

# Chemical evolution (aging) of toluene and benzene SOA

E. Kostenidou<sup>1,2</sup>, E. Louvaris<sup>1,2</sup>, C. Kaltsonoudis<sup>1,2</sup> and S.N. Pandis<sup>1,2,3</sup>

<sup>1</sup>Department of Chemical Engineering, University of Patras, Patras, 26504, Greece

<sup>2</sup>Institute of Chemical Engineering Sciences, ICE-HT, Patras, 26504, Greece

<sup>3</sup>Department of Chemical Engineering, Carnegie Mellon University, PA, 15213, USA

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Presenting author email: v\_kostenidou@chemeng.upatras.gr

Secondary organic aerosol (SOA) is produced by the transfer of the lower volatility oxidation products of volatile, intermediate volatility, and semi-volatile organic compounds (VOCs) to the particulate phase. SOA may contribute up to 70% to the total aerosol organic carbon mass (Hallquist et al., 2009). Though model simulations suggest that anthropogenic SOA contributes only around 10% to the global SOA budget (Tsigaridis and Kanakidou, 2003), there are indications that this fraction may be a lot higher especially over polluted areas (e.g. Volkamer et al., 2006; Platt et al., 2014). Toluene and benzene are two of the major aromatics VOCs that are emitted by anthropogenic sources such as motor vehicles, industry and biomass burning. Atmospheric organic aerosol (OA) is often highly oxidized as its components undergo multiple generations of oxidation reactions in the atmosphere. These reactions, often termed chemical aging, take place both in the gas and particle phase through functionalization and fragmentation steps. While the details of these chemical aging processes are yet to be elucidated, model calculations suggest that they can be important sources of SOA.

In this study laboratory experiments were performed in the ICE-HT environmental chamber in an effort to shed light on the aging of toluene and benzene photo-oxidation SOA products. Atmospheric levels of OH radicals were produced by HONO photolysis under UV illumination. Particle and gas-phase concentrations were measured by a combination of instruments. An Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and a Scanning Mobility Particle Sizer (SMPS) characterized the particulate phase. A thermodenuder system was deployed for the measurement of the SOA volatility changes. A Proton Transfer Reaction Mass Spectrometer (PTR-MS) was used to measure the VOC levels, while NO<sub>x</sub> and O<sub>3</sub> were monitored by the corresponding analyzers. The effects of the OH exposure, the pre-existing particle concentration and surface area, the initial precursor levels and UV intensity on the SOA yield and oxidation state were quantified.

The O:C ratio was lower for lower SOA loadings and varied between 0.55 and 0.95. For toluene photo-oxidation experiments the O:C did not practically change as the exposure to OH radicals was increased. However, for benzene photo-oxidation SOA the O:C ratio increased with OH addition when the initial mass concentration was low (0.5 μg m<sup>-3</sup>), but it did not have any effect for higher SOA concentrations (>5 μg m<sup>-3</sup>).

Positive matrix factorization (PMF) applied to the chamber data indicated that the aromatic SOA composition can be explained by more than one factor with different oxidation states (Figure 1). The concentration of the less oxygenated factor was higher at the beginning of the SOA formation and decreased with time. The concentration of the more oxygenated factor increased during most experiments.

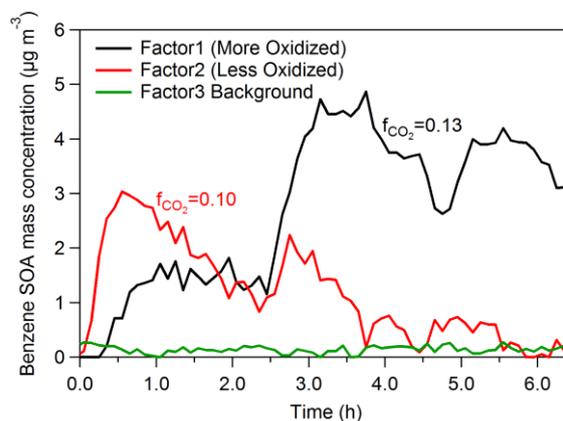


Figure 1. PMF analysis of the AMS organic aerosol spectra for a typical benzene photo-oxidation experiment.

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