Peroxy radicals in the oxidation process of Glyoxal, Methylglyoxal and Hydroxyacetone in aqueous solution: Spectroscopy and Kinetics

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Volatile organic compounds (VOCs) are introduced into the troposphere in large amounts from biogenic as well as anthropogenic sources. For example, the oxidation of isoprene results in the formation of semivolatile carbonyl compounds such as glyoxal and methylglyoxal, while biomass combustion can lead to hydroxyacetone. Furthermore, these oxygenated VOC oxidation products might be important for the formation of secondary organic aerosol (SOA) by partitioning between gas- and liquid phase of pre-existing particles. Glyoxal, methylglyoxal, and hydroxyacetone can be further oxidized by radicals, e.g., OH and NO_3, in the aqueous phase (cloud droplets, fog, rain, deliquescent particles) leading to substituted organic acids.

In case of glyoxal, two concepts exist in the literature to describe the oxidation pathway via alkyl radical to the peroxy radical by the addition of molecular oxygen. The first one[1] states that for dilute solutions (< 1 mM, typical concentration for cloud water) the peroxy radical is formed with a rate constant of $k = 1 \times 10^9\ M^{-1}\ s^{-1}$. The second concept[2] assumes that for solutions with higher concentrations > 1 mM the formation of the peroxy radicals is a minor reaction pathway because of a lower rate constant of $k = 1 \times 10^6\ M^{-1}\ s^{-1}$ estimated after Guzman et al., 2006[3].

The difference in the rate constants of the oxygen addition is of about three orders of magnitude and thus leads to different oxidation products and yields in the aqueous solution. In order to investigate the importance of the peroxy radical formation and alkyl radical recombination in more detail laboratory studies have been performed oxidizing glyoxal with varying oxygen concentrations. By means of spectroscopic experiments the decay of the formed glyoxyl radicals and glyoxyl peroxy radicals were studied in low and high concentrated oxygen solutions using a laser photolysis long path absorption setup (LP-LPA).

The spectroscopic investigations of the peroxy radicals were performed with a LP-LPA setup including a gated ICCD camera coupled with a grating spectrograph in combination with a deuterium lamp. For the kinetic investigation of the peroxy radicals, an argon-ion laser (λ = 244 nm) and a HeCd-laser (λ = 325 nm) was used.

The results of the spectroscopic and kinetic measurements will be presented. Additionally, the T-dependent decay of the peroxy radicals formed in the oxidation of methyglyoxal and hydroxyacetone was also studied using the same experiment.

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