

PHOTOLYSIS OF HYDROGEN PEROXIDE. PHOTOCATALYTIC EFFECTS OF Cu(II) AND REACTION KINETICS

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The quantum yield of hydrogen peroxide photolysis has been measured as a function of the concentration of photocatalytically active Cu^{2+} ions, intensity of photolytic radiation, temperature, and hydrogen peroxide concentration. The results obtained are consistent with the concept that high quantum yields of hydrogen peroxide photolysis ($\Phi \gg 1$) are due to thermal decomposition of hydrogen peroxide catalyzed by photochemically generated copper ions in oxidation states which are catalytically active.

We have shown recently¹⁻⁴ that quantum yields of hydrogen peroxide photolysis are affected by transition metal ions. The photocatalytic effects of Cu^{2+} are so strong that they are important even at trace concentrations (10^{-8} mol dm⁻³) of cupric ions^{1,2}. We have demonstrated² that with decreasing concentration of photocatalytically active Cu^{2+} ions there is a drop in the quantum yield of hydrogen peroxide photolysis from the initial $\Phi \gg 1$ to $\Phi < 1$. It is likely that the photocatalytic effects of transition metal ions are alone responsible for high quantum yields ($\Phi \gg 1$). This finding is in direct contradiction to the classical Haber-Weiss mechanism^{5,6}, which assumes that high quantum yields are due to a long kinetic chain length.

According to some literature data⁷, photolytic radiation intensity is the controlling factor in determining whether the photolysis of hydrogen peroxide proceeds by a chain ($\Phi > 1$) or a non-chain ($\Phi < 1$) mechanism. It has been stated⁷ that at $I_{\text{abs}} < 10^{17}$ quantum dm⁻³ s⁻¹ hydrogen peroxide photolysis occurs by a free radical chain mechanism.

The aim of the present work was to investigate the relationship between the quantum yield of hydrogen peroxide photolysis and the concentration of photocatalytically active Cu(II) ions at various intensities of photolytic radiation, hydrogen peroxide concentrations and reaction temperatures, and to confront the observations with both the classical free radical chain mechanism⁵⁻⁷ and our concept of photochemical generation of catalyst of hydrogen peroxide thermal decomposition^{2,4}.

EXPERIMENTAL

Chemicals

Most experiments were carried out with commercial hydrogen peroxide of analytical grade (Chemical Works, Sokolov). Comparative measurements were made using unstabilized hydrogen peroxide taken directly off production line. No significant differences were found between results obtained with the two sorts of hydrogen peroxide. Cupric sulphate (analytical grade; Lachema, Brno) was purified before use by recrystallization from redistilled water.

Special care was taken to ensure high purity of water used in experiments. Impurities present in redistilled water markedly affect the kinetics of hydrogen peroxide photolysis. The method used to purify redistilled water has been described in a previous paper².

Experimental Arrangement and Procedure

Two methods were used to follow the course of hydrogen peroxide photolysis: measurement of changes in the UV absorption spectrum of the reaction solution, and measurement of the volume of evolved oxygen.

In the spectrophotometric investigation, 3.5 ml of reaction solution was irradiated in a 1 cm quartz cell placed in a thermostatted block with a window for irradiation. The irradiation was interrupted at regular time intervals, and UV absorption spectra of the reaction solution were recorded.

In addition, the photolysis of hydrogen peroxide was followed volumetrically, *i.e.* by measuring the amount of evolved oxygen. The photolysis was carried out in a thermostatted, vigorously shaken quartz vessel connected to a gas burette.

In most experiments the photolytic radiation was obtained from a low-pressure mercury lamp (Spectral Lamp Philips 93109 E). Under the given conditions, this lamp functions essentially as a monochromatic source of radiation with a wavelength of 254 nm. As indicated by the value of the molar absorption coefficient ($\epsilon_{254} = 17.5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$), more than 99% of the incident radiation is absorbed in a 1 cm layer of reaction solution containing hydrogen peroxide in concentrations higher than $0.115 \text{ mol dm}^{-3}$. Thus, the 254 nm radiation was practically completely absorbed at all hydrogen peroxide concentrations used in our measurements.

In a few comparative experiments, the photolysis of hydrogen peroxide was initiated by the whole spectrum of a high-pressure mercury lamp (HBO 200 W, Narva, Berlin). The molar absorption coefficients for the main emission lines of this lamp are given in Table I, along with percentages of radiation absorbed by hydrogen peroxide solution. Comparison of the emission spectrum of the lamp⁸ with percentages of absorbed radiation shows that the majority of absorbed photons has a wavelength of 313 nm. For the most prominent 365 nm line, the absorption in 2 mol dm^{-3} hydrogen peroxide solution is relatively weak (only about 1% in a 1 cm layer).

The amount of photolytic radiation incident upon the reaction cell was measured by means of ferrioxalate actinometer.

In order to achieve a strict resolution of the thermal and the photoinitiated decomposition, we always performed two parallel measurements, one to determine the overall reaction rate on irradiation and the other to establish the reaction rate in the absence of photolytic radiation. The rate of photolysis was obtained as the difference between the overall rate on irradiation and the rate of thermal reaction. The quantum yield was expressed as the number of decomposed hydrogen peroxide molecules per light quantum absorbed by the irradiated reaction system. The rigorous approach in which only the quanta absorbed by the photochemically active species

are taken into account is rarely feasible in studies of photocatalyzed reactions. In general, the radiation is absorbed by both the catalyst precursor (photocatalyst) and the reacting substrate (here hydrogen peroxide).

RESULTS AND DISCUSSION

Effect of Cu(II) Concentration

The effect of cupric ions on the photolysis of hydrogen peroxide has been known for a relatively long time⁹. Recently, we have demonstrated^{1,2} that even trace concentrations of cupric ions (of the order of 10^{-9} mol dm⁻³) can markedly affect the quantum yields. However, the quantum yield is rather variable at these concentrations, being markedly affected by fluctuations in the content of trace impurities in the water used. A regular increase in quantum yield with increasing amount of added Cu(II) could only be observed from an addition of $1 \cdot 10^{-8}$ mol dm⁻³ upwards.

According to some literature sources⁷, the intensity of photolytic radiation is the basic criterion for determining whether a reaction will go by a chain or a non-chain mechanism. It has been stated⁷ that at intensities of absorbed radiation above 10^{17} quantum dm⁻³ s⁻¹ the photolysis of hydrogen peroxide occurs by a non-chain mechanism. We have therefore investigated the variation in the quantum yield of hydrogen peroxide photolysis with the concentration of added cupric sulphate at various intensities of photolytic radiation, using different experimental arrangements. The results (Fig. 1 and Table II) indicate that reaction conditions, including the intensity, do not greatly influence the functional relationship between the quantum yield and the Cu(II) concentration. Generally, decreasing the irradiation intensity

TABLE I

Molar absorption coefficients (mol⁻¹ dm³ cm⁻¹) of an aqueous solution of hydrogen peroxide, and proportions of radiation absorbed in a 1 cm layer of hydrogen peroxide solution ($1 \cdot 97$ mol . dm⁻³) for the wavelengths (nm) of mercury lamp emission lines

λ	ϵ	per cent of absorbed radiation
254	17.5	100
265	9.45	100
297	1.26	99.7
303	0.800	97.4
313	0.378	82.0
334	0.076	29.2
365	0.0023	1.04

causes a very slight increase in the slope of the quantum yield *vs* Cu(II) concentration plot. Even a marked change in the initial concentration of hydrogen peroxide or a change in the experimental technique does not produce any pronounced change in the dependence of the quantum yield on the concentration of added Cu(II).

The results obtained indicate that the quantum yield of hydrogen peroxide photolysis is critically dependent on the concentration of photocatalytically active species, the cupric ions. Considering that a distinct effect is observed even on addition of cupric ions in such concentrations as can be expected to occur naturally in any real reaction system, it is probable that the quantum yields reported in the literature were determined simply by random concentrations of cupric ions in the reaction systems.

Effect of Photolytic Radiation Intensity

In accord with literature data⁷, the quantum yield of hydrogen peroxide photolysis was found to increase with decreasing intensity of photolytic radiation. Usually, the increase in quantum yield is interpreted as being due to radical deactivation through mutual recombination, and the quantum yield is related to the radiation intensity by

$$\Phi = \text{constant} \cdot I^{-1/2} . \quad (1)$$

As can be seen from Fig. 2, the dependence expressed by Eq. (1) has not been confirmed. The experimental results show systematic deviations from Eq. (1) even

TABLE II

Variation in the quantum yield of hydrogen peroxide photolysis with the concentration of added Cu²⁺ ions (mol dm⁻³) for various intensities of photolytic radiation; *T* = 298 K

Reaction conditions ^a	[Cu ²⁺]	Φ molecules H ₂ O ₂ /quantum
<i>a</i>	3 · 10 ⁻⁸ – 1 · 10 ⁻⁵	4 · 17 · 10 ³ · [CuSO ₄] ^{0.400}
<i>b</i>	1 · 10 ⁻⁷ – 3 · 10 ⁻⁴	9 · 33 · 10 ³ · [CuSO ₄] ^{0.416}
<i>c</i>	3 · 10 ⁻⁶ – 1 · 10 ⁻⁴	1 · 54 · 10 ⁴ · [CuSO ₄] ^{0.422}
<i>d</i>	1 · 10 ⁻⁷ – 3 · 10 ⁻⁴	3 · 89 · 10 ⁵ · [CuSO ₄] ^{0.516}

^a *I* · 10⁻¹⁶ (quantum dm⁻³ s⁻¹): *a* – 35·4; *b* – 4·57; *c* – 1·74; *d* – 2·81; [H₂O₂]₀: *a*, *b*, *c* – 0·2 mol dm⁻³; *d* – 5·1 mol dm⁻³; *a*, *b*, *c* – 1 cm quartz cell, followed spectrophotometrically, quantum yield determined after 60 min irradiation; *d* – cylindrical quartz vessel, followed volumetrically, quantum yields determined after 10 min irradiation.

under conditions where $\Phi \gg 1$, *i.e.* where the photolysis should occur by a free radical chain mechanism.

Assuming that the absorption of radiation not only can give rise to catalytically active species but also cause their decay, we can explain the dependence of the quantum yield on the radiation intensity in terms of photocatalytic effects.

Effect of Temperature

The effect of temperature on the quantum yield of hydrogen peroxide photolysis has been studied at three levels of added cupric ions (0 ; $1 \cdot 10^{-6}$ mol dm $^{-3}$; $1 \cdot 10^{-5}$ mol dm $^{-3}$). As seen from Fig. 3, the variation in the quantum yield with temperature for each level follows the Arrhenius relation. The mean relative deviations from the linearized plot of $\ln \Phi$ against $1/T$ are low, *viz.* 2.9%, 1.0%, and 0.2%.

The observed temperature dependence indicates that the rate-controlling step of hydrogen peroxide photolysis is some of the thermal reactions that follow the absorption of a light quantum and the primary photophysical and photochemical

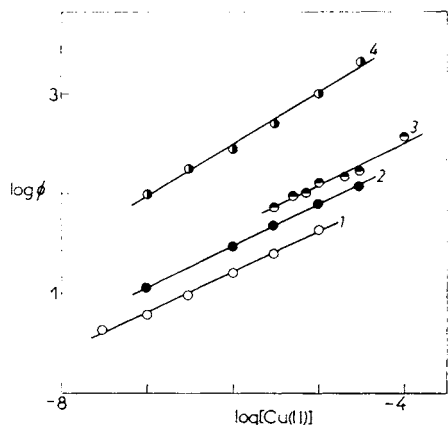


FIG. 1

Dependence of the quantum yield, Φ (molecules H_2O_2 /quantum), of hydrogen peroxide photolysis on the concentration of added Cu(II) for various reaction conditions. Average quantum yield after 60 min (curves 1–3) or 10 min (curve 4) irradiation. $\lambda = 254$ nm; $T = 298$ K; $[\text{H}_2\text{O}_2]_0: 0.2$ mol dm $^{-3}$ (curves 1–3); 5.1 mol dm $^{-3}$ (curve 4). $I \cdot 10^{-16}$ (quantum dm $^{-3}$ s $^{-1}$): 1 35.4; 2 4.57; 3 1.74; 4 2.81

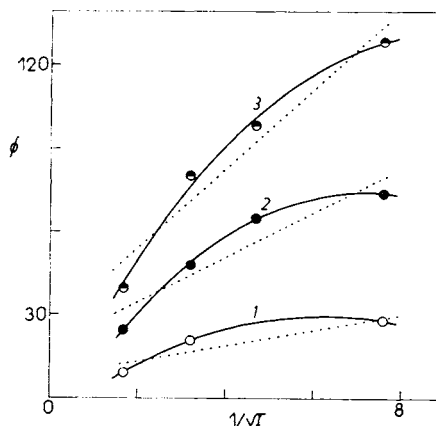


FIG. 2

Dependence of the quantum yield, Φ (molecules H_2O_2 /quantum), of hydrogen peroxide photolysis on the reciprocal of the square root of photolytic radiation intensity for various concentrations of added Cu(II) . Average quantum yield after 60 min irradiation. $\lambda = 254$ nm; $T = 298$ K; $[\text{Cu(II)}]: 1.0$; $2.3 \cdot 10^{-6}$ mol dm $^{-3}$; $3.1 \cdot 10^{-5}$ mol dm $^{-3}$

processes. The apparent activation energies were found to be as follows: 23 kJ mol^{-1} for photolysis without added cupric ions; 20 kJ mol^{-1} for an addition of $1 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3} \text{ Cu(II)}$; and 15 kJ mol^{-1} for $1 \cdot 10^{-5} \text{ mol dm}^{-3} \text{ Cu(II)}$. Apparently, the photocatalytic effect of cupric ions is (at least partly) to lower the activation energies of the thermal reactions.

Effect of Initial Concentration of Hydrogen Peroxide

According to the literature⁷, the reaction rate (quantum yield) is directly proportional to the concentration of hydrogen peroxide. We have verified this dependence for low concentrations of hydrogen peroxide ($0.2\text{--}0.8 \text{ mol dm}^{-3}$). For $5 \cdot 10^{-6} \text{ mol dm}^{-3} \text{ Cu(II)}$, 254 nm , $I = 3.54 \cdot 10^{14} \text{ quantum dm}^{-3} \text{ s}^{-1}$, 298 K and an irradiation period of 60 min, for example, we have established the relation

$$\Phi = 17.7 + 43.1 [\text{H}_2\text{O}_2]. \quad (2)$$

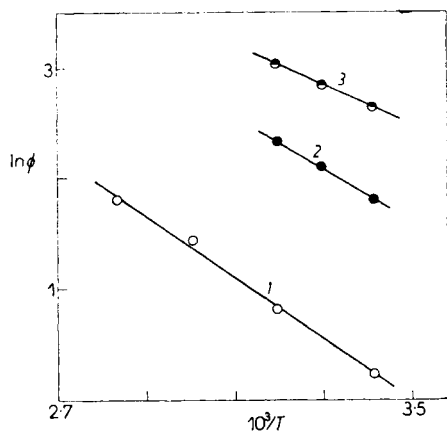


FIG. 3

Verification of the Arrhenius relation for hydrogen peroxide photolysis. A plot of $\ln \Phi$ vs $1/T$. Average quantum yield after 60 min irradiation. Φ (molecules H_2O_2 /quantum); $\lambda = 254 \text{ nm}$; $I = 3.97 \cdot 10^{17} \text{ quantum dm}^{-3} \text{ s}^{-1}$. $[\text{H}_2\text{O}_2]_0 = 9.7 \cdot 10^{-2} \text{ mol dm}^{-3}$; $[\text{Cu(II)}]_{\text{added}}$: 1 0; 2 $1 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$; 3 $1 \cdot 10^{-5} \text{ mol dm}^{-3}$

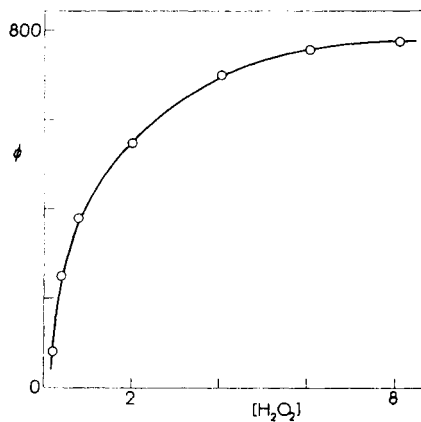


FIG. 4

Effect of the initial concentration of hydrogen peroxide on the quantum yield, Φ (molecules H_2O_2 /quantum), of hydrogen peroxide photolysis at a constant addition of $[\text{Cu(II)}] = 5 \cdot 10^{-6} \text{ mol dm}^{-3}$. Average quantum yield after 60 min irradiation. $\lambda = 254 \text{ nm}$; $I = 2.81 \cdot 10^{16} \text{ quantum dm}^{-3} \text{ s}^{-1}$; $T = 298 \text{ K}$

At $[\text{H}_2\text{O}_2]_0 > 1 \text{ mol dm}^{-3}$, the rate of increase in the quantum yield slows down compared to the linear dependence until, at $[\text{H}_2\text{O}_2]_0 > 6 \text{ mol dm}^{-3}$, the quantum yield becomes almost independent of hydrogen peroxide concentration.

A possible explanation of the observed increase of the quantum yield with increasing concentration of hydrogen peroxide is in terms of gradual saturation of the coordination sphere of photocatalytically active copper ions. The limiting value of quantum yield would then correspond to completely saturated coordination sphere (Fig. 4).

Inhibiting Effect of Sulphide and Hydrogen Phosphate

The photocatalytic effect of added transition metal compounds on the photolysis of hydrogen peroxide has been conclusively established^{1-4,9}. Trace concentrations of the compounds are also known to produce photocatalytic effects^{1,2}. Every reaction system contains trace concentrations of transition metals, some of which are photocatalytically active. We performed experiments in which substances (a sulphide and a phosphate) which bind transition metal ions into weakly dissociated compounds were added to a solution of hydrogen peroxide. As can be seen from Table III, the addition of these substances distinctly lowers the quantum yield of photolysis of "pure" hydrogen peroxide. This finding is evidence that the quantum yield of photolysis of pure hydrogen peroxide solution alone is determined by the level of photocatalytically active metal ions naturally occurring in these systems.

TABLE III

Effect of added potassium sulphide and sodium hydrogen phosphate on the quantum yield of hydrogen peroxide photolysis ($9.7 \cdot 10^{-2} \text{ mol dm}^{-3}$); irradiated at 254 nm; $I = 3.94 \cdot 10^{17} \text{ quantum dm}^{-3} \text{ s}^{-1}$; $T = 293 \text{ K}$; Φ in (molecules $\text{H}_2\text{O}_2/\text{quantum}$) units

Time min	Addition			
	0	$5 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{ K}_2\text{S}$	$0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{HPO}_4^a$	$0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{HPO}_4^b$
120	1.16	0.958	—	0.468
150	—	—	0.843	—
240	1.06	0.719	—	0.381
360	1.05	0.659	0.683	0.390
420	—	0.669	0.585	—
480	—	—	—	0.424

^a Irradiated immediately upon mixing; ^b irradiated after standing for 12 h.

Reaction Mechanism

As has been shown above, there is no reason to assume that the photochemical decomposition of hydrogen peroxide occurs by two mechanisms, a chain and a non-chain one, and that the intensity of absorbed radiation determines which mechanism will predominate. It has been demonstrated that the quantum yield of photochemical reaction depends critically and under all conditions on the concentration of photocatalytically active species present in the solution.

The photocatalytic activity has been established for copper^{1,2,4,9,10} and $\text{ircn}^{2-4,11,12}$ ions. Of particular importance is the observation that these ions show a marked photocatalytic activity even when present in trace concentrations^{1,2} (*i.e.*, below 10^{-7} mol dm⁻³). Such concentrations of transition metal ions occur even in very pure hydrogen peroxide solutions.

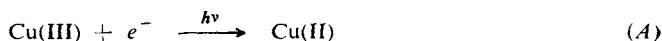
In drawing up the mechanism of photocatalyzed decomposition of hydrogen peroxide, consideration must be given to the fact that this reaction shows a marked dependence on temperature. The relevant experimental data suggest that the rate-determining step of photochemical decomposition is the thermal reaction, which is catalyzed by transition metal ions.

In a previous paper² we discussed the mechanism of hydrogen peroxide photolysis involving the photocatalytic effect of ferric ions. It was shown that radiation reduced the poorly photocatalytically active ferric ions to ferrous ions with increased photocatalytic activity. It may be expected, and there is experimental evidence to suggest, that the photocatalytic effect of copper likewise consists in photochemical generation of an unstable, catalytically active oxidation state of copper.

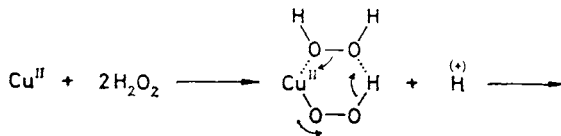
Cupric aquo ions, which are effective in catalyzing the decomposition of hydrogen peroxide, are unstable in hydrogen peroxide solutions. UV-VIS and EPR spectra of the reacting solutions have proved that cupric ions in hydrogen peroxide solutions rapidly undergo a transition to Cu(I) or Cu(III) ions.

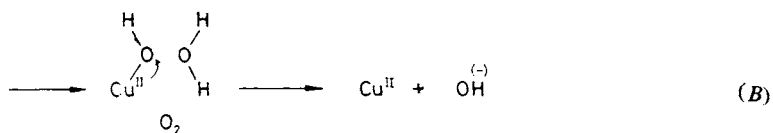
On the basis of experimental observations and literature data on the mechanism of thermal decomposition of hydrogen peroxide, we propose the following mechanism of photochemical decomposition of hydrogen peroxide catalyzed by copper ions.

Photochemical generation of catalytically active oxidation state



Catalyzed thermal decomposition of hydrogen peroxide¹³





Decay of catalytically active oxidation state



The proposed reaction scheme assumes that hydrogen peroxide oxidizes Cu(II) to Cu(III). In the first step of the photochemical reaction, Cu(III) ions are photochemically reduced to Cu(II), which are unstable in hydrogen peroxide solution but catalyze the thermal decomposition of hydrogen peroxide. However, we cannot rule out the possibility that hydrogen peroxide reduces Cu(II) to Cu(I) which, in turn, is oxidized photochemically to unstable Cu(II). It seems that both the CTTL ($\text{M} \rightarrow \text{H}_2\text{O}_2$) and CTTM ($\text{M} \leftarrow \text{H}_2\text{O}_2$) electron transfers can occur in complexes of hydrogen peroxide with transition metal ions.

A good account of the catalyzed thermal decomposition of hydrogen peroxide has been given by the mechanism proposed by Sigel¹³ (reaction B), which assumes that the reaction occurs within the coordination sphere of the catalyzing metal. As has been shown, there is no reason to assume that the photochemical decomposition of hydrogen peroxide occurs by the Haber-Weiss free radical chain mechanism⁵.

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