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On the atmospheric degradation of multifunctional organic compounds by NO_3 and SO_4^- radicals in aqueous solution

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The atmospheric decomposition and transformation of a large number of organic compounds is initiated by radicals in the gas and aqueous phase. With increasing degree of oxidation and functionalization, organics become less volatile and more water soluble and partition into aqueous particles and cloud droplets where the oxidation by radicals continues. NO_3 and SO_4^- radicals dominate the atmospheric aqueous phase besides OH radicals. Within this work, temperature dependent kinetic investigations were conducted by use of a laser flash photolysis laser long path absorption (LFPLLPA) setup. Second order rate constants for the reactions of 3-methoxy-1-propanol, diethylether, methylpropylether, 2-methyloxirane-2-carbaldehyde, 2,3-dihydroxy-2-methylpropanal, pyruvic, glyoxylic and glycolic acid as well as glyoxal, methylglyoxal and glycolaldehyde with NO_3 and SO_4^- radicals were measured in a temperature range of 278 and 318 K applying pseudo-first order kinetics. The reactivity of the acids and their anions were investigated separately adjusting the pH to pH 1 or pH 8 for the acid or the anion form, respectively. From these measurements, activation parameters were derived. Measured k_{2nd} range from 10^6 - 10^8 M^1 s^1. The kinetic and thermodynamic parameters as well as reaction mechanisms will be discussed within this contribution.