

# Kinetic and Product Study of the Reaction of the $\text{NO}_3\cdot$ Radical with Phenol, Benzoic Acid and their Nitration Products in Aqueous Solution

H. Herrmann<sup>(1,2)</sup> Th. Umschlag<sup>(1)</sup> and K. Müller<sup>(2)</sup>

1: Institut für Physikalische und Theoretische Chemie, Universität GH Essen, FB8

Universitätsstr. 5, D-45117 Essen, Germany

Phone: +49-(0)201-183 3205, Fax: +49-(0)201-183 3228, E-mail: hartmut.herrmann@uni-essen.de

2: Institut für Troposphärenforschung, Permoserstr. 15, D-04303 Leipzig, Germany

E. Bolzacchini, S. Meinardi and B. Rindone

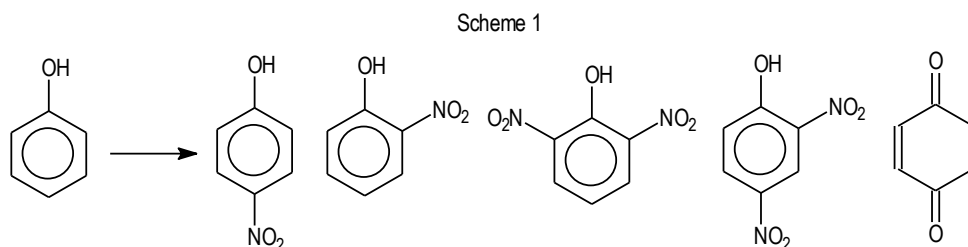
Department of Environmental Sciences, University of Milano, Via L. Emanuelli, 15, I-20126

Milano, Italy.

Phone: (x39) 2 64474303, Fax: (x39) 2 64474300, E-mail: Ezio.Bolzacchini@unimi.it

Kinetic studies of the reaction of the  $\text{NO}_3\cdot$  radical with phenol and its nitration products were performed applying a laser-photolysis laser long path absorption apparatus. For the reaction of  $\text{NO}_3\cdot$  with phenol a second order rate constant of  $k_{\text{phenol}} = (1.8 \pm 0.3) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$  ( $\text{pH} = 0$ ,  $T = 298 \text{ K}$ ) was found. The Arrhenius expression for this reaction was determined in the temperature range  $288 \text{ K} \leq T \leq 328 \text{ K}$ :  $k(T) = (1.4 \pm 0.2) \cdot 10^{12} \cdot \exp [-(2050 \pm 480) \text{ K}/T] \text{ M}^{-1} \text{ s}^{-1}$ , corresponding to an energy of activation of  $E_a = (17 \pm 4) \text{ kJ mol}^{-1}$ . For the reaction of  $\text{NO}_3\cdot$  with 4-nitrophenol a second order rate constant of  $k_{4\text{-nitrophenol}} = (7.1 \pm 0.4) \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$  ( $\text{pH} = 0$ ,  $T = 298 \text{ K}$ ) and for the reaction of  $\text{NO}_3\cdot$  with 2,4 dinitrophenol a rate constant of  $k_{2,4\text{ dinitrophenol}} = (5.3 \pm 0.6) \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$  ( $\text{pH} = 0$ ,  $T = 298 \text{ K}$ ) was derived.

Products studies of the reaction of the  $\text{NO}_3\cdot$  radical with phenol were performed. The  $\text{NO}_3\cdot$  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).



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