

T-dependent oxidation of hydroxyaldehydes in the aqueous phase with atmospherically relevant radicals

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Aromatic aldehydes are a major gas-phase constituents of troposphere, which play a fundamental role in the chemistry of polluted regions. They can be directly emitted from vast variety of anthropogenic and biogenic sources. Apart from those, they could be also transformed in the atmosphere by photolysis and/or can get oxidized in presence of atmospheric oxidants such as radicals, yielding hydroxyaldehydes as the main final products. Even though the formation process takes place primarily in the atmospheric gas phase, the produced hydroxyaldehydes are considered as water-soluble compounds due to their Henry's Law constants, and are therefore capable of undergoing efficient phase transfer to cloud droplets, fog, haze, rain, and deliquescent aerosols, commonly referred as atmospheric aqueous phase. Dissolved organic gases can additionally be oxidized in the aqueous phase, where they contribute to aerosol mass production during cloud evaporation event, forming aqueous-phase secondary organic aerosols (aqSOAs). The potential formation of SOAs in the aqueous phase was estimated by a model prediction, where net global production rate accounts for 10 Tg yr⁻¹ to 50 Tr yr⁻¹. Additionally, there is a lack of aqueous-phase kinetic data with atmospherically relevant radicals that could be used to achieve an accurate description and model prediction of multiphase tropospheric chemistry. Accordingly, in the present study the second-order rate constants for the oxidation reactions of glyceraldehyde, glycolaldehyde, and lactaldehyde with hydroxyl radicals ($\cdot\text{OH}$), sulfate radicals ($\text{SO}_4\cdot^-$), and nitrate radicals ($\text{NO}_3\cdot$) in the aqueous phase were determined. In case of glycolaldehyde, the subsequent radical-initiated second-order rate constants ($k_{2\text{nd}}$) at 298 K were obtained: $k(\cdot\text{OH}) = (1.3 \pm 0.1) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, $k(\text{SO}_4\cdot^-) = (2.9 \pm 0.2) \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$, and $k(\text{NO}_3\cdot) = (3.9 \pm 1.1) \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$, respectively. In addition, the temperature-dependencies of the rate constants were determined in ranges between 278 and 318 K. Through the obtained rate constants and their T-dependencies, the degradation of hydroxyaldehydes with atmospherically relevant radicals in the aqueous-phase can be currently assigned, by which the predictive capabilities of models could be reached. These findings reveal the importance of aqueous phase conversion of gaseous oxidation products, contributing to the budget of important tropospheric aqueous phase carbonyls, which are important for better understanding the formation pathway of in-cloud processed SOAs.