by using an Agilent 1100 series LC/MSD Ion trap spectrometer. A total of 10µL solution was introduced into a Liquid chromatography (LC) column for chromatographic separation prior to MS analysis. Column flow was adjusted to 0.400 mL min^{-1} and a 60% water/40% methanol mixture was used as the carrier solvent. The LC/MS ion source was operated in the Electrospray Ionization (ESI) mode to obtain mass spectra.

Results and Discussion

FTIR spectra of ozonated soot showed no indication of any oxidized products even after long time O_3 exposures (60 ppbv) on diesel soot at 300K, i.e. no measureable product formation was observed (spectra not shown). The experimental observation was used to calculate an upper level limit on the uptake coefficient (γ) for this soot-O_3 reaction. The experimentally obtained low γ value i.e., $\gamma_{300K}=2\times10^{-7}$ of soot-O_3 reaction indicated a low probability of irreversible O_3 loss from gas phase to surface adsorbed products (particle phase). By analyzing uptake-coefficient value, it can be concluded that at ambient temperature soot is unreactive to atmospheric oxidant. An upper-estimate of the O_3 uptake coefficient, γ value was calculated from eq.1;

$$\gamma = 4KV/\omega S \qquad (1)$$

Where K = rate constant of O_3 loss, $7.2\times10^4\,min^{-1}ppm^{-1}$ at 300K (experimentally obtained); V = volume of reaction zone, $1.437\times10^{-6}m^3$; ω = average molecular speed or root mean square (r.m.s.) velocity, 23690 $mmin^{-1}$; S = specific surface area of soot;80-87$m^2\,gm^{-1}$.

IR stretching bands at 1730 and 2850 cm^{-1} in Fig. 3 indicated the presence of carbonyl group (aldehyde or ketone) (Marley et al 1993) and some alkane compounds in the water soluble oxidized product respectively which was produced during ozonolysis reaction of Beta-caryophyllene. The band at 1640 cm^{-1}

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is basically a peak from liquid water adsorption (Marley et al.1994). UV-Vis spectra in Fig. 4 supported this fact by indicating a shift of absorbance maxima to longer wavelength; from 250 to 300 nm. This bathochromic shift may occur due to the presence of some conjugated species in this oxidized sample.

LC-MS, FTIR and UV-Vis spectroscopies were used to identify the products including low molecular weight highly volatile and water soluble products such as formaldehyde, acetaldehyde, acetic acid and acetone. Component of low molecular weight like formaldehyde was reported in a recent paper (Winterhalter et al. 2009).
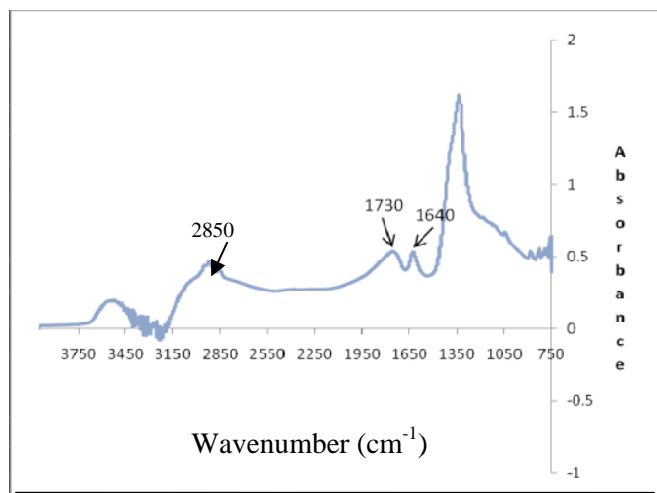

Figure 3. FTIR-ATR spectrum of water soluble oxidized products of β-caryophyllene.

Also identified were high molecular weight macromolecules (~350 Da) with lower water solubility and lower vapor pressure, which may have formed due to oligomerization.

This oxidation reaction may result in formation of some polar compounds which facilitates the partition of gas phase volatile organic compounds to the particle phase. These products may condense on soot and make it hydrophilic in nature. These SOA coated soot may influence climate directly through light scattering and absorbing or indirectly by serving as cloud condensation nuclei (CCN). For small aerosols that are less than 200 nm in size, these organic coatings will be predominantly adding to atmospheric absorption and heating of the atmosphere.
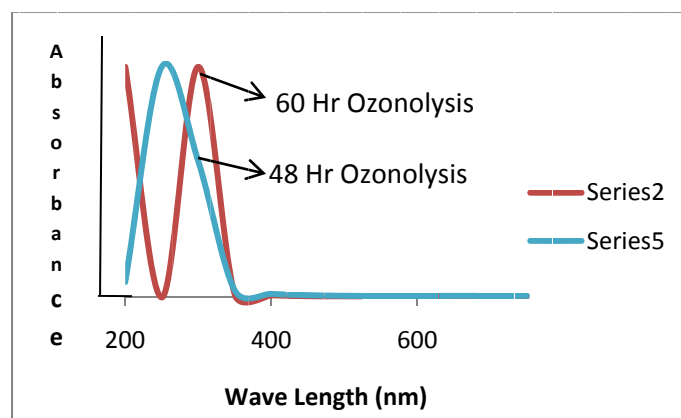

Figure 4. UV-Vis spectra of oxidized products of β-caryophyllene..

Further work is underway to examine the effects of acid catalyzed carbonaceous seed particles which may increase the formation of SOA and to determine the gas/particle partitioning coefficient of β-caryophyllene-ozonolysis reaction products in presence of soot surface or carbonaceous aerosol and to establish the organic reaction mechanisms (e.g. aldol condensation reaction, etc.) to determine the possible pathways for oligomer formation.

Acknowledgments

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