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Aromatic organosulfates in atmospheric aerosols: Synthesis, characterization, and abundance



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HIGHLIGHTS

- Homologous series of benzyl and phenyl sulfates were synthesized.
- Aromatic organosulfates were identified and quantified in ambient aerosol.
- Major ESI fragments of aromatic organosulfates are sulfite and sulfate radicals.
- Toluene chamber experiments did not generate aromatic organosulfates.

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ABSTRACT

Aromatic organosulfates are identified and quantified in fine particulate matter (PM_{2.5}) from Lahore, Pakistan, Godavari, Nepal, and Pasadena, California. To support detection and quantification, authentic standards of phenyl sulfate, benzyl sulfate, 3- and 4-methylphenyl sulfate and 2-, 3-, and 4-methylbenzyl sulfate were synthesized. Authentic standards and aerosol samples were analyzed by ultra-performance liquid chromatography (UPLC) coupled to negative electrospray ionization (ESI) quadrupole time-of-flight (ToF) mass spectrometry. Benzyl sulfate was present in all three locations at concentrations ranging from 4 to 90 pg m⁻³. Phenyl sulfate, methylphenyl sulfates and methylbenzyl sulfates were observed intermittently with abundances of 4 pg m⁻³, 2–31 pg m⁻³, 109 pg m⁻³, respectively. Characteristic fragment ions of aromatic organosulfates include the sulfite radical ($\cdot\text{SO}_3^-$, m/z 80) and the sulfate radical ($\cdot\text{SO}_4^-$, m/z 96). Instrumental response factors of phenyl and benzyl sulfates varied by a factor of 4.3, indicating that structurally-similar organosulfates have significantly different instrumental responses and highlighting the need to develop authentic standards for absolute quantitation organosulfates. In an effort to better understand the sources of aromatic organosulfates to the atmosphere, chamber experiments with the precursor toluene were conducted under conditions that form biogenic organosulfates. Aromatic organosulfates were not detected in the chamber samples, suggesting that they form through different pathways, have different precursors (e.g. naphthalene or methyl-naphthalene), or are emitted from primary sources.

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1. Introduction

Sulfate esters (a.k.a. organosulfates) are ubiquitous in atmospheric aerosols, having been detected in remote, urban, forested, marine, and arctic locations worldwide (Romero and Oehme, 2005; Surratt et al., 2007; Frossard et al., 2011; Kristensen and Glasius,

2011; Mazzoleni et al., 2012; Stone et al., 2012). Monosulfate esters are strong acids with pK_a values estimated below -3 (Guthrie, 1978), so they are deprotonated ($R-O-SO_3^-$) in environmental systems. These negatively charged molecules are highly water-soluble and non-volatile, such that they remain in the particle phase in the atmosphere. Organosulfates may play a role in climate forcing, by direct light absorption (Nguyen et al., 2012) and/or by affecting aerosol hygroscopicity due to their acidic and amphiphilic nature. They also help to reconcile the under-predictions of particle-phase organic carbon in atmospheric models by providing a means to account for acid-catalyzed secondary organic aerosol (SOA) formation (Iinuma et al., 2013; Pye et al., 2013).

The total atmospheric abundance of organosulfates has been estimated to range from 4 to 30% of fine particle organic mass (Surratt et al., 2008; Frossard et al., 2011; Stone et al., 2012). These estimates remain highly uncertain due to the lack of quantitation standards and direct measurement techniques. Tolocka and Turpin (2012) calculate the upper limit of organosulfate contributions to fine particle ($PM_{2.5}$) organic mass at 5–10% for background locations in the United States. Meanwhile, individual organosulfate species account for less than 1% of organic mass (Iinuma et al., 2009; Olson et al., 2011; Kundu et al., 2013), indicating that organosulfate concentrations are not dominated by a few highly abundant species and, instead, are present in a wide range of chemical forms.

The chemical structures of organosulfates range from small molecules to high-molecular weight organic matter (Stone et al., 2009), with a high oxygen-to-carbon ratio (Mazzoleni et al., 2012; Stone et al., 2012). Qualitative surveys of organosulfates have revealed that they are largely aliphatic in structure and also contain hydroxy, carboxylic acid, and nitrooxy functional groups (Lin et al., 2012). Among the most abundant and ubiquitous organosulfates are those derived from isoprene and isoprene oxidation products (Zhang et al., 2012; Lin et al., 2013b); these small, multi-functional organosulfates have been widely observed in ambient aerosol (Surratt et al., 2007; Kristensen and Glasius, 2011; Stone et al., 2012), and used as markers of isoprene-derived SOA in field experiments (Zhang et al., 2012; Lin et al., 2013b).

Aromatic organosulfates, containing an intact aromatic ring, have recently been observed in ambient aerosol in Lahore, Pakistan (Stone et al., 2012; Kundu et al., 2013) and in urban sites in East Asia in low abundance (Lin et al., 2012). Kundu et al. (2013) unequivocally identified benzyl sulfate against a synthesized authentic standard, quantified its monthly-average concentration in $PM_{2.5}$ ($0.05\text{--}0.50\text{ ng m}^{-3}$).

The current study builds on the tentative identification of homologous series of phenyl and benzyl sulfates with methyl substituents by Kundu et al. (2013). Series of phenyl and benzyl sulfates were synthesized and confirmed as constituents of fine particulate matter. These standards were used to study their mass spectra and response factors under negative ESI, and to evaluate their abundance in atmospheric aerosols from three distinct urban locations: Lahore, Pakistan, Godavari, Nepal, and Pasadena, California, USA. The potential for secondary formation of aromatic organosulfates from toluene was also examined (Zhang et al., 2012).

2. Materials and methods

2.1. Synthesized product characterization

Aromatic organosulfates standards were characterized by high resolution mass spectrometry (HRMS, Micromass Q-ToF Premier, Waters) with negative ESI and 1H nuclear magnetic resonance (NMR, Bruker DRX, 400 MHz). Phenyl sulfates were also characterized by ^{13}C NMR. Standardization of the aromatic organosulfates

was performed in D_2O using 1H NMR (Varian 300 MHz). For quantification purposes, dichloroacetic acid (DCA) was used as an internal standard, following Olson et al. (2011). Phenols and benzyl alcohols were obtained from Acros Organics or Sigma Aldrich and were used without further purification.

2.2. General procedure for the synthesis of phenyl sulfates

The reagent 2,2,2-trichloroethyl chlorosulfate (TCE) was prepared from trichloroethanol and sulfuryl chloride following Hedayatu et al. (1971). A solution of TCE in dry tetrahydrofuran (THF, 10 mL) was added dropwise to phenols (1.0 equiv), triethylamine (1.2 equiv), 4-dimethylaminopyridine (DMAP, 1.2 equiv), in dry THF (40 mL) and was stirred for 2 h (Liu et al., 2004; Li et al., 2010). The reaction mixture was then extracted with ethyl acetate and washed with H_2O , 1.0 N HCl, and saturated brine. The organic layer was then dried with Na_2SO_4 and solvent removed under vacuum. The resulting white residue was purified by silica gel column chromatography with hexane and ethyl acetate (10:1, v/v) as mobile phase. The TCE-sulfate ester was then dissolved in methanol and excess ammonium formate and zinc powder were added to generate the free sulfate ester. Reaction progress was monitored with thin-layer chromatography. The product was purified with column chromatography on silica gel with dichloromethane, methanol, and ammonium hydroxide (30:6:1, v/v/v) as mobile phase. Following vacuum filtration, excess solvent was removed under reduced pressure and the product dried with light heating. The reaction scheme is shown in Fig. 1.

2.2.1. Phenyl sulfate, ammonium salt

Yield: 31%; purity: 93%; white solid; 1H NMR (400 MHz, CD_3OD): δ /ppm 7.12–7.38 (m, 5H); ^{13}C NMR (400 MHz, CD_3OD): δ /ppm 122.2, 125.5, 129.8, 153.7; HR-MS (ESI, negative) m/z (relative intensity, %): 172.9903 (17, $C_6H_5O_4S^-$), 93.0328 (100), 79.9559 (10).

2.2.2. 3-Methylphenyl sulfate, ammonium salt

Yield: 64%; purity 85%; white solid; 1H NMR (400 MHz, CD_3OD): δ /ppm 2.32 (s, 3H), 6.97–7.21 (m, 4H); ^{13}C NMR (400 MHz, CD_3OD): δ /ppm 21.3, 119.3, 122.9, 126.8, 129.9, 140.4, 153.6; HR-MS (ESI, negative) m/z (relative intensity, %): 187.0061 (17, $C_7H_7O_4S^-$), 107.0484 (100), 79.9561 (10).

2.2.3. 4-Methylphenyl sulfate, ammonium salt

Yield: 39%; purity: 85%; white solid; 1H NMR (400 MHz, CD_3OD): δ /ppm 2.24 (s, 3H), 7.05–7.10 (m, 4H); ^{13}C NMR (400 MHz, CD_3OD): δ /ppm 20.9, 122.5, 130.7, 135.7, 151.8; HR-MS (ESI, negative) m/z (relative intensity, %): 187.0061 (19, $C_7H_7O_4S^-$), 107.0486 (100), 79.9560 (17).

2.3. General procedure for the synthesis of benzyl sulfates

Benzyl and methylbenzyl sulfates were synthesized following Olson et al. (2011), wherein benzyl alcohol, 2-, 3-, and 4-methylbenzyl alcohols were dissolved in acetonitrile with N,N -diisopropylethylamine (DIEA). The solution was cooled to $0\text{ }^\circ C$ before slow addition of chlorosulfonic acid. The reaction was allowed to proceed in an ice bath for 3 h, prior to removal of acetonitrile under reduced pressure. The resulting product mixture was liquid and was not subjected to further purification.

2.3.1. Benzyl sulfate

Purity: 44%; 1H NMR (400 MHz, D_2O): δ /ppm 5.03 (s, 2H), 7.37–7.44 (m, 5H); HR-MS (ESI, negative) m/z (relative intensity, %): 187.0049 (58, $C_7H_7O_4S^-$), 107.0483 (4), 95.9507 (100), 80.9639 (21), 79.9553 (11).

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