

## METHYLENE-BLUE-SENSITIZED PHOTOCHEMICAL HYDROXYLATION OF 2-HYDROXYBENZOIC ACID BY HYDROGEN PEROXIDE: PHOTOCATALYTIC EFFECT OF FERRIC CHLORIDE

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### Summary

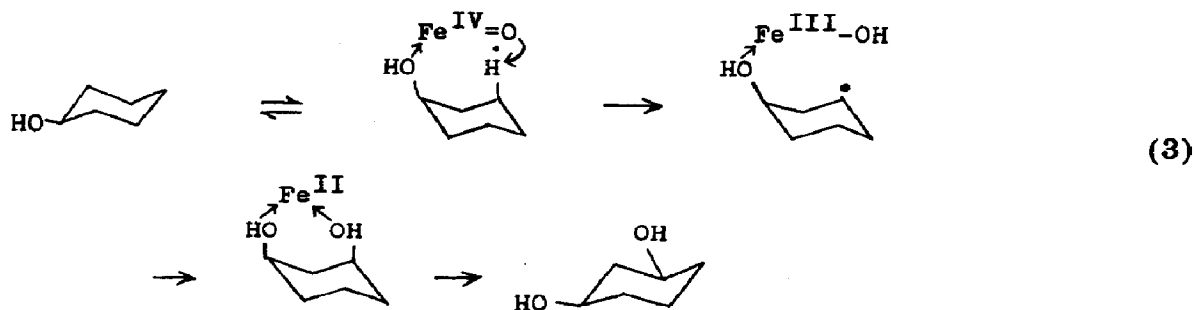
The methylene-blue-sensitized hydroxylation of 2-hydroxybenzoic acid by hydrogen peroxide initiated by visible radiation and catalysed by ferric chloride has been investigated. The major reaction product is 2,3-dihydroxybenzoic acid. In the absence of iron(III), the reaction occurs extremely slowly. Iron(III) is observed to have an appreciable catalytic effect on the photosensitized reaction at concentrations as low as  $10^{-8}$  M. The first step of the reaction is the photochemical reduction of iron(III) to iron(II), *i.e.* the generation of Fenton's reagent.

### 1. Introduction

The hydroxylation of organic compounds by hydrogen peroxide catalysed by ferrous ions (hydroxylation by Fenton's reagent) has received much attention in the past [1]. Despite a very large amount of work on the subject [2], there remain differences of opinion about the mechanism of the reaction. Besides the generally accepted mechanism in which it is assumed that the organic compound is attacked by hydroxyl radical [1]

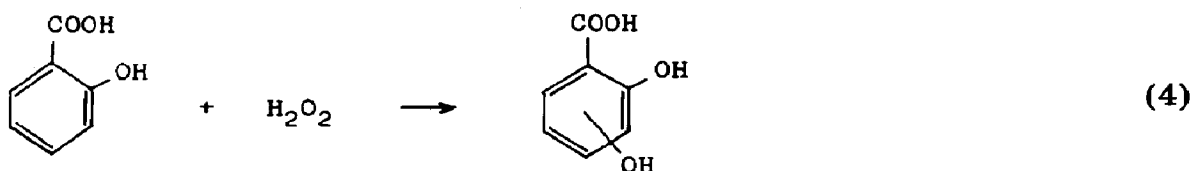


there are papers in which it is assumed that iron in the +4 oxidation state in the form of the ferryl ion  $\text{FeO}^{2+}$  bound to the oxidized substrate is the active species [3]. For instance, the following reaction scheme has been proposed for the hydroxylation of cyclohexanol [3]:



This mechanism receives support from the stereoselective incorporation of the hydroxyl group and from the origin of the hydroxyl-group hydrogen.

The classical method of hydroxylation employing Fenton's reagent [4] consists of slow addition of small quantities of hydrogen peroxide to a well-stirred solution containing  $\text{Fe}^{2+}$  and an organic compound [1]. This method has been used for quantitative studies [1] although it is clear that it can hardly ensure homogeneity of the reaction system. An elegant way to eliminate this difficulty is to generate Fenton's reagent in the reaction system photochemically. The simplest method is direct photochemical reduction of iron(III) to iron(II). We have tested [5] this method with the hydroxylation of 2-hydroxybenzoic acid described by Grinstead [6]:



The photochemical reaction was initiated by the emission lines of a mercury lamp with wavelengths around 300 nm (297 nm, 303 nm and 313 nm). However, the radiation was absorbed not only by the iron(III) compounds but also by 2-hydroxybenzoic acid and hydrogen peroxide. The result was rapid hydroxylation even without adding iron(III).

In the present work, we excited photochemically only the sensitizer, methylene blue, and compared the course and products of the sensitized and the directly initiated reaction. The aim of this work was to make a step towards the elucidation of the mechanisms of thermal and photoinitiated hydroxylations by hydrogen peroxide.

## 2. Experimental details

### 2.1. Chemicals

Hydrogen peroxide of analytical grade (Chemical Works, Sokolov), ferric chloride of analytical grade (Cambrian Chemicals), methylene blue (Merck, Darmstadt) and 2-hydroxybenzoic acid (Reanal, Budapest) were

used as received. 2,3- and 2,5-dihydroxybenzoic acids were synthesized at the Faculty of Sciences, Palacký University, Olomouc; their spectral data have been published previously [7]. The other chemicals used were of analytical grade (Lachema, Brno).

Special care was taken to ensure that the water was of high purity. Double distilled water was mixed with potassium permanganate (about  $0.2 \text{ g l}^{-1}$ ), raised to the boil and held there for 10 h. The purification was completed by fractional distillation on a column, with the middle fraction being collected. Experiments with water treated in this way showed good reproducibility.

## 2.2. Experimental arrangement

The spectrophotometric investigation of the photosensitized reaction was carried out in a 1 cm cell placed in a thermostatted aluminium block. Irradiation was interrupted at regular time intervals and UV absorption spectra of the reaction mixture were recorded on an SP 800B spectrophotometer (Unicam, Cambridge).

For product identification, the photosensitized reaction was run in a thermostatted glass cylindrical vessel (volume, about 150 ml) with a sodium arc located at the centre. The reaction initiated by UV radiation was carried out in a quartz cylindrical vessel placed in a thermostatted aluminium block, and the reaction mixture was irradiated by an arc located outside the reaction vessel.

The radiation sources were an NaE 16 sodium arc (Narva, Berlin), an HBO 200 high pressure mercury arc (Osram, Munich) and a 93110E medium pressure mercury arc (Philips, Eindhoven). An OG 5 filter (Zeiss, Jena) was used to cut off wavelengths shorter than 550 nm. The radiation intensity was determined using potassium diaminetetrakis(thiocyanato-*N*) chromate (potassium form of Reinecke's salt) by a procedure described in the literature [8].

Since singlet oxygen might be involved in the mechanism of the reaction sensitized by methylene blue and because oxygen is known to act as a quencher of a number of excited states, the reaction course for saturation of the solution with oxygen was compared with that in an inert atmosphere of argon. Oxygen was found to have no measurable effect on the reaction rate. Subsequent experiments were therefore performed in the presence of atmospheric oxygen.

In order to distinguish strictly the catalytic and photocatalytic effects, we always followed the thermal reaction in parallel with the photochemical reaction. The rate of the photochemical reaction was obtained as the difference between the overall rate during irradiation and the contribution from the thermal reaction.

## 2.3. Product analysis

The product analysis was performed as described by Grinstead [6]. After irradiation, the reaction solution was acidified to pH 2.5 and shaken with chloroform, the unreacted 2-hydroxybenzoic acid being extracted into

the chloroform phase. Dihydroxybenzoic acids were extracted from the thus-treated solution with diethyl ether. The ether was subsequently evaporated in a vacuum vaporizer and the residue was dissolved in water. The UV absorption spectrum was recorded and the wavelengths of the isosbestic points on changing the pH were compared with literature data [9].

In addition to UV absorption spectroscopy, thin-layer chromatography was used to identify the reaction products. The chromatographic analysis was carried out on Merck plates (DC-Fertigplatten Kiesegel F<sub>254</sub>) and 254 nm radiation was used to detect the products. Good separation was achieved with a benzene-acetic acid-water (7:3:0.5 by volume) developing system. The  $R_f$  for the individual substances were as follows: 0.53 for 2-hydroxybenzoic acid, 0.23 for 2,3-dihydroxybenzoic acid and 0.20 for 2,5-dihydroxybenzoic acid. Methylene blue remained at the starting line.

#### 2.4. Quantum yield determination

The quantum yield of the sensitized reaction was expressed in terms of the number of molecules of reacted 2-hydroxybenzoic acid ( $j \equiv S$ ) or the number of molecules of the 2,3-dihydroxybenzoic acid produced ( $j \equiv D$ ):

$$\Phi_j \text{ (molecules } j \text{ quantum}^{-1}) = \frac{N_A c_j V}{1000\tau I(1 - 10^{A_{588}})} \quad (5)$$

where  $N_A$  is Avogadro's number,  $V$  (ml) is the irradiated volume,  $\tau$  (s) is the irradiation time,  $A_{588}$  is the absorbance of the reaction solution at 588 nm and  $I$  (quanta  $s^{-1}$ ) is the radiation intensity determined as described by Wegner and Adamson [8]. The molar concentrations  $c_j$  were determined by two methods. For large volumes of irradiated solutions, they were established directly by measuring UV spectra of the various fractions extracted from the reaction solution (see Section 2.3). In studying the kinetics of the sensitized reaction, the concentrations were evaluated from changes in the absorption spectrum of the solution in the region of the 297 nm absorption maximum due to 2-hydroxybenzoic acid. However, all components of the reaction system, *i.e.* 2-hydroxybenzoic acid ( $A_S$ ), methylene blue ( $A_{MB}$ ), reaction products ( $A_X$ ), hydrogen peroxide ( $A_H$ ) and ferric chloride, absorb at this wavelength. The absorbance of ferric chloride was very low at the concentrations used and was therefore neglected in further calculations. The absorbance of hydrogen peroxide was taken as constant because hydrogen peroxide was present in large excess relative to 2-hydroxybenzoic acid and, moreover, its absorbance never exceeded 5% of the total absorbance of the reaction mixture. The calculation of the absorbance  $A_{MB}$  of methylene blue at 297 nm was based on the observation that the ratio of the decolouration rates at 297 nm and 667 nm is a constant. The other components of the reaction solution showed practically no absorption at 667 nm, making it possible to calculate the absorbance of methylene blue at 297 nm. The concentrations of 2-hydroxybenzoic ( $c_S$ ) and 2,3-dihydroxybenzoic ( $c_D$ ) acids were calculated as

$$c_S = c_{S,0} \frac{\Delta A_{KOR}}{\Delta A_{MAX}} \quad (6)$$

$$c_s = c_s p \quad (7)$$

where  $c_{s,0}$  is the initial concentration of 2-hydroxybenzoic acid,  $p$  is the mole fraction of 2-hydroxybenzoic acid in the hydroxylation products ( $p$  was determined by extraction as described by Grinstead [6]),  $\Delta A_{KOR}$  is the change in absorbance resulting from the conversion of 2-hydroxybenzoic acid to products in the given experiment and  $\Delta A_{MAX}$  is the change in absorbance resulting from total conversion of 2-hydroxybenzoic acid to products. In the cases where the thermal reaction occurred at a measurable rate,  $\Delta A_{KOR}$  was calculated as

$$\Delta A_{KOR} = (\Delta A - \Delta A_{MB}) - (\Delta A_T - \Delta A_{MB,T}) \quad (8)$$

where  $\Delta A$  is the measured total change in absorbance at 297 nm during the course of an irradiation experiment and  $\Delta A_T$  is the measured change in absorbance for the corresponding thermal reaction. The changes in methylene blue absorbance on irradiation ( $\Delta A_{MB}$ ) and in the thermal reaction ( $\Delta A_{MB,T}$ ) were calculated from changes at 667 nm obtained by parallel measurements.  $\Delta A_{MAX}$  in eqn. (6) is a limiting value for time  $\tau \rightarrow \infty$ . Moreover, consecutive degradation reactions start to play a role after long periods of irradiation. Therefore, the magnitude of  $\Delta A_{MAX}$  is not accessible to direct experimental determination and was calculated from the equation

$$\Delta A_{MAX} = A_{S,0} - A_X \frac{c_{S,0}}{c_S} \quad (9)$$

where  $A_{S,0}$  is the initial absorbance of 2-hydroxybenzoic acid and  $A_X$  is the absorbance of products after  $c_S$  mol  $\text{dm}^{-3}$  2-hydroxybenzoic acid have reacted in the given experiment. The value of  $A_X$  was calculated as

$$A_X = A - (c_{S,0} - c_S)\epsilon_S l - A_{MB} - A_H \quad (10)$$

where  $(c_{S,0} - c_S)$  is the concentration of unreacted 2-hydroxybenzoic acid (determined by extraction of the reaction mixture [6]),  $l$  is the cell thickness,  $\epsilon_S$  is the molar absorption coefficient of 2-hydroxybenzoic acid at 297 nm and  $A$ ,  $A_{MB}$  and  $A_H$  are the absorbances of the reaction mixture, methylene blue and hydrogen peroxide respectively, on termination of irradiation.

Thus the value of  $\Delta A_{MAX}$  was determined for a given series of experiments. Subsequently, absorption spectra of the reaction mixture were measured for individual runs and  $\Delta A_{KOR}$  was calculated from eqn. (8). Substitution into eqns. (6), (7) and (5) gave the quantum yields.

### 3. Results and discussion

#### 3.1. Reaction products

Grinstead [6] has demonstrated that the thermal reaction of hydrogen peroxide with 2-hydroxybenzoic acid catalysed by iron(II) complexes involves the formation of 2,3- and 2,5-dihydroxybenzoic acids. No 2,4- or

2,6-dihydroxybenzoic acid is formed, even in trace concentrations. In a previous work [5] we showed that the photochemical activation of the system 2-hydroxybenzoic acid–hydrogen peroxide–ferric chloride by wavelengths around 300 nm yields 2,5-dihydroxybenzoic acid as the main product.

In the present work, we initiated the photochemical reaction by employing radiation from the visible region of the spectrum, using methylene blue as the sensitizer. A typical course of the sensitized reaction, as characterized by changes in the UV absorption spectrum of the reaction mixture, is shown in Fig. 1. The main product of the reaction is 2,3-dihydroxybenzoic acid. Its formation was confirmed both by thin-layer chromatographic analysis and by measuring the UV absorption spectra of products extracted from the reaction mixture as described by Grinstead [6]. Figure 2 shows spectra of extracted products from the reaction initiated by UV radiation (yielding predominantly 2,5-dihydroxybenzoic acid) and from the reaction initiated by visible radiation and sensitized by methylene blue (yielding predominantly 2,3-dihydroxybenzoic acid).

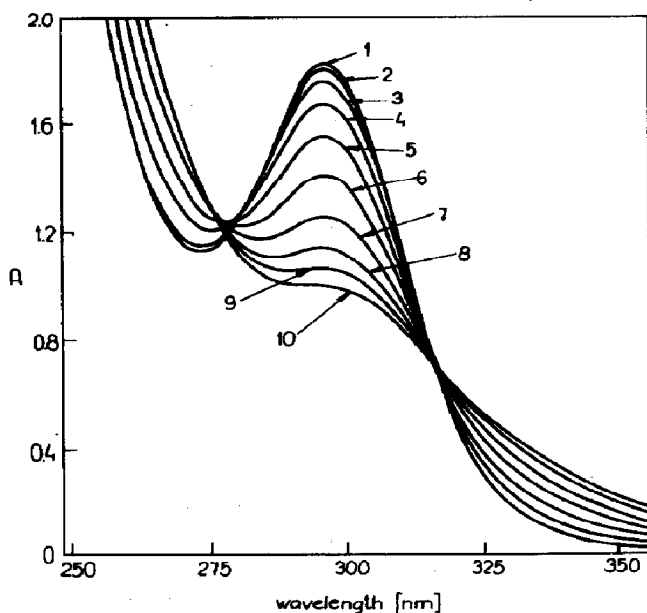
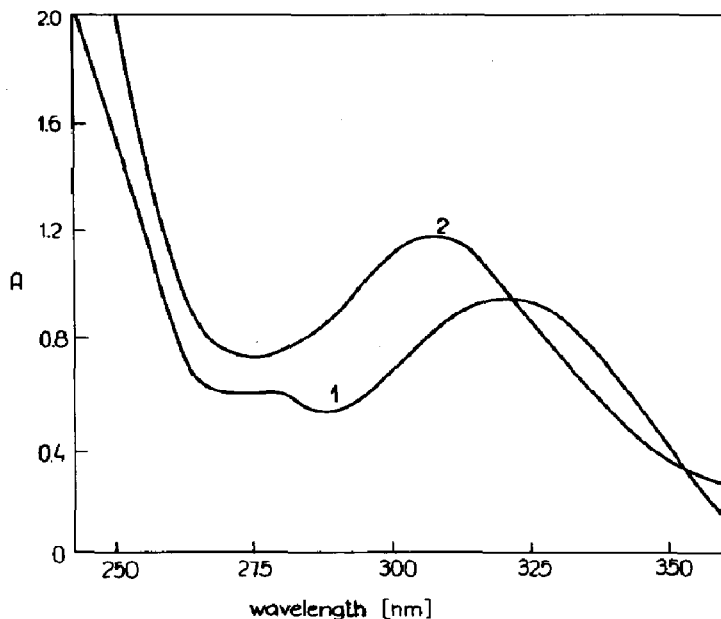


Fig. 1. Changes in the absorption spectra of the reaction solution. Irradiation by an HBO 200 arc (Osram) with an OG 5 filter (Zeiss),  $\lambda > 550$  nm;  $T = 298$  K;  $[2\text{-hydroxybenzoic acid}]_0 = 4 \times 10^{-4}$  M;  $[\text{hydrogen peroxide}]_0 = 0.1$  M;  $[\text{methylene blue}]_0 = 1 \times 10^{-5}$  M;  $[\text{FeCl}_3]_0 = 1 \times 10^{-5}$  M. Irradiation time: curve 1, 0 min; curve 2, 20 min; curve 3, 30 min; curve 4, 40 min; curve 5, 50 min; curve 6, 60 min; curve 7, 70 min; curve 8, 80 min; curve 9, 90 min; curve 10, 100 min.

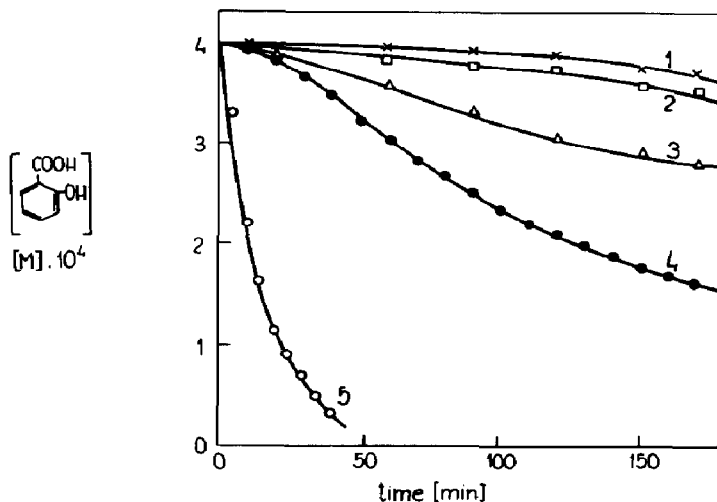
### 3.2. Reaction kinetics

#### 3.2.1. Effect of ferric chloride concentration

Ferric chloride exerts a marked photocatalytic effect on the hydroxylation of 2-hydroxybenzoic acid by hydrogen peroxide initiated by visible



**Fig. 2.** Absorption spectra of hydroxylation products extracted from the reaction mixture.  $[2\text{-hydroxybenzoic acid}]_0 = 4 \times 10^{-4} \text{ M}$ ;  $T = 298 \text{ K}$ . Curve 1:  $[\text{hydrogen peroxide}]_0 = 2 \times 10^{-3} \text{ M}$ ; irradiation by a Philips 93110E spectral lamp. Curve 2:  $[\text{hydrogen peroxide}]_0 = 0.01 \text{ M}$ ;  $[\text{methylene blue}]_0 = 1 \times 10^{-5} \text{ M}$ ;  $[\text{FeCl}_3]_0 = 1 \times 10^{-6} \text{ M}$ ; irradiation by a Narva NaE sodium arc.



**Fig. 3.** Variation in the concentration of 2-hydroxybenzoic acid during hydroxylation for various amounts of added  $\text{FeCl}_3$ . Irradiation by an HBO 200 arc (Osram) with an OG 5 filter (Zeiss),  $\lambda > 550 \text{ nm}$ ;  $T = 298 \text{ K}$ ;  $[2\text{-hydroxybenzoic acid}]_0 = 4 \times 10^{-4} \text{ M}$ ;  $[\text{hydrogen peroxide}]_0 = 0.1 \text{ M}$ ;  $[\text{methylene blue}]_0 = 1 \times 10^{-5} \text{ M}$ .  $[\text{FeCl}_3]_0$ : curve 1,  $0 \text{ M}$ ; curve 2,  $1 \times 10^{-8} \text{ M}$ ; curve 3,  $1 \times 10^{-7} \text{ M}$ ; curve 4,  $1 \times 10^{-6} \text{ M}$ ; curve 5,  $1 \times 10^{-5} \text{ M}$ .

radiation ( $\lambda > 550 \text{ nm}$ ) and sensitized by methylene blue. A plot of the concentration of unreacted 2-hydroxybenzoic acid against time (Fig. 3) shows that, without the addition of iron(III), the reaction proceeds very slowly. As

the iron(III) concentration is increased, there is an increase in the rate of the photochemical reaction. The photocatalytic effect is noticeable even for very small additions of ferric chloride, of the order of  $10^{-8}$  M. Such low concentrations of iron(III) are inevitably present as impurities in any real reaction system. That the reaction occurs slowly even without any added ferric chloride is probably a result of a photocatalytic effect of iron(III) naturally occurring in the reaction system. In the complete absence of iron(III) and/or other photocatalytically active transition metals, the hydroxylation sensitized by methylene blue would probably not occur at all. The addition of  $10^{-8}$  -  $10^{-5}$  M does not result in an appreciable increase in the amount of absorbed radiation of wavelength longer than 550 nm. Hence, an increase in the rate signifies an increase in the total quantum yield of the reaction.

### 3.2.2. Effect of methylene blue concentration

As seen in Fig. 4, the reaction occurs, although very slowly, even in the absence of methylene blue. This is because the absorption of  $\lambda > 550$  nm radiation by iron(III) complexes, although very small, is not negligible. For instance, the absorbance at 577 nm of the reaction mixture for which curve 1 in Fig. 4 was obtained was found to be 0.012. As the methylene blue concentration is increased, there is an increase in the reaction rate. Figure 4 shows that the rate of the reaction with no added sensitizer is negligible compared with that sensitized by methylene blue at concentrations of  $10^{-6}$  M and higher.

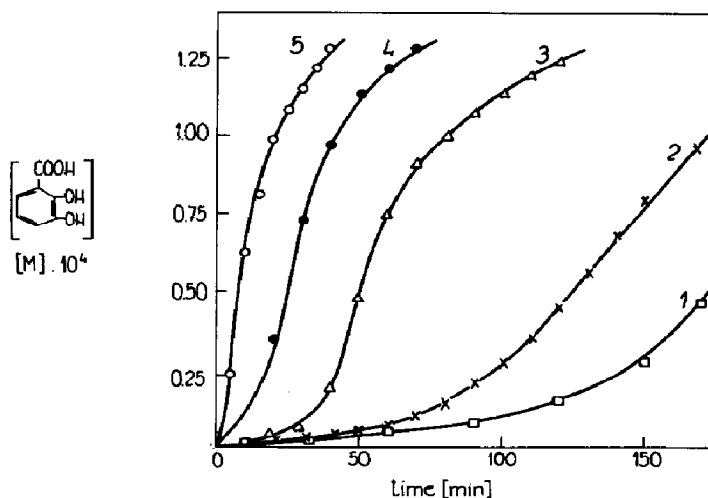


Fig. 4. Variation in the concentration of 2,3-dihydroxybenzoic acid with time for various amounts of added methylene blue. Irradiation by an HBO 200 arc (Osram) with an OG 5 filter (Zeiss),  $\lambda > 550$  nm;  $T = 298$  K;  $[2\text{-hydroxybenzoic acid}]_0 = 4 \times 10^{-4}$  M;  $[\text{hydrogen peroxide}]_0 = 0.1$  M;  $[\text{FeCl}_3]_0 = 1 \times 10^{-5}$  M.  $[\text{Methylene blue}]_0$ : curve 1, 0 M; curve 2,  $1 \times 10^{-8}$  M; curve 3,  $1 \times 10^{-7}$  M; curve 4,  $1 \times 10^{-6}$  M; curve 5,  $1 \times 10^{-5}$  M.

### 3.3. Effect of reaction temperature

The effect of temperature on photoinitiated reactions has not as yet received due attention. This is especially true for reactions that involve



photocatalytic effects even though these may increase with increasing temperature [10] in the same way as catalytic effects in thermal reactions [11]. The effect of temperature on the quantum yield of photosensitized hydroxylation of 2-hydroxybenzoic acid is documented in Fig. 5 and Table 1. It can be seen that the quantum yield increases with increasing temperature for both series of experiments, indicating that the rate-determining step in the hydroxylation of 2-hydroxybenzoic acid is a reaction with a high activation energy. Such a reaction can hardly be the attack on 2-hydroxybenzoic acid by hydroxyl radicals.

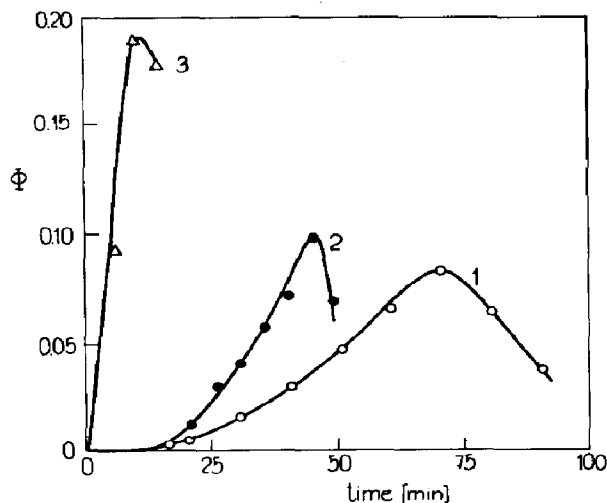


Fig. 5. Quantum yield  $\Phi$  of the formation of 2,3-dihydroxybenzoic acid as a function of irradiation time at various temperatures. Irradiation by a Narva NaE sodium arc;  $I_0 = 4.51 \times 10^{15}$  quanta  $s^{-1}$ ;  $[2\text{-hydroxybenzoic acid}]_0 = 4 \times 10^{-4}$  M;  $[\text{hydrogen peroxide}]_0 = 0.1$  M;  $[\text{methylene blue}]_0 = 1 \times 10^{-5}$  M;  $[\text{FeCl}_3]_0 = 1 \times 10^{-5}$  M;  $T$ : curve 1, 298 K; curve 2, 313 K; curve 3, 343 K.

TABLE 1

Quantum yields of 2,3-dihydroxybenzoic acid produced by the photosensitized hydroxylation of 2-hydroxybenzoic acid

$\tau$ (min)	$\Phi$ (molecules of 2,3-dihydroxybenzoic acid per quantum) at the following temperatures		
	298 K	313 K	343 K
30	0.006	0.006	0.026
60	0.006	0.012	0.069
90	0.006	0.017	0.035
120	0.006	0.012	0.087
150	0.006	0.023	0.156
180	0.006	0.006	0.104

Irradiation by a Narva NaE sodium arc;  $I_0 = 4.51 \times 10^{15}$  quanta  $s^{-1}$ ;  $[2\text{-hydroxybenzoic acid}]_0 = 4 \times 10^{-4}$  M;  $[\text{hydrogen peroxide}]_0 = 0.1$  M;  $[\text{methylene blue}]_0 = 1 \times 10^{-6}$  M;  $[\text{FeCl}_3]_0 = 1 \times 10^{-6}$  M.

### 3.4. Post-irradiation effect

The variations in the product concentrations and in the concentration of the reacting 2-hydroxybenzoic acid with time show autocatalytic character, particularly at low methylene blue concentrations. This kinetic feature is due to a gradual accumulation of the iron(II) produced by photosensitized reduction of iron(III). Consistent with this concept is the observation documented in Fig. 6, namely that on termination of irradiation the reaction proceeds much more rapidly than does the thermal reaction not preceded by irradiation. This post-irradiation effect is typical of reactions involving the photochemical generation of a catalyst of a thermal reaction with a non-negligible lifetime. In our case, the photochemically generated catalyst is iron(II) (the formation of iron(II) was also proved spectrophotometrically by reaction with 1,10-phenanthroline).

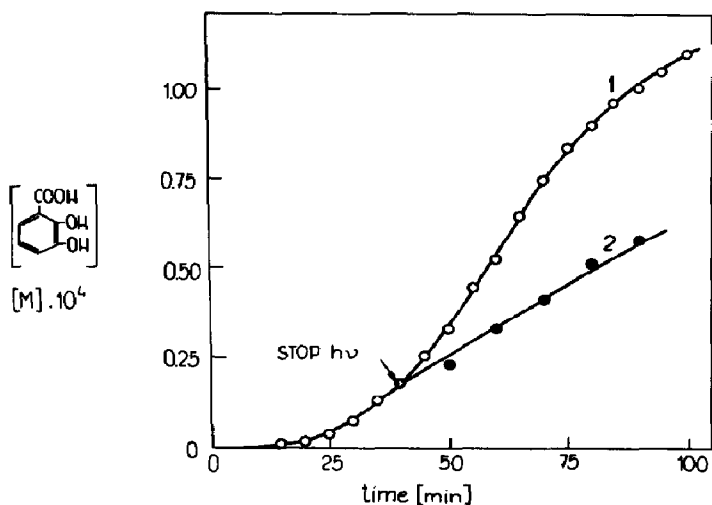


Fig. 6. Post-irradiation effect. Irradiated by a Narva NaE sodium arc;  $I_0 = 4.51 \times 10^{15}$  quanta  $s^{-1}$ ;  $T = 298$  K;  $[2\text{-hydroxybenzoic acid}]_0 = 4 \times 10^{-4}$  M;  $[\text{hydrogen peroxide}]_0 = 0.1$  M;  $[\text{methylene blue}]_0 = 1 \times 10^{-5}$  M;  $[\text{FeCl}_3]_0 = 1 \times 10^{-5}$  M. Curve 1, irradiation for the whole time; curve 2, irradiation interrupted for 40 min.

### 3.5. Formation of the leuco form of methylene blue

When a reaction solution containing 2-hydroxybenzoic acid, hydrogen peroxide, methylene blue and ferric chloride is irradiated, methylene blue turns colourless, *i.e.* its leuco form is produced. In the visible region, the decolouration occurs only in the presence of all the four reaction components. No leuco form is produced when hydrogen peroxide, ferric chloride or 2-hydroxybenzoic acid is absent. The rate of hydroxylation of 2-hydroxybenzoic acid is directly proportional to the rate of decolouration of methylene blue. This is documented in Fig. 7, which shows absorbance changes at 667 nm (methylene blue) and at 297 nm (hydroxylation of 2-hydroxybenzoic acid). If no decolouration takes place there is no hydroxylation either.

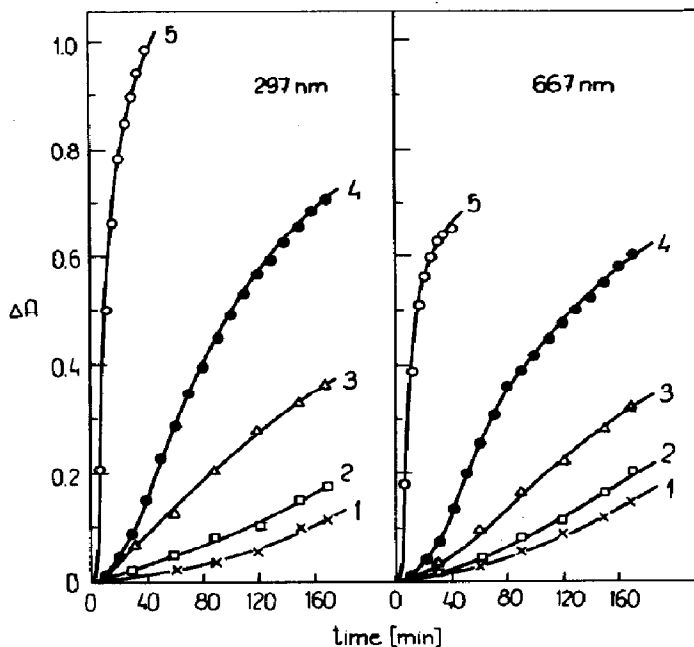


Fig. 7. Absorbance of the reaction solution as a function of time at 667 nm (methylene blue) and at 297 nm (hydroxylation). Irradiation by an HBO 200 arc (Osram) with an OG 5 band filter (Zeiss),  $\lambda > 550$  nm;  $T = 298$  K;  $[2\text{-hydroxybenzoic acid}]_0 = 4 \times 10^{-4}$  M;  $[\text{hydrogen peroxide}]_0 = 0.1$  M;  $[\text{methylene blue}]_0 = 1 \times 10^{-5}$  M.  $[\text{FeCl}_3]_0$ : curve 1, 0 M; curve 2,  $1 \times 10^{-8}$  M; curve 3,  $1 \times 10^{-7}$  M; curve 4,  $1 \times 10^{-6}$  M; curve 5,  $1 \times 10^{-5}$  M.

One could assume that the decolouration occurs by one-electron reduction to give the leuco form which, in turn, interacts with iron(III) to re-form methylene blue with simultaneous reduction of iron(III) to iron(II). Our experiments did not confirm this assumption and the decolouration of methylene blue was found to be irreversible. Thus, the leuco form is probably a product of oxidation or hydroxylation of methylene blue.

#### 4. Reaction mechanism

The photocatalytic effect in the methylene-blue-sensitized photochemical hydroxylation of 2-hydroxybenzoic acid undoubtedly originates in the photochemical generation of iron(II), *i.e.* in the generation of a catalyst of the thermal reaction.

An important clue to the reaction mechanism is the observed difference between the products of the reaction initiated by UV radiation (predominantly 2,5-dihydroxybenzoic acid) and those of the methylene-blue-sensitized reaction initiated by visible radiation (predominantly 2,3-dihydroxybenzoic acid). The difference cannot be explained in terms of the classical mechanism, which assumes the formation of a free hydroxyl radical (reaction (1)) followed by attack on 2-hydroxybenzoic acid by this radical (reaction (2)). If the product were formed by reaction (2), the path in which

the OH<sup>•</sup> radical is produced would not matter and the sensitized and UV-initiated reactions should yield the same product.

An acceptable explanation for all the experimental observations is provided by a mechanism which assumes that the hydroxylation occurs within the coordination sphere of the iron. This assumption is supported by the high stability constants of the complexes of both iron(III) and iron(II) with 2-hydroxybenzoic acid [12]. For instance, in a solution containing iron and 2-hydroxybenzoic acid at typical concentrations of  $10^{-5}$  M and  $4 \times 10^{-4}$  M respectively, there would be a free ferrous ion concentration of  $7 \times 10^{-9}$  M for iron in the +2 oxidation state and the concentration of iron in the +3 oxidation state would be  $1 \times 10^{-18}$  M. Clearly, ferrous ions at such a low concentration can hardly produce significant concentrations of OH<sup>•</sup> radicals through reaction (1). The assumption that the reaction involves mixed ligand ferric or ferrous ion complexes with 2-hydroxybenzoic acid, hydrogen peroxide and methylene blue as intermediate compounds receives further support from the simultaneous occurrence of 2-hydroxybenzoic acid hydroxylation and methylene blue decolouration. In no experiment did hydroxylation occur without simultaneous decolouration and, conversely, decolouration never took place alone without the acid being hydroxylated.

## 5. Conclusions

It has been demonstrated that it is feasible to sensitize efficiently the hydroxylation of 2-hydroxybenzoic acid by hydrogen peroxide initiated by visible light and catalysed by ferric chloride. Other organic compounds can probably be hydroxylated or oxidized in the same way. This opens up a wide variety of possibilities for accomplishing controlled oxidations and hydroxylations of organic compounds by using hydrogen peroxide.

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