

NO₃-radical reactions of poly-substituted phenols in aqueous solution

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The degradation and conversion of organic compounds, such as phenols, in the atmosphere is often initiated by radical reactions. The NO₃-radical is a known night-time oxidant and one of the most important radical in the atmosphere besides OH. Sources of the investigated poly-substituted phenols can be either direct emissions (e.g., from combustion processes) or secondary atmospheric oxidation reactions of benzene derivatives. Oxidation reactions of poly-substituted phenols with NO₃-radicals in atmospheric aqueous phase (cloud droplets, fog, rain, deliquescent particles) can be as fast as in the gas phase, due to the possibility of a direct electron transfer mechanism in aqueous solution. The objective of this work was the description of the reactivity of the following substituted phenols (a) 4-hydroxy-3,5-dimethoxybenzoic acid, (b) 4-hydroxy-3,5-dimethoxybenzaldehyde, (c) 4-hydroxy-3-methoxybenzoic acid, (d) 3-hydroxy-4-methoxybenzoic acid, (e) 4-hydroxy-3-methoxybenzaldehyde, (f) 1,2,3-trihydroxybenzene, (g) 2,6-dimethoxyphenol, (h) 2,6-dimethylphenol, (i) 2,6-dichlorophenol and (10) 2,6-dinitrophenol towards the NO₃-radical in aqueous solution as a function of temperature. To investigate the temperature-dependent reactions a laser flash photolysis - long path laser absorption (LFP – LPLA) setup has been used. NO₃-radicals were generated by HNO₃ - photolysis at a wavelength of $\lambda = 248$ nm in aqueous solution (pH = 0.5 with HClO₄). The obtained kinetic parameter will be presented, discussed and correlated to properties of the investigated phenols, such as the bond dissociation energy (BDE), and the energy of the highest occupied molecular orbital (E_{HOMO}). The correlations obtained indicate a dominating direct electron transfer mechanism during the oxidation of the investigated phenols in aqueous solution, which is contrary to the known gas-phase reaction mechanism. Furthermore, the presented correlations can be used to assess kinetic data of NO₃-radical reactions in aqueous phase.