

Formation of organosulfates from the sulfate radical induced oxidation of methacrolein and methyl vinyl ketone

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Keywords: Isoprene, Sulfate radical, SOA
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Recent studies show that organosulfates are an important fraction of ambient secondary organic aerosol (SOA). The contribution to the organic mass was estimated to be up to 30% in ambient aerosols and up to 20% for isoprene-derived organosulfates (Froyd et al., 2010, Surratt et al., 2008). The isoprene-derived organosulfate with m/z 215 ($C_5H_{11}O_7S^-$) is often reported to be the most abundant single organosulfate compound. Its formation 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 (Paulot et al., 2009, Iinuma et al., 2007).

C_2 to C_4 organosulfates are found in ambient and laboratory generated SOA that can be related to isoprene oxidation products (Froyd et al., 2010, Surratt et al., 2007, Gómez-González et al., 2008). These compounds have been suggested to form from the sulfate radical induced oxidation of semi-volatile isoprene oxidation products in the particle phase (Galloway et al., 2009, Perri et al., 2010, Nozière et al., 2010). Here, the formation of organosulfates originating directly from methacrolein (MACR) or methyl vinyl ketone (MVK) with m/z of 199 and 183, are of interest because their existence was shown in studies of ambient aerosols (Froyd et al., 2010, Gómez-González et al., 2008). A sulfate radical reaction with unsaturated compounds is as fast as other organosulfate formation mechanisms and is even competitive to the reaction with hydroxyl radicals (Nozière et al., 2010, Buxton et al., 2000). Supporting the theory of the contribution of a radical mechanism in the formation, a very recent study reports a dependency of the fraction of organosulfates in particle mass on the season and photochemical activity (Tolocka and Turpin, 2012). This might indicate the involvement of solution phase radical chemistry.

In the present study, experiments on the sulfate radical induced oxidation of methacrolein and methyl vinyl ketone were performed in bulk aqueous phase as well as in an aerosol chamber, to investigate their relevance in aqueous phase SOA formation. Samples from aqueous phase experiments and extracts from filters collected after chamber experiments were analysed with UPLC/(-)ESI-IMS-QTOFMS.

All the samples showed the abundance of highly oxidized organosulfates with m/z values corresponding to the species found in ambient particle samples (see Table 1). Chamber experiments showed a distinct increase in particle mass for experiments with sulfate radical precursor ($K_2S_2O_8$) in the seed particles (see Figure 1).

Table 1. Selected organosulfate species of MACR and MVK with elemental composition.

Reactant	m/z [M-H]	Formula
MVK/	153	$C_3H_5O_5S$
MACR	183	$C_4H_7O_6S$
	199	$C_4H_7O_7S$

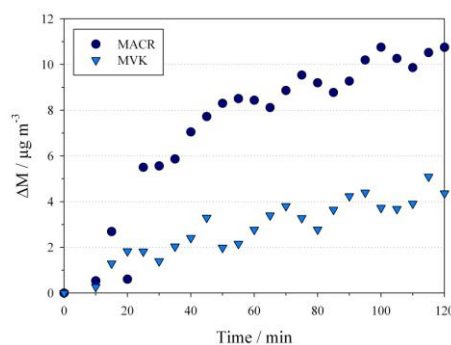


Figure 1. Time series of particle mass increase (ΔM) for MACR and MVK with $K_2S_2O_8/H_2SO_4$ as seed particles.

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.

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