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Supplement of

Determination of atmospheric organosulfates using HILIC chromatography with MS detection

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Extended discussion of the observation and formation of multiple isomers of organosulfates with formulas $C_5H_{11}O_7S^-$, $C_5H_9O_7S^-$, and $C_5H_7O_7S^-$

Proposed structures for organosulfates with molecular formulas of $C_5H_{11}O_7S^-$ (m/z 215), $C_5H_9O_7S^-$ (m/z 213) and $C_5H_7O_7S^-$ (m/z 211) are shown in Tables S1, S2 and S3, respectively. One enantiomeric form of each isomer is shown. The BEH amide column is achiral and will not resolve enantiomers, but is capable of resolving diastereomers and conformational isomers. The proposed structures for $C_5H_{11}O_7S^-$ are based upon the acid-catalyzed ring-opening of each of the four isomers of IEPOX observed as photooxidation products of isoprene: β 1-IEPOX, β 4-IEPOX, δ 1-IEPOX and δ 4-IEPOX (Paulot et al., 2009). In the presence of acid and sulfate, IEPOX will undergo ring-opening with sulfate as a nucleophile, forming methyltetrol sulfates (Surratt et al., 2010). The epoxide ring opening is regioselective; the nucleophile preferentially attacks tertiary carbons, inverting the stereochemistry at this carbon. If a tertiary carbon is part of the epoxide, the nucleophile preferentially attacks the least substituted carbon (i.e., primary > secondary).

Considering the ring-opening of the four IEPOX isomers elucidated by Paulot et al. (2009) and the regioselectivity of epoxide ring opening, four major isomers of $C_5H_{11}O_7S^-$ (m/z 215) are expected to form, as shown in Table S1. Specifically, β 1-IEPOX yields product **1**, β 4-IEPOX yields product **1**, δ 1-IEPOX yields products **3** and **4**, and δ 4-IEPOX yields products **1** and **2**. These major products are expected to correspond to the four major peaks observed for $C_5H_{11}O_7S^-$ (m/z 215) in Figure 4. Additional products **5-8** are suggested to form as minor products due to nucleophile attack on the secondary carbon of β 1-IEPOX, β 4-IEPOX and δ 1-IEPOX, and the primary carbon of δ 4-IEPOX. These expected minor products likely contribute to the two minor chromatographic peaks for $C_5H_{11}O_7S^-$ (m/z 215) eluting at 4.51 and 4.81 minutes in Figure 4.

Organosulfates with the formula $C_5H_9O_7S^-$ (m/z 213) have been shown to form in chamber studies with isoprene as the precursor gas (Surratt et al., 2008) and are related to the organosulfates with formula $C_5H_{11}O_7S^-$ (m/z 215) by loss of H_2 and an increase of one unit of unsaturation. It is plausible to consider that one of the primary alcohols in the $C_5H_{11}O_7S^-$ (m/z 215) organosulfate is oxidized to an aldehyde in

the atmosphere, losing one unit of unsaturation and giving the product $C_5H_9O_7S^-$ (m/z 213). The resulting oxidation product for either **1** or **2** is a γ -hydroxyaldehyde, which is in equilibrium with the intramolecular hemiacetal form (a.k.a. lactol form) shown in Table S2. The formation of five- and six-membered ring is thermodynamically favored over the straight-chain form. Hence, products **9** - **16** in Table S2 are proposed as structures for $C_5H_9O_7S^-$ (m/z 213), and are suggested to form from the oxidation of products **1** and **2** to an aldehyde, followed by intramolecular hemiacetal formation. The order of elution of $C_5H_9O_7S^-$ (m/z 213) and $C_5H_{11}O_7S^-$ (m/z 215) from the BEH amide column supports this structural assignment, as the proposed $C_5H_9O_7S^-$ (m/z 213) product contains one less hydroxyl group, decreasing the strength of hydrogen-bonding interactions with the stationary phase compared to $C_5H_{11}O_7S^-$ (m/z 215), causing it to elute from the column earlier.

Similarly, organosulfates with formulas $C_5H_7O_7S^-$ (m/z 211) have been shown to form in chamber studies with isoprene as the precursor gas (Surratt et al., 2008) and are related to the organosulfates with formula $C_5H_9O_7S^-$ (m/z 213) with an increase of one unit of unsaturation. It is plausible to consider that the γ -hydroxyaldehyde from products **1** and **2** is further oxidized to a carboxylic acid in the atmosphere, by addition of oxygen. The resulting product is a γ -hydroxycarboxylic acid, which in the presence of dilute acids immediately undergoes cyclization and loss of water to form a lactone shown in Table S3. The formation of the five-membered lactone ring imparts stability on the molecule compared to the straight chain form, making the ring the thermodynamically favored product. Hence, products **17** – **24**, shown in Figure S2 are proposed structures for $C_5H_7O_7S^-$ (m/z 211). The order of elution from the BEH amide column again supports this assignment, with $C_5H_7O_7S^-$ (m/z 211) having only one fewer hydroxyl group than $C_5H_9O_7S^-$ (m/z 213) and two fewer hydroxyl groups than $C_5H_{11}O_7S^-$ (m/z 215). With fewer hydrogen-bond donor sites, the strength of the interactions between $C_5H_7O_7S^-$ (m/z 211) and the stationary phase decrease, causing it to elute earlier.

Table S1: Proposed structures for $C_5H_{11}O_7S^-$ (m/z 215) that can be formed by acid catalyzed IEPOX ring opening in the presence of sulfate. Only one enantiomeric form of each isomer is shown.

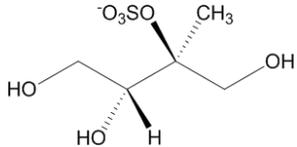
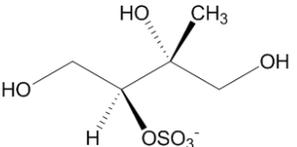
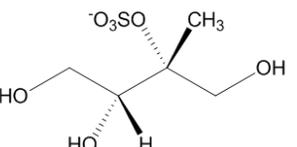
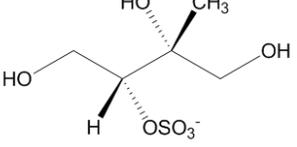
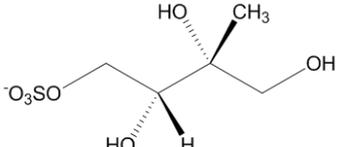
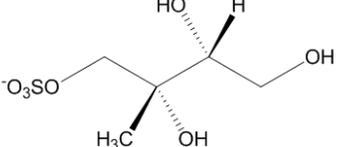
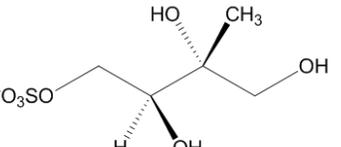
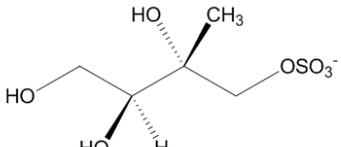
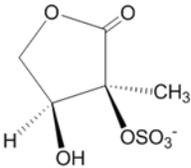
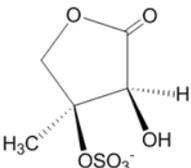
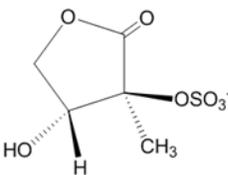
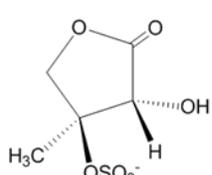
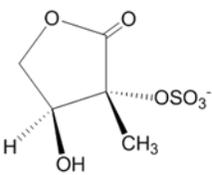
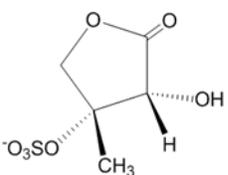
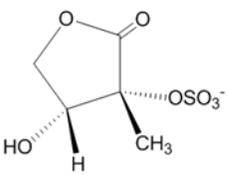
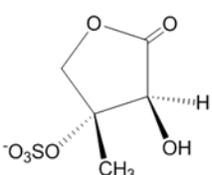
Major isomers of $C_5H_{11}O_7S^-$ (m/z 215)	Minor isomers of $C_5H_{11}O_7S^-$ (m/z 215)
<p>1</p>  <p>(2<i>S</i>,3<i>R</i>)-1,3,4-trihydroxy-2-methylbutyl-2-sulfate</p>	<p>5</p>  <p>(2<i>S</i>,3<i>R</i>)-1,3,4-trihydroxy-3-methylbutyl-2-sulfate</p>
<p>2</p>  <p>(2<i>R</i>,3<i>R</i>)-1,3,4-trihydroxy-2-methylbutyl-2-sulfate</p>	<p>6</p>  <p>(2<i>R</i>,3<i>R</i>)-1,3,4-trihydroxy-3-methylbutyl-2-sulfate</p>
<p>3</p>  <p>(2<i>R</i>,3<i>R</i>)-2,3,4-trihydroxy-3-methylbutyl sulfate</p>	<p>7</p>  <p>(2<i>R</i>,3<i>R</i>)-2,3,4-trihydroxy-2-methylbutyl sulfate</p>
<p>4</p>  <p>(2<i>S</i>,3<i>R</i>)-2,3,4-trihydroxy-3-methylbutyl sulfate</p>	<p>8</p>  <p>(2<i>R</i>,3<i>S</i>)-2,3,4-trihydroxy-2-methylbutyl sulfate</p>

Table S2: Proposed structures for $C_5H_9O_7S^-$ (m/z 213), that are proposed to form from the oxidation of a primary alcohol in $C_5H_{11}O_7S^-$ (m/z 215) to an aldehyde, followed by intramolecular hemiacetal formation. Only one enantiomeric form of each isomer is shown.

Major isomers of $C_5H_9O_7S^-$ (m/z 213)	
<p>9</p> <p>(2S,3S,4S)-2,4-dihydroxy-3-methyltetrahydrofuran-3-yl-3-sulfate</p>	<p>13</p> <p>(3S,4S,5R)-4,5-dihydroxy-3-methyltetrahydrofuran-3-yl-3-sulfate</p>
<p>10</p> <p>(2S,3S,4R)-2,4-dihydroxy-3-methyltetrahydrofuran-3-yl-3-sulfate</p>	<p>14</p> <p>(3S,4R,5R)-4,5-dihydroxy-3-methyltetrahydrofuran-3-yl-3-sulfate</p>
<p>11</p> <p>(2S,3R,4S)-2,4-dihydroxy-3-methyltetrahydrofuran-3-yl-3-sulfate</p>	<p>15</p> <p>(3R,4R,5R)-4,5-dihydroxy-3-methyltetrahydrofuran-3-yl-3-sulfate</p>
<p>12</p> <p>(2S,3R,4R)-2,4-dihydroxy-3-methyltetrahydrofuran-3-yl-3-sulfate</p>	<p>16</p> <p>(3R,4S,5R)-4,5-dihydroxy-3-methyltetrahydrofuran-3-yl-3-sulfate</p>

Table S3: Proposed structures for $C_5H_7O_7S^-$ (m/z 211) that is proposed to form from the oxidation of a primary alcohol in $C_5H_{11}O_7S^-$ (m/z 215) to a carboxylic acid, followed by intramolecular lactone formation and loss of water. Only one enantiomeric form of each isomer is shown.

Major isomers of $C_5H_7O_7S^-$ (m/z 211)	
<p>17</p>  <p>(3S,4S)-4-hydroxy-3-methyl-tetrahydro-2-furanone-3-sulfate</p>	<p>21</p>  <p>(3S,4S)-4-hydroxy-3-methyl-tetrahydro-5-furanone-3-sulfate</p>
<p>18</p>  <p>(3S,4R)-4-hydroxy-3-methyl-tetrahydro-2-furanone-3-sulfate</p>	<p>22</p>  <p>(3S,4R)-4-hydroxy-3-methyl-tetrahydro-5-furanone-3-sulfate</p>
<p>19</p>  <p>(3R,4S)-4-hydroxy-3-methyl-tetrahydro-2-furanone-3-sulfate</p>	<p>23</p>  <p>(3R,4R)-4-hydroxy-3-methyl-tetrahydro-5-furanone-3-sulfate</p>
<p>20</p>  <p>(3R,4R)-4-hydroxy-3-methyl-tetrahydro-2-furanone-3-sulfate</p>	<p>24</p>  <p>(3R,4S)-4-hydroxy-3-methyl-tetrahydro-5-furanone-3-sulfate</p>

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