

A new source of methyl glyoxal in the aqueous phase

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Volatile organic compounds (VOCs) are emitted from biogenic and anthropogenic sources in large quantities (1300 Tg carbon year⁻¹; Goldstein and Galbally, 2007). The oxidation of VOCs in the atmosphere leads to the formation of semivolatile organic compounds which can partition into the particle phase and thus they contribute to the formation of secondary organic aerosol (SOA). However, several literature studies have shown a discrepancy of the global SOA mass between model predictions and field studies (Hallquist *et al.*, 2009). So far unknown SOA sources are a possible reason for this discrepancy. Thus the oxidation within the aqueous particle phase (aqSOA) can be considered as an additional source of SOA (Ervens *et al.*, 2011, Herrmann *et al.*, 1999). Tentative aqSOA precursor compounds are carbonyl compounds because they are ubiquitous in the atmospheric multiphase system and they directly participate in gas-, particle- and aqueous phase chemistry. Methyl ethyl ketone (MEK) is one important atmospheric relevant carbonyl compounds as it is detected in significant amounts in the gas phase as well as in cloud water, ice, fog and rain (Grosjean, 1982; van Pinxteren *et al.*, 2005). Based on this it can be expected that MEK contribute to the aqSOA formation processes.

For this reason, numerous experiments were conducted to investigate the reaction of MEK and its oxidation products in the aqueous phase. The oxidation was conducted over a reaction period of four hours with a 0.1 mmol L⁻¹ aqueous MEK solution and 2 mmol L⁻¹ H₂O₂ as OH radical source. In addition the photolysis and the non-radical reaction of MEK with H₂O₂ was conducted. Oxidation products were identified and quantified after derivatisation of the carbonyl compounds with PFBHA (O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride) by gas chromatography connected to mass spectrometry (GC/MS).

Several oxidation products were identified from the oxidation with OH radicals including 2,3-butanedione, (25% molar yield), hydroxyacetone (3% molar yield) and methyl glyoxal (3% molar yield). The comparatively low molar yield of methyl glyoxal can be explained by further reactions with OH radicals and thus it can be assumed that the real molar yield is significantly higher. For this reason a reaction mechanism was developed based on the obtained results.

Methyl glyoxal is often related to the aqSOA formation (Herrmann *et al.*, 1999; Ervens *et al.*, 2011), consequently the OH radical oxidation of MEK has to be considered as an additional aqSOA source.

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