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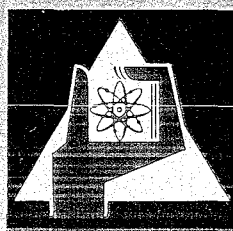
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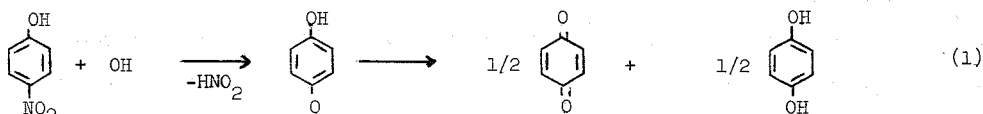
OH-Radical Induced Denitration of Nitrophenols

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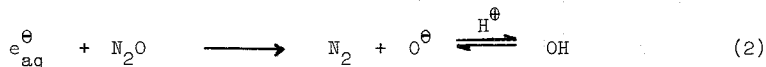
We wish to report that OH-radicals eliminate nitrous acid from 4-Nitrophenol to yield 1,4-Benzo-semiquinone as an intermediate, which subsequently disproportionates into 1,4-Hydrobenzoquinone and 1,4-Benzoquinone (1).



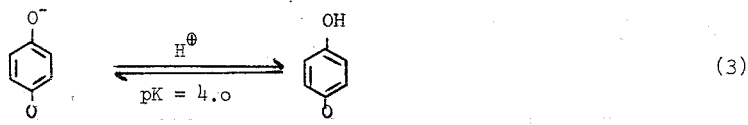
Experimental evidence for reaction (1) has been obtained from the ESR-detection of semiquinone radicals, as well as the analytical determination of Nitrite and 1,4-Benzoquinone.

ESR measurements

The insitu ESR technique⁴⁾ was employed as described earlier³⁾. A N₂O saturated aqueous solution of 3-Nitrophenol (2x10⁻⁴ molar) was investigated in the pH range 5 - 12. Radiation produces hydrated electrons, which in this solution are all converted into hydroxyl radicals (2)^{4,5)}.

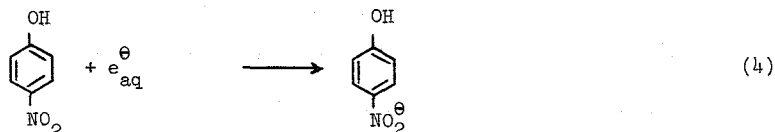


We observed a 1:4:6:4:1 ESR-quintet with hf-splitting of 2.35 Gauss and g = 2.0044. This radical was unambiguously identified as the radical anion of the 1,4-Benzo-semiquinone (3)⁶⁾.



We obtained the same radical signal when 4-Nitrophenol reacted with OH-radicals, produced by mixing an aqueous solution of Ti³⁺ (5x10⁻³ molar and complexed with EDTA⁷⁾) in the pH range 6 - 9 with aqueous H₂O₂ (10⁻¹ molar, containing 0.14% 4-Nitrophenol). Using 2-Nitrophenol in the Ti/H₂O₂-system we obtained the ESR-spectrum of the 1,2-Benzo-semiquinone radical, which is characterized by two triplets of a_{4,5} = 3.6 and a_{3,6} = 0.76 Gauss⁶⁾.

The irradiation of N_2 - or Ar -saturated 4-Nitrophenol solution yields a new ESR-spectrum which is superimposed on, and approximately twice as intense as, the radical signal of the 1,4-Benzo-semiquinone. The additional ESR-signal was identified as the anion radical of the 4-Nitrophenol⁸⁾, which is generated by the reaction of hydrated electrons with 4-Nitrophenol (4).



Analytical and G-value determinations

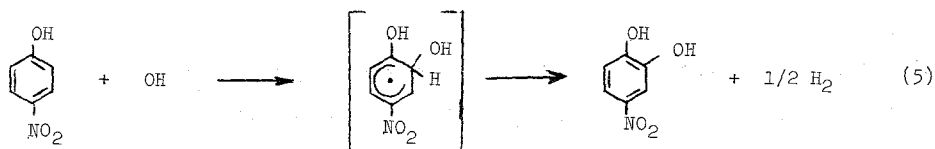
N_2O - or N_2 -saturated solutions of 4-Nitrophenol (2×10^{-4} - 2×10^{-2} molar) were irradiated in a Co-60-Gamma source with doses up to 5×10^{17} eV/ml. Nitrous acid was determined photometrically using the method of Griess-Ilovay⁹⁾. The test of Nitrate with Brucine was negative⁹⁾. The total yield of Quinone - after aerial oxidation of the Hydroquinone in the irradiated solution - was determined with 2,4-Dinitrophenylhydrazine¹⁰⁾. The resulting blue coloured indophenone derivate was measured photometrically.

Corrections were applied to the Quinone yield because of the presence of 4-Aminophenol, a reduced product in irradiated 4-Nitrophenol solutions^{4,5)}. 4-Nitropyrocatechol, the product of hydroxylation of 4-Nitrophenol^{4,5)}, was determined in alkaline solutions, where a strong absorption at 512 nm is obtained. The observed G-values are presented in table 1.

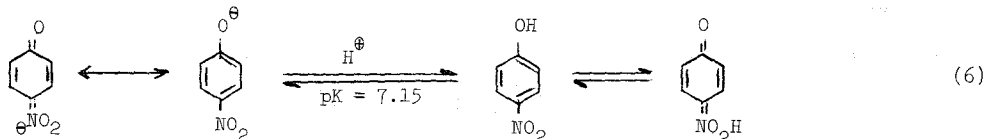
Table 1 Yields of products of the OH induced denitration and hydroxylation of aqueous 4-Nitrophenol (Dose: 5×10^{17} eV/ml)

pH	Gas	conc. (mol/l)	G_{HNO_2}	$G_{1,4\text{-Benzoquinone}}$	$G_{4\text{-Nitropyrocatechol}}$
5	N_2	5×10^{-4}	0.30	0.33	1.88
5	N_2	2×10^{-2}	0.39		2.42
5	N_2O	5×10^{-4}	0.66	0.65	3.84
8	N_2	5×10^{-4}	0.68	0.70	1.50
8	N_2	2×10^{-2}	0.77		1.94
8	N_2O	5×10^{-4}	1.32	1.42	2.98

The yields of nitrous acid and 1,4-Benzoquinone are equal, within experimental error, demonstrating the validity of equation (1). The yields are doubled when N_2O is used as electron scavenger (2) proving that OH radicals are the precursors of the reaction. In addition the results show a remarkable dependence on the pH. At pH 5 the OH-induced denitration amounts to 14% while 86% of the OH radicals react to form 4-Nitrocatechol (5)^{4,5}.



In alkaline solution (pH 8) the yield of denitration is more than doubled (31%) while the hydroxylated product decreases by the same amount. This pH-effect may be related to the acid-base equilibrium of 4-Nitrophenol (6).



The electronic structure of the 4-Nitrophenolate differs from the neutral molecule in so far as the assumed electrophilic attack of the OH radical occurs with equal probability at the ortho and para positions of the molecule. In acid solutions OH-addition at the ortho position of the ring seems to be preferred.

Evidence for OH-induced denitration has been obtained for Nitrobenzene¹¹). We observed denitration of Nitrobenzaldehydes and Nitrobenzoicacids. Thus this type of reaction seems to be of general importance during the hydroxylation of aromatic nitrocompounds.

Acknowledgements

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- 2) Summer student of the Staatliche Ingenieurschule, Aalen, Germany
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