Evidence for Unrecognized Anthropogenic Sources of Organosulfates and Sulfonates: Gas-Phase Oxidation of Anthropogenic Precursors in the Presence of Sulfate Aerosol

Matthieu Riva[1], Sophie Tomaz[2], Tianqu Cui[1], Ying-Hsuan Lin[1], Emilie Perraudin[2], Avram Gold[1], Elizabeth A. Stone[3], Eric Villenave[2] and Jason D. Surratt[1]

[1]Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, The University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, USA
[2]Univ. Bordeaux, EPOC-CNRS, UMR 5805, F-33405 Talence Cedex, France
[3]Department of Chemistry, University of Iowa, Iowa City, IA 52242, USA
Keywords: Organosulfates, SOA, Sulfonate, gas-phase.
Presenting author email: m.riva@unc.edu

Organosulfates are important components of atmospheric fine organic aerosol. However, many of their chemical structures, abundances and sources remain unclear. Formation of organosulfates from the oxidation of biogenic compounds (isoprene, monoterpenes, 2-methyl-3-buten-2-ol (MBO)) (Surratt et al., 2007; Iinuma et al., 2009), in the presence of acidified sulfate aerosol has been characterized in both laboratory-generated and ambient secondary organic aerosol (SOA). Enhancements of SOA mass due to increased aerosol acidity have been partially explained by the presence of organosulfates in the aerosol phase (Surratt et al., 2007; Offenberg et al., 2009).

Recent recent studies have identified and quantified aromatic organosulfates in the fine aerosol collected from several major urban locations (Staudt et al., 2014; Tao et al. 2014). Preliminary smog chamber experiments using toluene, nitrogen oxides, and acidified sulfate aerosol did not produce some of these recently identified organosulfates.

The aim of the present work was to examine the organosulfate and sulfonate formation potential arising from the photooxidation of polycyclic aromatic hydrocarbons (PAHs), which are recognized to be one of the "missing" sources of SOA, particularly in urban areas. Naphthalene and 2-methyl-naphthalene, which are two of the most abundant PAHs emitted into the gas phase and have been shown to form SOA upon photooxidation (Kautzman et al., 2010), were selected for photooxidation experiments in the UNC outdoor smog chamber in the presence of non-acidified and acidified sulfate seed aerosol. Impacts of seed aerosol composition ($MgSO_4$ or $(NH_4)_2SO_4$) and relative humidity on organosulfur compound formation were examined.

Chemical characterization of filters collected from all experiments using ultra performance liquid chromatography coupled to electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (UPLC/ESI-HR-QTOFMS) revealed the formation of organosulfates and sulfonates from the gas-phase photooxidation of the selected PAHs in the presence of sulfate aerosol (Figure 1).

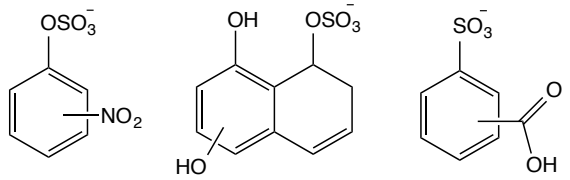

Figure 1. Structures of select organosulfates and sulfonates arising from the photooxidation of PAHs

Organosulfates and sulfonates identified in the smog chamber experiments were also measured in urban fine aerosol collected at Lahore, Pakistan, and Pasadena, USA. This work suggests that the gas-phase oxidation of PAHs in the presence of sulfate aerosol is a hitherto unrecognized source of anthropogenic secondary organosulfur, and providing new anthropogenic SOA tracers.

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