Chemical composition and volatility distribution of SOA formed by ozonolysis of β-caryophyllene between 213-313 K

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Introduction

- β-Caryophyllene is the most common and abundant of the sesquiterpenes emitted into the atmosphere and more reactive and larger in size than monoterpenes. (Duhl et al., 2008).

- Their aerosol mass yields are large and result in a significant contribution to the SOA budget in the atmosphere (Tasoglou and Pandis, 2015).

- Therefore, we studied the composition of both gas and particle phases as well as phase partitioning of SOA from ozonolysis of β-caryophyllene in presence and absence of NOx at five temperatures (213 K, 243 K, 273 K, 298 K and 313 K) in the AIDA aerosol simulation chamber (Wagner R et al., 2006).

- This work focusses on the characterization and volatility analysis of the SOA by mass spectrometry employing a FIGAERO-HR-TOF-CIMS (Lopez-Hilfiker et al., 2013) operated with iodide ions as well as a HR-TOF-AMS (Canagaratna M et al., 2007).
β-Caryophyllene was oxidized by an excess of 317 ppb ozone in presence of 37 ppb of NO₂.
Results: Mass spectrum of SOA formed at 273 K

Main components are $C_{15}H_{24}O_{3-6}$, $C_{14}H_{22}O_{3-6}$, $C_{14}H_{24}O_{5-6}$, $C_{15}H_{25}O_{7-8}N$.

Nitrogen containing species are marked in red.
Results: Mass spectra of SOA formed at 213K-313K

With decreasing temperature the SOA contains more heavier masses at m/Q(400-540, dimers) and less at m/Q(200-400, monomers) as well as m/Q(540-700, trimers).

More compounds in C_xH_yO_zN_j(j≥1) are formed at higher temperatures. Their mass peaks are strongest at 298 K.
Results: Desorption of SOA from Filters

- The maximum of desorption temperatures ($T_{\text{max}}$) of sum C$_x$H$_y$O$_z$ and sum C$_x$H$_y$O$_z$N$_j$ compounds show similar trends with temperature, going down from 213 K to 273 K, and then going up from 298 K to 313 K.

- Bimodal structures could be explained by two volatile groups (e.g. m/Q 200-400 and 600-700 at 273 K) for each filter. The fragmentation of heavier compounds during the heating procedure could also contribute to the first peak.

- At 213 K, the single but wide peak may be influenced significantly by the compounds at m/Q of 488.3 (excluding I') and 489.3 (excluding I'), as these two compounds contribute most to C$_x$H$_y$O$_z$ group and C$_x$H$_y$O$_z$N$_j$ group, respectively.
The $T_{\text{max}}$ goes down from experiments at 213 K to 273 K, and then goes up from 298 K to 313 K. The $T_{\text{max}}$ keeps the lowest in experiments at 273 K. The mass peaks are more concentrated in the experiment at 273 K.

At low temperatures, the product spectrum is smaller, which means these compounds have larger individual contributions to total mass.

Maximum circle size means the mass fraction is 0.11%
Calculation of the saturation concentration $C_{sat}^*$

$$\lg C_{sat}^*(298K) = (n_{c0} - n_c) \cdot b_c - n_o \cdot b_o - 2 \cdot ((n_c \cdot n_o) / (n_c + n_o)) \cdot b_{co} - n_N \cdot b_N; \quad (Li \ et \ al., 2016)$$

where $n_{c0}$ is the reference carbon number; $n_c$, $n_o$ and $n_N$ denote the numbers of carbon, oxygen and nitrogen atoms, respectively; $b_c$, $b_o$ and $b_N$ denote the contribution of each atom to $\lg C_{sat}^*$, respectively, and $b_{co}$ is the carbon–oxygen nonideality.

$$\Delta H_{vap} = (-5.7 \cdot \lg C_{sat}^*(298K) + 129) \cdot 1000;$$

Where $\Delta H_{vap}$ is the enthalpy of vaporization, kJ/mol;

Clausius – Clapeyron equation:

$$\lg C_{sat}^*(T) = \lg C_{sat} \cdot (298K) + (\Delta H_{vap} / (R \cdot \ln10)) \cdot ((1/298) - (1/T));$$
Particles formed at higher temperatures contain more volatile compounds.

Nitrogen containing compounds $C_xH_yO_zN_j$ contribute mainly to LVOC and SVOC for particles formed at higher temperatures, while to ELVOC for lower temperatures.
Conclusion

- Particle phase analysis shows three groups of compound masses with m/z 200-400, (C_{5-16}), (m/z 400-540, (C_{20-34}), and m/z 540-700, (C_{35-40}) classified as monomers, dimers, and trimers, respectively.

- Trimeric compounds were observed preferentially in SOA formed at higher temperatures (273 K, 298 K, 313 K), while only monomeric and dimeric compounds were detected at lower temperatures (243 K and 213 K). Interestingly, dimeric compounds, including C_xH_yO_z and C_xH_yO_zN_j, contribute more to SOA mass for the lower temperatures.

- Comparing volatility distributions for the five different temperatures and thermal desorption information from FIGAERO-CIMS (298-473 K), more compounds with lower volatilities are found for lower SOA formation temperatures.

- Nitrogen containing compounds C_xH_yO_zN_j contribute mainly to LVOC and SVOC for particles formed at higher temperatures, while to ELVOC for lower temperatures.
Reference


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