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MECHANISM OF HOMOLYTIC AROMATIC HYDROXYLATION III (1)

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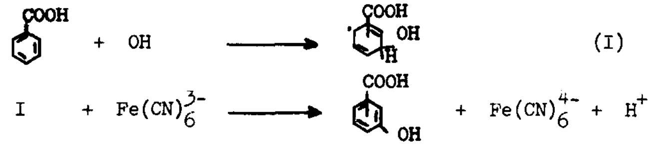
The homolytic hydroxylation of benzoic acid in aqueous solution yields ortho, meta and para hydroxy-benzoic acids. The published data for the isomeric distribution of these compounds vary from 5:2:10 to 2:1:1 (2). We have studied the γ-irradiation of an aqueous solution of benzoic acid in the presence of N_2O as a function of $K_3Fe(CN)_6$ concentration. The mechanism of the hydroxylation under these conditions is:

$$H_2O \xrightarrow{\sim\sim\sim} OH,\ H,\ e^{\ominus}_{aq},\ H_2,\ H_2O_2 \qquad (1)$$

$$e^{\ominus}_{aq} + N_2O \xrightarrow{H^{\oplus}} OH + N_2 \qquad (2)$$



(3)

(4)

$$H_2O_2 + Fe(CN)_6^{4-} \longrightarrow Fe(CN)_6^{3-} + OH + OH^- \qquad (5)$$

In N_2O-saturated solutions e^-_{aq} is completely converted into OH (reaction 2). The OH-radicals then add to the benzoic acid to form the cyclohexadienylradicals (reaction 3) (3) which are oxidized by $K_3Fe(CN)_6$ to the final product the hydroxy-benzoic acid (reaction 4). The proposed mechanism (reaction 1-5) is in good agreement with the material balance. The sum of the experimentally obtained initial G-values of the three isomeric hydroxy-benzoic acids is 5.4 ± 0.5, $G(CO_2)$ is 0.29, $G(-Fe^{III})$ is 5.4 + 0.2 and $G(N_2)$ is 2.7 (smallest dose $5x10^{17}$ eV/g). The theoretically expected G-values are $G(\text{hydroxy-benzoic acids}) + G(CO_2) = G_{OH} + G_{e^{\ominus}} + G_{H_2O_2} = 5.9$ (4) and $G(-Fe^{III}) = G_{OH} + G_{e^-} + G_H = 5.8$.

The G-values for the sum of the hydroxylated products as well as the $G(CO_2)$ and the $G(-Fe^{III})$-values do not vary with the $K_3Fe(CN)_6$ concentration, as is predicted by the mechanism. However, the ratio of the ortho/meta/para products changes strongly with the $K_3Fe(CN)_6$ concentration (Fig. 1)

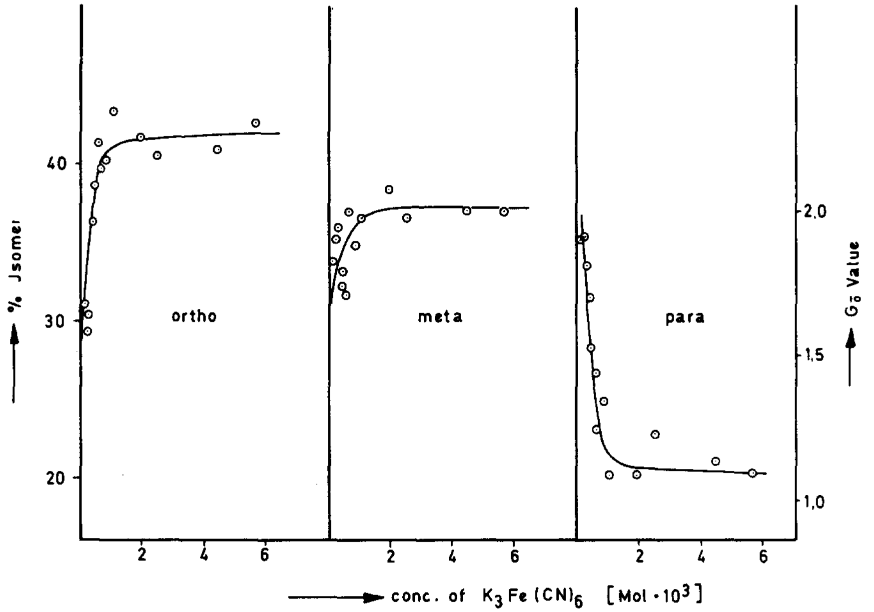
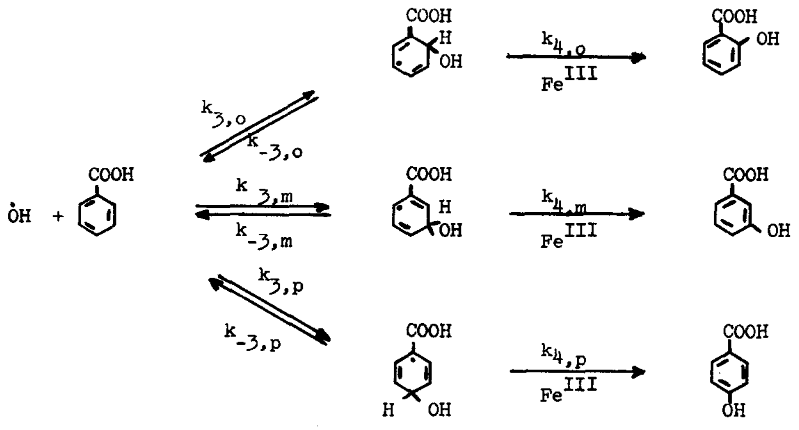


Fig. 1 Initial G-values for ortho, meta and para hydroxy-benzoic acids as function of the $K_3Fe(CN)_6$ concentration (experimental conditions: concentration: benzoic acid 1,5x1o^{-3}Mol, N_2O 2.2x1o^{-2} Mol; dose rate 2x1o^{17} eV/g.min Co-6o-γ; analysis of the hydroxy-benzoic acids by radio paper chromatography. The pH-value was 3.6 ± o.o2 independent of the $K_3Fe(CN)_6$ concentration. The amount of the benzoic acid anion was calculated from this to about (17%).

This result is unexpected and shows, that the additon of an OH-radical to the aromatic ring is not the only determining step of the isomer distribution. In addition the ratio of the isomers is influenced by the rate of the oxidation-step. The result can be explained by the following mechanism:



The formation of the three isomeric cyclohexadienylradicals (CHD-radicals) is reversible and leads to an equilibrium. In a subsequent reaction the CHD-radicals are oxidized forming the corresponding hydroxylated compounds. Whether the OH-radical on the left side of the equilibrium is truly a "free" radical or whether it remains somehow attached in a weak complex to the aromatic is not yet known. In the case of Cl-atoms, the formation of charge transfer complexes has been observed (5). However, the assumption of such a complex does not change the kinetic equations.

The isomer distribution is determined by the ratio of the over-all-rate constants $k_{o,o}/k_{o,m}/k_{o,p}$ where $k_{o,o} = \frac{k_{3,o} \cdot k_{4,o} \; Fe^{III}}{k_{-3,o} + k_{4,o} \; Fe^{III}}$ etc. At high concentration of Fe^{III} this ratio approaches $k_{3,o}/k_{3,m}/k_{3,p}$, which is the true ratio of the primary addition step. A ratio of 1.05/0.95/1.0 is obtained experimentally (Fig. 1) (The values are corrected for two ortho and meta positions). At low concentrations of Fe^{III} the ratio approaches

$$\frac{k_{3,o} \cdot k_{4,o}}{k_{-3,o}} \quad \frac{k_{3,m} \cdot k_{4,m}}{k_{-3,m}} \quad \frac{k_{3,p} \cdot k_{4,p}}{k_{-3,p}}$$

showing, that under these conditions the ratio of isomers is determined by the rate of the back reaction and the rate of the oxidation, too. At the lowest $K_3Fe(CN)_6$ concentration used in our experiments a ratio of 1/1.1/2.4 was obtained.

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