

## Sulfate radical-initiated formation of isoprene-derived organosulfates in atmospheric aerosols

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Recent studies show that organosulfates contribute significantly to the mass of ambient secondary organic aerosol (SOA). Up to 80% of the particles collected in the free troposphere above tropical regions and even 95% of particles in urban regions can contain organosulfates<sup>1,2</sup>. The contribution to the organic mass was estimated to be up to 30% in ambient aerosols and up to 20% for isoprene-derived organosulfates<sup>1,3</sup>. The formation of the isoprene-derived organosulfate with  $m/z$  215 ( $C_5H_{11}O_7S^-$ ) is explained by the acid catalyzed sulfation of isoprene epoxydiol (IEPOX) that is suggested to form from the OH oxidation of isoprene under  $NO_x$ -free conditions<sup>4,5</sup>.

Apart from the  $m/z$  215 of the IEPOX originating organosulfate,  $C_2$  to  $C_4$  organosulfates that can be related to isoprene oxidation products are found in ambient and laboratory generated SOA<sup>1,2,6</sup>. These compounds have been suggested to form from the isoprene oxidation originating semi-volatile polar compounds that react with sulfate radicals in the particle phase<sup>7</sup>. Very recent study reports a dependency of the fraction of organosulfates in particle mass on the season and photochemical activity, supporting the aqueous phase formation mechanism of these organosulfates through the reaction of semi-volatile polar compounds with sulfate radicals<sup>8</sup>.

In the present study, laboratory experiments were performed to study the sulfate radical initiated oxidation of methacrolein and methyl vinyl ketone in the aqueous phase. Furthermore, a series of smog chamber experiments were performed to investigate their relevance in aqueous phase isoprene, methacrolein and methyl vinyl ketone SOA formation. Samples from aqueous phase experiments and extracts from filters collected after chamber experiments were analysed with UPLC/(-)ESI-IMS-QTOFMS.

Highly oxidized organosulfates were found in all the samples with  $m/z$  values corresponding to the species found in ambient particle samples. This study shows that sulfate radical reactions in the aqueous phase can partly explain the formation of these organosulfates from methacrolein and methyl vinyl ketone.

Organosulfate formation plays an important role in atmospheric aerosol processing as they do not only increase organic particle mass but also influence the CCN activity and, deplete the fraction of acidic sulfate in the ambient particle matter<sup>1,7</sup>.

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