

High- m/z ion signal to total mass signal ratios measured for secondary organic aerosol using aerosol mass spectrometer

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A volatility basis-set (VBS) model in which oligomerizations are taken into account has recently been tested for further improvements of conventional VBS models.¹⁾ In order to study the oligomerization rates during secondary organic aerosol (SOA) formation and the ratio of high- m/z ion to total SOA mass spectrum ion signal, SOA particles produced during laboratory chamber experiments were analyzed by using an Aerodyne aerosol mass spectrometer (AMS). Photooxidation of α -pinene, isoprene, toluene, and 1,3,5-trimethylbenzene (TMB) was investigated in the presence of NO_x . Ozonolysis of α -pinene and isoprene was also studied. A stainless steel tube was used as a collection tube for AMS. A mass spectrum measured for organic aerosol (OA) in the region $m/z = 10 - 675$ was divided into seven mass regions; the total signal of each mass region was studied as a function of time. Increase in the signal intensity was observed with increasing of the OA level in a region $m/z < 500$. The oligomer signals increased up to substantial levels within one hour after nucleation. After substantial amounts of oligomers were produced, the ratio of the total signal of each mass region to total OA signal was constant. Next, the ratio of total mass signal in the region $m/z > m_1$ to total OA mass signal, ϕ , was determined:

$$\phi = \text{OA} (m/z > m_1) / \text{OA}(\text{total}),$$
$$m_1 = n m_C (\text{OM}/\text{OC}),$$

where n is the number of carbon atoms in SOA precursor, m_C is the carbon atomic mass, and OM/OC is organic matter to organic carbon mass ratio measured by AMS. The m_1 values of α -pinene, isoprene, toluene, and TMB were determined to be 217, 147, 180, and 204, respectively. We assumed that a contribution from monomer signals is low in a region $m/z > m_1$. Signals measured by electron ionization of AMS contain both the fragment and parent ions of organic compounds. Note that the value, ϕ , is an index of oligomer to total SOA ratio, but does not represent an absolute value of that ratio. The ϕ value of SOA from the same precursor decreased with increasing of SOA mass loading (Fig. 1), showing that oligomer formation is suppressed under high mass loading conditions. In a region $10 - 100 \mu\text{g m}^{-3}$, the ϕ value of toluene SOA was the highest, whereas that of α -pinene SOA was the lowest. No apparent effect of oxidation method (photooxidation or ozonolysis) was observed.

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References: ¹⁾ Trump and Donahue, Oligomer formation within secondary organic aerosol: equilibrium and dynamic considerations. *Atmos. Chem. Phys. Discuss.*, **13**, 24605 - 24634 (2013).

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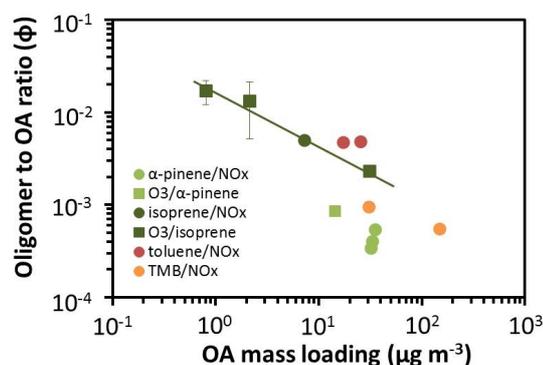


Fig. 1. Effects of OA mass loading on the oligomer to OA signal ratio (ϕ).