COMPARISON OF PHOTOCATALYTIC ACTIVITIES OF 3d TRANSITION METAL IONS FOR HYDROGEN PEROXIDE PHOTOLYSIS AND PHOTOINITIATED HYDROXYLATION OF 2-HYDROXYBENZOIC ACID

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Quantum yields of hydrogen peroxide photolysis and photoinitiated hydroxylation of 2-hydroxybenzoic acid in the presence of 3d transition metal ions have been measured. Marked photocatalytic effects were only observed for Cu(II) in hydrogen peroxide photolysis, and for Fe(III) in photoinitiated hydroxylation of 2-hydroxybenzoic acid. No photocatalytic activity was detected for the other 3d transition metal ions investigated. Fe(III) and Cu(II) differ in their photocatalytic activities, suggesting that the simple concept of free OH$^\cdot$ radical formation cannot explain the mechanisms of their action.

In previous studies, we investigated the photocatalytic effects of Cu(II) and Fe(III) on the photolysis of hydrogen peroxide[1-4] and of Fe(III) on the photoinitiated hydroxylation of 2-hydroxybenzoic acid by hydrogen peroxide[5,6].

Classical interpretation[7-9] of the mechanisms of catalytic effects assumes the intermediate formation of a hydroxyl radical by the action of transition metal ions:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\cdot \qquad (A)$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + OH^- + OH^\cdot . \qquad (B)$$
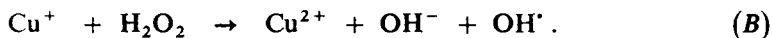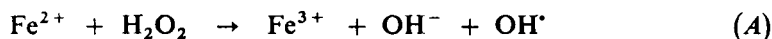
In the case of photolysis[7,8], it is assumed that the hydroxyl radical starts the propagation cycle

$$OH^\cdot + H_2O_2 \rightarrow H_2O + HO_2^\cdot \qquad (C)$$

$$HO_2^\cdot + H_2O_2 \rightarrow H_2O + O_2 + OH^\cdot . \qquad (D)$$
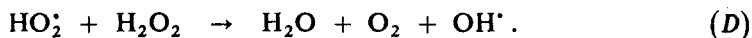
In hydroxylation[9,10], the hydroxyl radical is supposed to start the reaction by abstracting hydrogen

$$R\text{---}H + OH^\cdot \rightarrow R^\cdot + H_2O . \qquad (E)$$
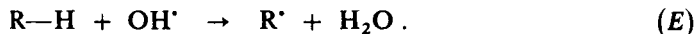
Clearly, if the concept of catalyzed generation of free hydroxyl radical were true, the catalytic activity for the photolysis should correlate with that for the hydroxylation.

In the past, hydrogen peroxide photolysis and photoinitiated hydroxylation were studied under different conditions. The aim of the present work was to examine the photocatalytic activities of transition metal ions for both reactions under identical conditions and so verify the existing mechanistic concepts.

EXPERIMENTAL

Chemicals

Hydrogen peroxide of analytical grade (Chemické závody, Sokolov), 2-hydroxybenzoic acid (Reanal, Budapest), and ferric chloride (Cambrian Chemicals) were used as received. Cupric sulphate of analytical grade (Lachema, Brno) was purified before use by recrystallization. The other chemicals used were of analytical grade (Lachema, Brno).

Since impurities contained in ordinary redistilled water markedly affect quantum yields of hydrogen peroxide photolysis, special care was taken to ensure high purity of water. The method used to purify redistilled water has been described previously[2].

Experimental Arrangement and Procedure

The reaction solution was irradiated in a 1 cm quartz cell placed in a thermostatted block. The radiation source was a low-pressure mercury arc (Spectral lamp Philips 93 109E). Under the conditions employed, the arc was virtually a monochromatic radiation source of 254 nm wavelength. UV absorption spectra were taken on Unicam SP-800 and Beckman Acta M-IV spectrophotometers.

The quantum yields of hydrogen peroxide photolysis (Φ_P, molecules of H_2O_2 *per* quantum) and photoinitiated hydroxylation of 2-hydroxybenzoic acid (Φ_H, molecules of $C_6H_4(OH)(COOH)$ *per* quantum) were expressed as the average numbers of molecules of the reacted substance *per* quantum of radiation absorbed by the reaction solution, the average being taken over the whole time of irradiation:

$$\Phi_P(\Phi_H) = \frac{N_A\,\Delta c_P(\Delta c_H)\,V}{1\,000\tau I_0(1-10^{-A})}\,,$$

where N_A is the Avogadro constant, V is the irradiated volume (ml), τ is the irradiation time (s), I_0 is the radiation intensity (quantum s^{-1}) (determined by using potassium tris(oxalato)ferrate-(III)[11]), and A is the average absorbance of the reaction solution over a given time interval at 254 nm.

The molar concentration of hydrogen peroxide decomposed by photolysis (Δc_P) was determined from changes in the absorption spectrum of the reaction solution. The molar concentration of 2-hydroxybenzoic acid that had undergone hydroxylation (Δc_H) was established by two methods. In comparative experiments, the reaction solution was treated after irradiation by the method described by Grinstead[12]. On acidifying to pH = 2·5, unreacted 2-hydroxybenzoic acid was extracted into chloroform. The reaction solution was then treated with diethyl ether to extract dihydroxybenzoic acids. The ether was evaporated in a vacuum vaporizer and the residue was dissolved in water. Measurement of the absorbances of individual phases and their volumes

provided a correlation between the change in the absorption spectra of reaction solutions and the amount of reacted 2-hydroxybenzoic acid. In further experiments of the series, changes in 2-hydroxybenzoic acid concentration during the reaction were determined from changes in absorption spectra.

In order to distinguish strictly the catalytic from photocatalytic effects, we always followed the thermal reaction in parallel with the photoinitiated reaction. Compared with the rate of the photochemical reaction, that of the thermal reaction was, however, negligible in all experiments.

RESULTS AND DISCUSSION

We have studied the effects of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions on the quantum yields of hydrogen peroxide photolysis and photo-initiated hydroxylation of 2-hydroxybenzoic acid by hydrogen peroxide. The results summarized in Table I show that Cu(II) and Fe(III) are the only species to exhibit photocatalytic effects under the conditions employed. Cu(II) is particularly efficient in increasing the quantum yields of the photolysis, while Fe(III) dominates in catalyzing the hydroxylation.

We have also investigated changes in the ratio of the photocatalytic activities of Cu(II) and Fe(III) with changing concentration of hydrogen peroxide and hence with changing ratio of the amounts of radiation absorbed by the components of the reaction solution. The amounts of radiation absorbed by individual components of the reaction solutions are given in Table II. The quantum yields of hydrogen peroxide photolysis and photoinitiated hydroxylation of 2-hydroxybenzoic acid are listed in Table III. As seen in this table, a decrease in hydrogen peroxide concentra-

TABLE I

Effect of added $3d$ transition metal compounds ($1 . 10^{-5}$ mol dm^{-3}) on the quantum yields of hydrogen peroxide photolysis (Φ_P) and hydroxylation of 2-hydroxybenzoic acid (Φ_H). Irradiated by a low-pressure mercury arc. $I_0 = 9.84 . 10^{14}$ quantum s^{-1}; $T = 298$ K; $[H_2O_2]_0 = 0.09$ mol . . dm^{-3}; Φ_P (molecules of H_2O_2/quantum): irradiation time 120 min; Φ_H (molecules of 2-hydroxybenzoic acid/quantum): irradiation time 60 min; [2-hydroxybenzoic acid]$_0 = 4 . 10^{-4}$ mol dm^{-3}

Added compound	Φ_P	Φ_H
—	1·43	0·081
KCr(SO$_4$)$_2$	2·06	0·071
MnSO$_4$	1·29	0·071
FeCl$_3$	4·29	0·169
NiSO$_4$	1·62	0·057
CuSO$_4$	22·5	0·126
ZnSO$_4$	1·29	0·076

tion results in decreased quantum yields of both the photolysis and the hydroxylation regardless of whether these are catalyzed or uncatalyzed reactions. There is also a slight variation in the ratio of the catalytic activities of Fe(III) and Cu(II). On the whole, however, it is observed that under all reaction conditions used cupric sulphate is superior in catalyzing the photolysis, whereas ferric chloride is more efficient in increasing the quantum yields of the hydroxylation.

TABLE II

Proportions of radiation absorbed by individual components of the reaction solution (percentages of the total radiation absorbed); $T = 298$ K

a) Hydrogen peroxide photolysis; [catalyst] $= 1 \cdot 10^{-5}$ mol dm^{-3}

$[H_2O_2]$ mol dm^{-3}	Catalyst	Percentage of radiation absorbed by	
		H_2O_2	Catalyst
0·9	CuSO$_4$	99·94	0·06
	FeCl$_3$	97·65	2·35
0·09	CuSO$_4$	99·94	0·06
	FeCl$_3$	97·58	2·42
0·009	CuSO$_4$	99·80	0·20
	FeCl$_3$	92·66	7·34

b) Photoinitiated hydroxylation of 2-hydroxybenzoic acid; [2-hydroxybenzoic acid] $= 4 \cdot 10^{-4}$ mol dm^{-3}; [catalyst] $= 1 \cdot 10^{-5}$ mol dm^{-3}

$[H_2O_2]$ mol dm^{-3}	Catalyst	Percentage of radiation absorbed by		
		H_2O_2	$C_6H_4(OH)(COOH)$	Catalyst
0·09	—	72·05	27·95	0
	CuSO$_4$	72·01	27·94	0·05
	FeCl$_3$	70·78	27·47	1·75
0·009	—	44·61	55·39	0
	CuSO$_4$	44·57	55·34	0·09
	FeCl$_3$	43·09	53·50	3·41
0·0009	—	8·61	91·39	0
	CuSO$_4$	8·60	91·25	0·15
	FeCl$_3$	8·14	86·35	5·51

There is a difference in the mechanisms of the photocatalytic effects of Fe(III) and Cu(II) on the above reactions, as documented by different variations in the quantum yield with irradiation time. In the case of hydroxylation of 2-hydroxybenzoic acid with added Fe(III), there is a steep increase in the reaction rate during the initial phase of the reaction as a result of accumulation of photochemically generated ferrous ions[5] (Fig. 1, curve 3). In the absence of any added photocatalyst (Fig. 1, curve 1) or if cupric sulphate is added (Fig. 1, curve 2), no accumulation of photochemically generated, catalytically active species occurs (the mean relative deviations

TABLE III

Effect of initial hydrogen peroxide concentration (mol dm^{-3}) on the quantum yields of hydrogen peroxide photolysis (Φ_P) and hydroxylation of 2-hydroxybenzoic acid by hydrogen peroxide (Φ_H). Irradiated by a low-pressure mercury arc. $I_0 = 9.84 \cdot 10^{14}$ quantum s^{-1}; $T = 298$ K; concentration of added salt, $1 \cdot 10^{-5}$ mol dm^{-3}; Φ_P (molecules of H$_2$O$_2$/quantum): irradiation time 120 min; Φ_H (molecules of 2-hydroxybenzoic acid/quantum): irradiation time 60 min [2-hydroxybenzoic acid]$_0 = 4 \cdot 10^{-4}$ mol dm^{-3}

Catalyst	[H$_2$O$_2$]$_0$							
	0·9		0·09		0·009		0·0009	
	Φ_P	Φ_H	Φ_P	Φ_H	Φ_P	Φ_H	Φ_P	Φ_H
—	4·33	—	1·43	0·081	2·24	0·065	—	0·025
FeCl$_3$	10·7	—	4·29	0·169	2·55	0·152	—	0·041
CuSO$_4$	98·1	—	22·5	0·126	6·68	0·069	—	0·030

FIG. 1

Variation in the quantum yield of photo-initiated hydroxylation of 2-hydroxybenzoic acid by hydrogen peroxide, Φ_H (molecules of 2-hydroxybenzoic acid/quantum), with time. Irradiated by a low-pressure mercury arc. $I_0 = 9.84 \cdot 10^{14}$ quantum s^{-1}; $T = 298$ K; [H$_2$O$_2$]$_0 = 0.09$ mol dm^{-3}; [2-hydroxybenzoic acid]$_0 = 4 \cdot 10^{-4}$ mol . . dm^{-3}; 1 no catalyst; 2 $1 \cdot 10^{-5}$ mol dm^{-3} CuSO$_4$; 3 $1 \cdot 10^{-5}$ mol dm^{-3} FeCl$_3$
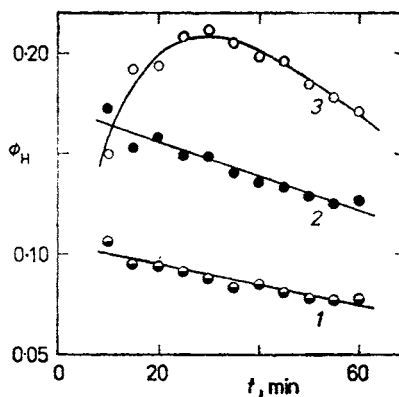
from the linear plot of the quantum yield against the irradiation time are $4\cdot0\%$ and $3\cdot2\%$, respectively).

A different situation arises in the case of hydrogen peroxide photolysis. Under the given conditions, the reaction shows no autocatalytic character, even in the presence of added ferric chloride. Thus no appreciable accumulation of Fe(II) occurs. The addition of ferric ions to the reaction system does not change the quantum yield to a large extent. (The mean relative deviation from the linear plot of the quantum yield against the irradiation time for the photolysis of $0\cdot009$ mol dm^{-3} hydrogen peroxide with $1 \cdot 10^{-5}$ mol dm^{-3} added ferric chloride was $4\cdot3\%$.)

Of the $3d$ transition metal ions studied, only Fe(III) and Cu(II) were found to exert marked photocatalytic effects. Ferric ions, which are efficient in catalyzing the photochemical hydroxylation, have only a small effect on the quantum yield of hydrogen peroxide photolysis. On the other hand, Cu(II), an efficient catalyst of the photolysis, has only a slight accelerating effect on the photoinitiated hydroxylation. This implies that the catalytic action of the transition metals is not limited to the production of free OH· radicals (if it were, both transition metals should accelerate photolysis as well as hydroxylation) and that both reactions occur within the co-ordination sphere of the catalyzing transition metal ion.

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