OH radical reactions with oxygenated organic compounds in aqueous solution: A laser flash photolysis investigation

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Oxygenated organic compounds are omnipresent in the troposphere, due to their strong emissions from either biogenic or anthropogenic sources. The degradation and conversion of these compounds is often initiated by radical reactions and will occur in the gas phase as well as in the aqueous phase of the troposphere, which is formed by cloud droplets, fog, haze, rain or hygroscopic particles containing 'aerosol liquid water (ALW)'.

In the present study, the temperature dependent OH radical reactions with oxygenated organic compounds in the aqueous phase have been investigated, by using a laser flash photolysis setup. To determine the rate constants, the OH radical - thiocyanate anion - competition kinetic method has been used. The following rate constants for OH radical oxidation reactions of the oxygenated organic compounds have been obtained: acetone (2-propanone) $k_{298 \text{ K}} = (1.2 \pm 0.2) \cdot 10^8 \text{ I mol}^{-1} \text{ s}^{-1}$, 1-hydroxypropan-2-one $k_{298} \, \text{K} = (1.1 \pm 0.1) \cdot 10^9 \, \text{I mol}^{-1} \, \text{s}^{-1}$, 1,3-dihydroxy-propan-2one $k_{298 \text{ K}} = (1.5 \pm 0.1) \cdot 10^9 \text{ I mol}^{-1} \text{ s}^{-1}$, 2,3-dihydroxypropanal $k_{298 \text{ K}} = (1.3 \pm 0.1) \cdot 10^9 \text{ I mol}^{-1} \text{ s}^{-1}$ 0.03) \cdot 10⁹ I mol⁻¹ s⁻¹, butane-1,3-diol k_{298 K} = (2.5 ± 0.1) \cdot 10⁹ I mol⁻¹ s⁻¹, butane-2,3diol $k_{298 \text{ K}} = (2.0 \pm 0.02) \cdot 10^9 \text{ I mol}^{-1} \text{ s}^{-1}$ and hexane-1,2-diol $k_{298 \text{ K}} = (4.6 \pm 0.4) \cdot 10^9$ I mol⁻¹ s⁻¹. The T-dependencies of the rate constants have also been studied. With the obtained rate constants and their T-dependencies source and sink processes of oxygenated organic compound in the troposphere might be better understood through implementation in model simulations such as the chemical aqueous-phase radical mechanism (CAPRAM) to elucidate the oxidative capacity of the tropospheric aqueous phase.

^{1.} M. Chin and P. H. Wine, *Journal of Photochemistry and Photobiology A - Chemistry*, 1992, 69, 17-25.