

Oxidation of Glyoxal in the Aqueous Phase

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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 form semivolatile carbonyl compounds. For example, the carbonyl compound glyoxal can be produced by the oxidation process of isoprene. 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. In the gas phase as well as in the aqueous phase (cloud droplets, fog, rain and deliquescent particles) these compounds can be further oxidized, e.g., by radicals (OH and NO₃) leading to peroxy radicals and then to substituted organics. Two concepts exist in the literature to describe the glyoxal oxidation pathway via alkyl radicals to the peroxy radicals by the addition of molecular oxygen. The first one^[1] states that peroxy radical formation occurs with a rate constant of $k = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The second concept^[2] assumes that this is a minor reaction pathway because of the lower rate constant of $k = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. The difference in the rate constants of the oxygen addition is of about three orders of magnitude which might lead to different oxidation products and yields in aqueous solution. In the present work, 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). To clarify the difference a method introduced by Adams et al., 1969^[3] to measure the rate constant of the oxygen addition on alkyl radical was modified for laser flash photolysis conditions and successfully applied. In this study a rate constant for the addition reaction of molecular oxygen of $k = 8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ was measured. This clearly indicates that the oxidation of glyoxal by OH radicals via H abstraction reaction to the glyoxyl alkyl radical followed by the addition of oxygen to the glyoxyl peroxy radical which, in conclusion, can be well described by the concept of Buxton et al., 1997^[1].

- 1 Buxton, G. V., T. N. Malone, and G. A. Salmon (1997), *J. Chem. Soc. Faraday Trans.*, 93 (16), 2889-2891.
- 2 Lim, Y. B., Y. Tan, M. J. Perri, S. P. Seitzinger, and B. J. Turpin (2010), *Atmos. Chem. Phys.*, 10, 10521-10539.
- 3 Adams, G. E., and R. L. Willson (1969), *Trans. Faraday Soc.*, 65, 2981-2987