

**Laboratory studies of the peroxy radicals in the oxidation process of Glyoxal,
Methylglyoxal and Hydroxyacetone in aqueous solution**

T. Schaefer and H. Herrmann

Leibniz Institute for Tropospheric Research, Leipzig

E-mail: schaefer@tropos.de

Large amounts of volatile organic compounds (VOCs) are emitted into the atmosphere from biogenic and anthropogenic sources. The emitted VOCs can be further oxidized in the gas phase as well as in the aqueous phase (cloud droplets, fog, rain and deliquescent particles) to semivolatile carbonyl compounds. For example, the carbonyl compounds glyoxal and methylglyoxal can be produced by the oxidation process of isoprene, whereas hydroxyacetone can be formed by the combustion of biomass. Additionally, these semivolatile carbonyl compounds might be important for the formation of secondary organic aerosol (SOA) by partitioning between gas- and liquid phase of pre-existing particles. The oxidation process can be initiated, e.g., by radicals (OH and NO₃), which lead to the formation of peroxy radicals and then to substituted organics. There are still uncertainties concerning the oxidation pathways of glyoxal, after H-atom abstraction by, e.g., OH radicals, via alkyl radical to the peroxy radical under addition of molecular oxygen. One concept^[1] claims that for dilute solutions (< 1 mM, typical concentration for cloud water) the peroxy radical is formed with a rate constant of $k = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. 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 $k = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ 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. Laboratory studies of glyoxal oxidation under varying oxygen concentrations have been performed in order to investigate the importance of the peroxy radical formation and alkyl radical recombination in more detail. The formation and 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 OH radicals were generated directly in the reaction cell by the photolysis of hydrogen peroxide (H₂O₂) at $\lambda = 248 \text{ nm}$. Additionally, the T-dependent decay of the peroxy radicals formed in the oxidation of methylglyoxal and hydroxyacetone was also studied using the same experiment.

- 1 Buxton, G. V., Malone, T. N. and Salmon, G. A., *J. Chem. Soc. Faraday Trans.*, 1997, 93, 2889–2891.
- 2 Guzman, M. I., Colussi, A. J. and Hoffmann, M. R., *J. Phys. Chem. A*, 2006, 110, 3619–3626.
- 3 Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P. and Turpin, B. J., *Atmos. Chem. Phys.*, 2010, 10, 10521-10539.