# Kinetic and Product Study of the Reaction of the $NO_3$· Radical with Phenol, Benzoic Acid and their Nitration Products in Aqueous Solution

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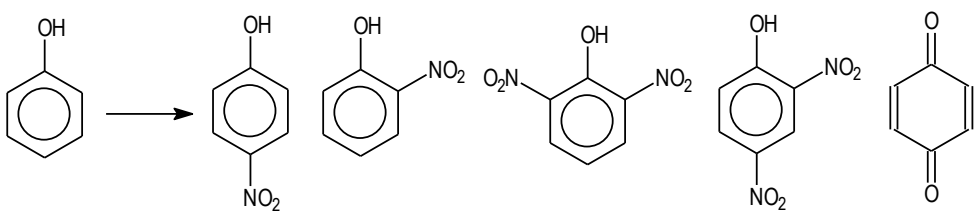
Kinetic studies of the reaction of the $NO_3$· radical with phenol and its nitration products were performed applying a laser-photolysis laser long path absorption apparatus. For the reaction of $NO_3$· with phenol a second order rate constant of $k_{phenol} = (1.8 \pm 0.3)\cdot 10^9$ $M^{-1}$ $s^{-1}$ (pH = 0 ,T = 298 K) was found. The Arrhenius expression for this reaction was determined in the temperature range 288 K ≤ T ≤ 328 K: $k(T) = (1.4 \pm 0.2)\cdot 10^{12} \cdot \exp[-(2050 \pm 480)\ K/T]$ $M^{-1}$ $s^{-1}$, corresponding to an energy of activation of $E_a = (17 \pm 4)$ kJ $mol^{-1}$. For the reaction of $NO_3$· with 4-nitrophenol a second order rate constant of $k_{4\text{-nitrophenol}} = (7.1 \pm 0.4) \cdot 10^8$ $M^{-1}$ $s^{-1}$ (pH = 0, T = 298 K) and for the reaction of $NO_3$· with 2,4 dinitrophenol a rate constant of $k_{2,4\ dinitrophenol} = (5.3 \pm 0.6) \cdot 10^8$ $M^{-1}$ $s^{-1}$ (pH = 0, T = 298 K) was derived.

Products studies of the reaction of the $NO_3$ radical with phenol were performed. The $NO_3$· radical was generated using the photolysis of cerium(IV) ammonium nitrate and the analysis was performed by HPLC-DAD and GC-MS. 4-nitrophenol, 2-nitrophenol, 2,6-dinitrophenol, 2,4-dinitrophenol and p-benzoquinone were identified as reaction products from phenol (Scheme 1).

Scheme 1

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