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PHOTOCATALYTIC EFFECTS OF Fe(III) COMPOUNDS ON THE HYDROXYLATION OF BENZOIC ACID BY HYDROGEN PEROXIDE INITIATED BY 589 nm RADIATION AND SENSITIZED BY METHYLENE BLUE

Stanislav Luňák,* Petr Sedlák, Jiřina Brodilová, and Pavel Lederer
Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences,
160 00 Prague 6, Czechoslovakia

Summary: The hydroxylation of benzoic acid by hydrogen peroxide initiated by 589 nm radiation is catalyzed by the following Fe(III) compounds: $FeCl_3$, $K_3[Fe(C_2O_4)_3]$, $Na_2[Fe(CN)_5NO]$, and $K_3[Fe(CN)_6]$. This photochemical reaction can be effectively sensitized by methylene blue.

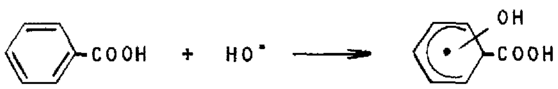
The hydroxylation of organic compounds by hydrogen peroxide is most frequently carried out using Fenton's reaction[1] (equation 1) or the photodissociation of hydrogen peroxide[2] (equation 2).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + HO^\bullet \qquad (1)$$

$$H_2O_2 \xrightarrow{h\nu} 2\ HO^\bullet \qquad (2)$$

In our previous studies on the photochemical hydroxylation of salicylic acid by hydrogen peroxide, we have shown that UV-radiation can also be used to generate photochemically Fenton's reagent from Fe(III) compounds[3,4] and that this photochemical generation can be sensitized by methylene blue if carried out using VIS-radiation[5].

Ogata and co-workers[6] have explained the formation of hydroxybenzoic acids in photochemical hydroxylation of benzoic acid by hydrogen peroxide by two consecutive reactions with $HO^\bullet$ radicals (equations 3 and 4).



(3)

(4)

The hydroxybenzoic acids that form are highly photochemically reactive and undergo consecutive reactions with hydrogen peroxide. The aim of the present work was to test the feasibility of benzoic acid hydroxylation with hydrogen peroxide by photochemical generation of Fenton's reagent sensitized by methylene blue and initiated by 589 nm radiation of a sodium arc. These conditions essentially excluded the direct photochemical excitation of hydroxybenzoic acids, so reducting markedly their loss by subsequent photochemical reactions.

The reaction was carried out in a sealed thermostatted cell.[7] The radiation was obtained from a SHC 400 W high-pressure sodium arc (Tesla Holešovice). The concentrations of benzoic acid and hydroxybenzoic acids were determined using a liquid chromatograph.[7] The kinetics of the hydroxylation was also followed by means of UV spectrophotometry. The most markable difference in absorbance of reaction solution was observed at 300 nm (ΔA_{300}).

In order to achieve a strict resolution of the thermal and the photochemical hydroxylation, we always performed two parallel measurements, one to determine the overall rate on irradiation and the other to establish the reaction rate in the absence of photolytic radiation. The rate of photochemical hydroxylation was obtained as the difference between the overall rate on irradiation and the rate of thermal reaction. However, the rate of thermal hydroxylation was low compared with the rate of photoinitiated reaction under the applied experimental conditions.

TABLE I. Effect of methylene blue (MB) and iron(III) chloride on the rate of benzoic acid hydroxylation characterized by changes in the reaction solution absorbance at 300 nm (ΔA_{300}). Irradiated by 589 nm; $[C_6H_5COOH]_o = 1 \times 10^{-3}$M; $[H_2O_2]_o = 2 \times 10^{-3}$M; T = 298 K

Addition	0	1×10^{-6}M MB	1×10^{-5}M $FeCl_3$	1×10^{-6}M MB + + 1×10^{-5}M $FeCl_3$
Irradiation time, h			ΔA_{300}	
1	-	0.02	0.07	0.11
2	-	0.04	0.13	0.23
3	0.02	0.07	0.23	0.48

Table I illustrates the photosensitizing effect of methylene blue and the photocatalytic effect of iron(III) chloride. The photosensitizing effect of methylene blue is linked with the photocatalytic effect of Fe(III) compounds. Indeed, when irradiated by a wavelength of 589 nm in the presence of methylene blue, hydrogen peroxide alone undergoes no photolysis at all. This is accord with published data on the energy of the first excited triplet of methylene blue[8] (142.3 kJ mol^{-1}) and the dissociation energy of the O-O bond in hydrogen peroxide[9] (213.4 kJ mol^{-1}).

TABLE II. Effect of Fe(III) compounds and methylene blue (MB) on the hydroxylation of benzoic acid by hydrogen peroxide initiated by 589 nm radiation. $[C_6H_5COOH]_o = 2 \times 10^{-3}M$; $[H_2O_2]_o = 2 \times 10^{-3}M$; T = 298 K; $p_i = 100 \times \Delta[C_6H_4(OH)(COOH)]/\Delta[C_6H_5COOH]$; i = 1 for 4-hydroxybenzoic acid; i = 2 for 3-hydroxybenzoic acid

Addition	Irradiation time, h	$[C_6H_5COOH] \times 10^{-3}$	p_1 %	p_2 %
$1 \times 10^{-4}M$	1	1.53	11.1	16.6
$FeCl_3$	5	0.95	8.2	13.1
$1 \times 10^{-4}M$	1	1.69	6.3	5.2
$K_3[Fe(CN)_6]$	5	1.36	8.0	8.3
$1 \times 10^{-4}M$	1	1.82	4.2	4.3
$Na_2[Fe(CN)_5NO]$	5	1.19	8.8	13.6
$1 \times 10^{-5}M$ MB +	1	1.78	8.3	2.7
$1 \times 10^{-5}M$ $FeCl_3$	5	1.21	10.5	13.9
$1 \times 10^{-5}M$ MB +	1	1.93	11.6	1.0
$1 \times 10^{-5}M$ $K_3[Fe(CN)_6]$	5	1.27	9.4	11.9
$1 \times 10^{-5}M$ MB +	1	1.85	7.2	19.2
$1 \times 10^{-5}M$ $Na_2[Fe(CN)_5NO]$	5	1.14	8.7	20.8

Table II compares the photocatalytic effectiveness of the Fe(III) compounds used and gives the amounts of 3- and 4-hydroxybenzoic acids in the products relative to that of the reacted benzoic acid. The table shows that the Fe(III) compounds used are comparable in the photocatalytic effectiveness and that the proportion of hydroxybenzoic acids in the reaction products is relatively high, especially when compared with that in the reaction initiated by UV-radiation.[7]

The photochemical generation of Fenton's reagent (i.e., photoinitiated reduction of Fe(III) to Fe(II)) has an advantage over the classical method in that uses a substantially lower iron concentrations. In the classical method, only a single HO$^•$ radical is formed for every added Fe^{2+} ion, whereas the photochemical reduction Fe(III)-Fe(II) is coupled to reaction (1) to close a cycle, thanks to which one Fe(II,III) ion produces many HO$^•$ radicals.

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