Reactivity of the NO_3-radical towards poly-substituted phenols in aqueous solution

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The NO_3-radical is one of the most important radicals in the atmosphere besides OH. The atmospheric decomposition or transformation of a variety of organic compounds such as phenols is initiated by these radicals. Sources of poly-substituted phenols can be direct emissions from combustion processes or secondary oxidation of benzene derivatives. In the liquid phase (cloud droplets, fog, rain, deliquescent particles), NO_3-radicals may react with substituted phenols faster than in the gas phase because there is the possibility for direct electron transfer besides the H-atom abstraction reaction mechanism [1]. It is important to investigate the fate of poly-substituted phenols because of their toxicity and the formation of toxic nitrated phenols in the liquid phase [2]. Kinetic data are necessary input parameters for tropospheric chemical modelling. For the kinetic investigation of the temperature dependent reactions of NO_3-radicals with substituted phenols a laser flash photolysis- long path laser absorption (LFP – LPLA) setup has been used. NO_3-radicals were generated in a reaction cell in aqueous solution (pH = 0.5 with $HClO_4$) by nitrate-anion photolysis ($[NO_3^-]$ = 0.05 M) at a wavelength of λ = 248 nm [3]. Second order rate constants for the reactions of NO_3 with (1) 4-hydroxy-3,5-dimethoxybenzoic acid $k_{298K} = (1{,}43 \pm 0{,}58)\cdot 10^9\ M^{-1}s^{-1}$, (2) 4-hydroxy-3,5-dimethoxybenzaldehyde $k_{298K} = (1{,}74 \pm 0{,}30)\cdot 10^9\ M^{-1}s^{-1}$, (3) 1,2,3-trihydroxybenzene $k_{298K} = (1{,}73 \pm 0{,}23)\cdot 10^9\ M^{-1}s^{-1}$, (4) 2,6-dimethoxyphenol $k_{298K} = (1{,}61 \pm 0{,}40)\cdot 10^9\ M^{-1}s^{-1}$, (5) 2,6-dimethylphenol $k_{298K} = (1{,}75 \pm 0{,}25)\cdot 10^9\ M^{-1}s^{-1}$and (6) 2,6-dichlorophenol $k_{298K} = (1{,}25 \pm 0{,}15)\cdot 10^9\ M^{-1}s^{-1}$ were determined between 278 and 318 K. Second order rate constants and the activation parameters were determined from these measurements. The obtained kinetic and the activation parameters will be discussed together with literature values.

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