Tetrahedron Letters No.3, pp. 251-254, 1971. Pergamon Press. Printed in Great Britain.

Hydroxylation of substituted phenols: an ESR-study in the Ti^{3+}/H_2O_2-System

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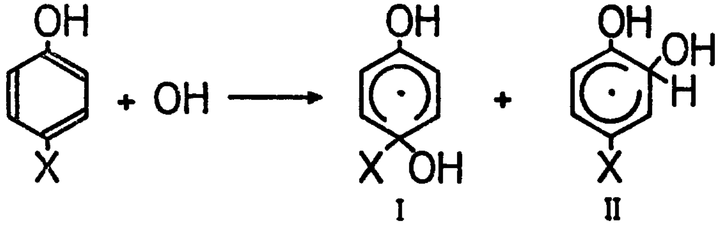
(Received in UK 25 November 1970; accepted for publication 17 December 1970)

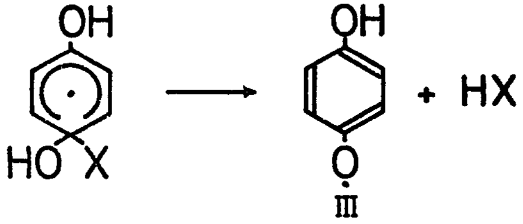
Hydroxy-cyclohexadienyl radicals are the primary products of the attack of hydroxyl radicals on aromatic compounds$^{1)}$. The existence of these intermediates in several systems has been demonstrated by pulse radiolysis$^{1,2)}$ and confirmed unambiguously by ESR-spectroscopy$^{3)}$. Several investigators have intimated that the OH-radical resembles standard electrophilic reagents in many of its reactions and that it consequently shows preference for attack at positions of high electron density in aromatic rings$^{4)}$.

Thus in phenols, owing to the strong +M-effect of the OH-group, the major points of attack are expected at the ortho and para positions (Reaction 1).

The intermediates I and II may then react by either dimerisation, disproportionation, oxidation or intramolecular displacement of HX. The displacement reaction (2) yields, besides the free acid HX, the 1,4-benzosemiquinone III



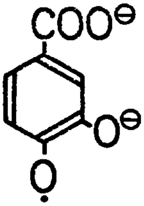
(1)



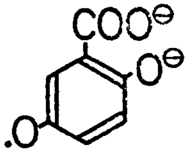
(2)

Jefcoate and Norman[5)] identified the 1,4-benzosemiquinone radical from the ESR-spectra produced by reaction of OH-radicals (from the Ti^{3+}/H_2O_2-system) with 4-Chloro- and 4-Fluorophenol. The Co-60-γ-radiolysis of aqueous solutions of 4-Nitrophenol provides another example in which similar intermediates are involved; nitrite is formed[6)], presumably by intramolecular fission from I ($X = NO_2$)[+].

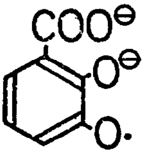
In order to determine the generality of such OH-induced replacement processes we have studied the reaction of OH-radicals (from Ti^{3+}/H_2O_2) with the following compounds: (2-bromo-, 2-nitro-, 2-chloro-, 2-fluorophenols; 4-bromophenol and 4-hydroxybenzaldehyde). In all cases within the pH-range 7-9, good spectra were obtained, which could be unambiguously assigned to the appropriate anion radicals of 1,4-[8)] or 1,2-benzosemiquinone[9)]. The ease of replacement of the CHO-group in the hydroxybenzaldehyde led us to try to decarboxylate the hydroxybenzoicacids. This reaction however, was found not to occur and with all three isomers the carboxyl substituted benzoquinone radicals (IV-VI) resulted.



IV



V



VI

[+] In this system as well as with other Nitrophenols it was found that oxygen profoundly effects the ratio of hydroxylation to denitration[7)].

Table I shows the relevant ESR-parameters for the proposed species

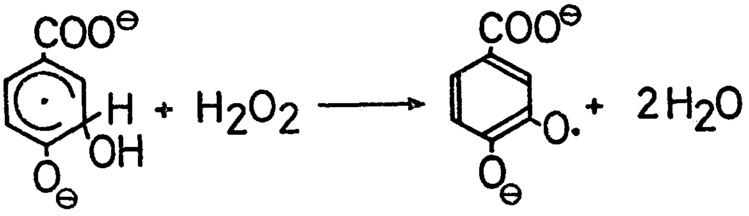
semiquinones observed from	g-factor	a_o	a_m	a_p	total splitting	proposed assignment
p-OH-C_6H_4COOH	2,0045	1,23±0,003	0,73±0,05	3,21±0,04	5,17	IV (100)
o-OH-C_6H_4COOH	2,0044	2,22±0,06	2,00±0,06	2,55±0,05	6,77	V (100)
					8,12	VI (24)
m-OH-C_6H_4COOH	2,00485	1,25±0,07	0,69±0,07	3,23±0,03	5,17	IV (100)
					6,70	V (33)
					8,12	VI (10)

(   ) = relative intensities of the separate components

In the case of p-hydroxybenzoicacid we obtained a single radical assigned to the structure IV. A similar species has been observed during alkaline oxidation of 3,4-dihydroxybenzoicacid[10].

In contrast, the ortho and meta hydroxy-substituted benzoic acids yield mixtures of two (V and VI) or three (IV-VI) radicals respectively. The relative intensities of the different components, reflecting their stationary state concentration in the solution, are shown in Table I.

The mechanism of formation of semiquinone radical anions assuming dihydroxy-carboxyl-cyclohexadienyl radicals as intermediates is however uncertain. Jephcoate and Norman[5] have rationalised similar results by postulating the intervention of excess H_2O_2 as a two electron oxidising agent. A similar mechanism may hold in our case (3).



(3)

A qualitative study of the dependence of signal intensity (Int.) on H_2O_2 was conducted. An empirical relationship of the form $\mathrm{Int.} \propto \left[H_2O_2\right]^n$ (n = 3/2-2) was noted as was expected from a steady state treatment, using reaction (3) as the quinone forming reaction. The expected changeover in spectral nature (i.e. semiquinone to cyclohexadienyl) at low H_2O_2 was however not observable under our conditions.

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