

HYDROGEN PEROXIDE PHOTOLYSIS. MECHANISM OF PHOTOCATALYTIC EFFECT OF TRANSITION METALS

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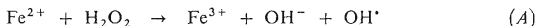
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The photochemical decomposition of hydrogen peroxide depends on the presence of transition metal ions in the reaction system. Photochemical reduction of the poorly catalytically active ions with higher oxidation states produces catalytically active ions of lower oxidation states which catalyze the thermal reaction. The quantum yield of hydrogen peroxide photolysis is proportional to the number of catalytic cycles occurring on the photochemically generated catalyst.

The original Haber-Weiss mechanism¹ of hydrogen peroxide decomposition (equations (A-E)), which was proposed to account for both the thermal and photochemical reactions, is only used nowadays to interpret the results of photolysis and radiolysis².

Initiation

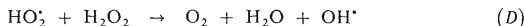
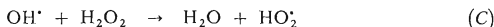
a) thermal



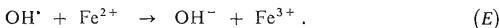
b) photochemical



Propagation



Termination



Serious objections were raised^{3,4} to reaction (D) being part of the scheme for the thermal reaction, and reaction (D) has been replaced by



The free radical chain reaction scheme for the photolysis, on the other hand, necessitates the participation of reaction (D), for otherwise there is no way of accounting for the formation of oxygen. The literature data² for the rate constant of reaction (D) show great scatter (over six orders of magnitude), suggesting that the reaction scheme does not give a true picture of the reaction mechanism.

We have shown recently⁵ that hydrogen peroxide photolysis is crucially affected by transition metal ions (Cu, Fe) present in the reaction system as impurities in trace concentrations. There are reasons to believe that in the absolute absence of transition metal ions the reaction would not take place at all.

This finding is in utter contradiction to the generally accepted Haber-Weiss mechanism of hydrogen peroxide decomposition. We have therefore undertaken a detailed study of the catalytic effects of transition metal ions on hydrogen peroxide photolysis, and of the mechanism by which this reaction proceeds.

EXPERIMENTAL

Chemicals

Hydrogen peroxide was mostly semiconductor grade (Chemické závody, Sokolov); in several experiments analytical grade (Chemické závody, Sokolov) was used.

In the study of the thermal as well as photoinitiated decomposition of hydrogen peroxide, the purity of the solvent, water, is of paramount importance. Specially treated redistilled water was therefore used in making up the solutions. Inhibiting residues of organic substances were eliminated by the following procedure: redistilled water with an addition of about 0.2 g KMnO_4 per litre was boiled for a minimum of 10 h, and then rectified on a 1 m column; the medium fraction (about half of the total volume) was collected. The purity of the water was checked by measuring the conductivity and the rate of thermal decomposition of hydrogen peroxide. Experiments using the water gave reproducible results, and permitted the effect of additions of transition metal compounds to be demonstrated even at very low concentrations (for Cu^{II} , *e.g.*, even at 10^{-8} mol dm^{-3}).

Potassium ferrioxalate, used as actinometer as well as sensitizer of hydrogen peroxide photolysis, was prepared following a published procedure⁶.

The other chemicals (mostly analytical grade, Lachema) were used without further purification.

Experimental Arrangement and Procedure

The course of hydrogen peroxide photolysis was followed volumetrically, by measuring the amount of evolved oxygen. The photolysis was carried out in a thermostatted quartz cell connected to a gas burette. The quartz cell was vigorously shaken. A HBO 200 high-pressure mercury arc (Narva, Berlin) was used as source of the photolytic radiation. Some experiments were initiated by the whole spectrum of the arc. In measurements of the quantum yields of direct photolysis, the radiation was monochromatized by a UV KS IF 313 interference filter (Carl Zeiss, Jena). From the HBO 200 spectrum, this filter transmits primarily the 313 nm line (22%), and also a minor amount of Hg-lines, namely 297 nm (2%), 303 nm (7%), and 334 nm (1.5%). A supplementary filter No 3 to an SPM 2 monochromator (Carl Zeiss, Jena) was used in experiments

exploring the effect of radiation with wavelengths that are not absorbed by hydrogen peroxide ($\lambda < 395$ nm). The spectral characteristics of the two filters, along with prominent emission lines of the HBO 200 high-pressure arc are shown in Fig. 1.

In experiments where quantum yields were determined, the intensity of the initiating radiation was measured using a ferrioxalate actinometer⁶.

As the reactions of thermal⁷ and photoionitiated⁵ decomposition of hydrogen peroxide are both trace-catalyzed, it was necessary to follow them separately in each experiment in order to discriminate exactly between the catalytic and photocatalytic* effects. It was important to carry the thermal reaction to a low conversion, so that the photoionitiated reaction could be started immediately at an initial hydrogen peroxide concentration not too different from that at the onset of the thermal reaction. These conditions were best fulfilled by using relatively concentrated solutions, about 8 mol dm^{-3} .

RESULTS AND DISCUSSION

Catalysis and Inhibition of the Photoionitiated Reaction

In order to ascertain whether the hydrogen peroxide photolysis would occur even at extremely low concentrations of photocatalytically active ions, we examined the effect of Cu(II) and EDTA additions. Fig. 2 shows changes in the reaction kinetics with the ratio $c_{\text{Cu}}/c_{\text{EDTA}}$ at various levels of c_{Cu} . The total quantum yields of the photoionitiated reaction, calculated from the amounts of oxygen evolved after 10 min reaction, at various ratios $c_{\text{Cu}}/c_{\text{EDTA}}$ are listed in Table I. The abrupt drop in both the reaction rate and the quantum yield at $c_{\text{Cu}}/c_{\text{EDTA}} = 1$ can only be explained in that the photocatalytically active cuprous ions combine with EDTA to form a poorly active Cu(II) EDTA complex.

The picture of EDTA inhibiting the photolysis by trapping OH^{\bullet} radicals can be completely excluded. For, if EDTA did act as a radical trap, then the quantum yield of hydrogen peroxide photolysis should vary with EDTA concentration according to the equation⁸ $\Phi = k/(k'c_{\text{EDTA}} + 1)$. Such a hyperbolic equation does not, however, fit the experimentally observed variation in the quantum yield with c_{EDTA} .

As opposed to this, a good agreement with experimental results is provided by a relation derived on the assumption that the inhibiting effect of EDTA consists in its binding with Cu(II) to form a photocatalytically poorly active Cu(II)EDTA complex, and that the rate of photolysis is proportional to the square root of the free Cu^{2+} ion concentration, as indeed has been observed experimentally⁵. This picture leads to the expression

$$\Phi = k_1[\text{Cu}^{2+}]^{0.5} = k_1[-A + (A^2 - 4Kc_{\text{Cu}})^{0.5}]^{0.5}, \quad (1)$$

* The term photocatalysis refers to the effect of a photocatalyst on the course of a photoionitiated reaction, *i.e.* to the enhancement of the total quantum yield of the reaction.

where $A = Kc_{\text{EDTA}} - Kc_{\text{Cu}} + 1$; $K = 10^{18.7}$ is the stability constant of the Cu(II) EDTA complex; c_{Cu} and c_{EDTA} are the total concentrations of copper and EDTA, respectively. The calculated values of $[\text{Cu}^{2+}]^{0.5}$ and the experimentally found quantum yields are plotted in Fig. 3 against EDTA concentration.

The results indicate that the hydrogen peroxide photolysis initiated by the 313 nm wavelength proceeds as a photocatalyzed reaction only.

Oxidation States of Catalytically Active Ions

A problem encountered in the investigation of the catalyzed photolysis of hydrogen peroxide is that the photocatalytically active ions and their complexes catalyze, to varying extent, also the thermal reaction, making an independent study of the photochemical reaction difficult. It has been found that potassium ferrioxalate is a photocatalyst that exerts a comparatively small effect on the thermal reaction.

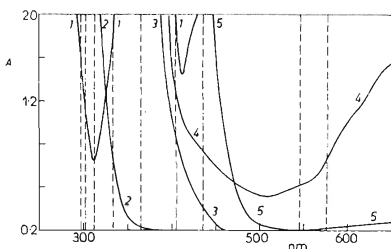


FIG. 1

Absorption spectra (10 mm cell, 20°C): 1 UVKSIF 313 filter; 2 8M-H₂O₂; 3 0.006M-K₃[Fe(C₂O₄)₃]; 4 supplementary filter No 3 to SPM 2; 5 0.15M-K₃[Fe(C₂O₄)₃]; dashed lines denote prominent emission lines of HBO 200 W arc

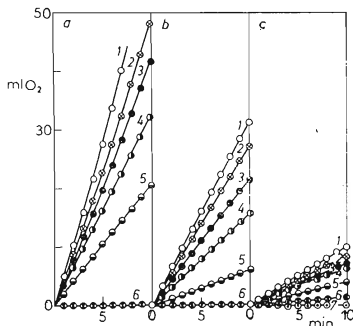


FIG. 2

Effect of the ratio $[\text{Cu(II)}]/[\text{EDTA}]$ on the amount of O₂ evolved in H₂O₂ photolysis (O₂ amounts formed by thermal reaction have been subtracted; in none of the runs did they exceed 10% of the total amount of evolved O₂); 20°C; $[\text{H}_2\text{O}_2]_0 = 8 \text{ mol} \cdot \text{dm}^{-3}$; irradiated by HBO 200 W combined with UVKSIF 313 filter; radiation intensity = $1.24 \cdot 10^{16} \text{ hv/s}$. $[\text{CuSO}_4]$: a $9.1 \cdot 10^{-4} \text{ mol dm}^{-3}$; b $9.1 \cdot 10^{-5} \text{ mol dm}^{-3}$; c $9.1 \cdot 10^{-6} \text{ mol dm}^{-3}$; $[\text{EDTA}]/[\text{Cu(II)}]$: 1 0; 2 0.2; 3 0.4; 4 0.6; 5 0.8; 6 1; 7 1.2

The catalytic effect of the ferrioxalate on the thermal and photoinitiated reactions is illustrated in Fig. 4. The reaction mixture was irradiated periodically by light

TABLE I

Effect of $c_{\text{Cu}}/c_{\text{EDTA}}$ on the quantum yield, ϕ (molecules $\text{O}_2/h\nu$), of hydrogen peroxide photolysis. $[\text{H}_2\text{O}_2]_0 = 8 \text{ mol dm}^{-3}$; initiated by 313 nm; radiation intensity = $1.42 \cdot 10^{16} \text{ hv/s}$. The table lists quantum yields after 10 min photolysis

$c_{\text{Cu}}, \text{mol dm}^{-3}$	$9.1 \cdot 10^{-4}$	$9.1 \cdot 10^{-5}$	$9.1 \cdot 10^{-6}$
$c_{\text{Cu}}/c_{\text{EDTA}}$	$\Phi_{10\text{min}}$ (molecules $\text{O}_2/h\nu$)		
1 : 0	169 ^a	91	29
1 : 0.2	142	79	24
1 : 0.4	123	62	20
1 : 0.6	94	46	18
1 : 0.8	61	18	11
1 : 1	0.7	0.1	3.7
1 : 1.2	—	—	0.1

^a Quantum yield after 7 min photolysis.

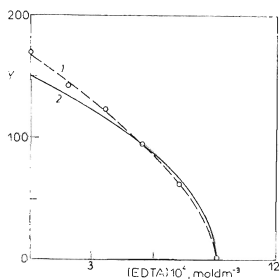


FIG. 3

Comparison of the variations in the observed quantum yield, ϕ , of photolysis and the calculated values for $[\text{Cu}^{2+}]^{0.5}$ as functions of EDTA concentration at constant $c_{\text{Cu}} = 9.1 \cdot 10^{-4} \text{ mol dm}^{-3}$; 20°C ; $[\text{H}_2\text{O}_2]_0 = 8 \text{ mol dm}^{-3}$; $1.42 \cdot 10^{16} \text{ hv/s}$; 1. $Y = \phi$ (molecules $\text{O}_2/h\nu$); 2. $Y = 5 \cdot 10^3 [\text{Cu}^{2+}]^{0.5}$ (calculated from Eq. (1))

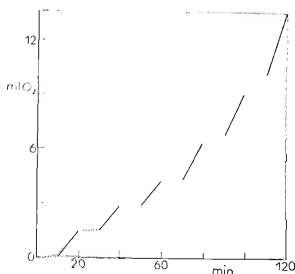


FIG. 4

Photocatalytic effect of $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$: $[\text{H}_2\text{O}_2]_0 = 7.8 \text{ mol dm}^{-3}$; $c(\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3])_0 = 0.13 \text{ mol dm}^{-3}$; 20°C ; irradiated by HBO 200 W arc combined with supplementary filter No 3 to SPM 2; dashed line — thermal reaction; solid line — photoinitiated reaction

of wavelength $\lambda > 395$ nm. This wavelength is absorbed by the ferrioxalate only, resulting in its photochemical reduction⁶. The formation of Fe(II) and its relatively long survival in the solution were demonstrated by reaction with *o*-phenanthroline (characteristic absorption maximum at 510 nm). Fig. 4 shows that unlike the initial Fe(III) complex, the photochemically generated Fe(II) complex catalyzes the decomposition of hydrogen peroxide. This finding is in agreement with literature data^{1,4,7} according to which Fe(II) is a very active catalyst of the thermal decomposition.

Apart from the pronounced photocatalytic effect of ferrioxalate, it can also be seen from Fig. 4 that the rate of the thermal reaction increases with increasing time of irradiation. This feature may be ascribed partly to accumulation of Fe²⁺ in the reaction solution, and partly to photoinitiated oxidation of the oxalate in the coordination sphere of Fe(III) (the free Fe³⁺ ions formed exert some effect on the thermal decomposition of hydrogen peroxide).

Quantum Yields of the Photocatalyzed Reaction

It is clear that the quantum yields of a photocatalyzed and an ordinary photoinitiated reaction have different physical meanings. For the system under consideration, *i.e.* for hydrogen peroxide photolysis sensitized and photocatalyzed by ferrioxalate, we may define

a) the quantum yield of the catalyst generation

$$\Phi_{\text{Fe}^{2+}} = (d[\text{Fe}^{2+}]/dt)/I_{\text{abs}}, \quad (2)$$

where $I_{\text{abs}} = d(h\nu)/t$ is the light flux absorbed by the photocatalytically active component, *i.e.* by the ferrioxalate, and

b) the total quantum yield of hydrogen peroxide photolysis

$$\Phi_{\text{O}_2} = (d[\text{O}_2]/dt)/I, \quad (3)$$

where $I = d(h\nu)/dt$ is the light flux absorbed by the reaction system.

The total quantum yield will only bear a direct relationship to the mechanism of the photolysis if $I = I_{\text{abs}}$, since then

$$\nu_c = \Phi_{\text{O}_2}/\Phi_{\text{Fe}^{2+}} = (d[\text{O}_2]/dt)(d[\text{Fe}^{2+}]/dt)^{-1}. \quad (4)$$

The ν_c represents the number of hydrogen peroxide molecules brought to reaction by one Fe²⁺ ion formed by the photochemical reduction of Fe³⁺ or, in other words, it gives the number of catalytic cycles (in analogy to the kinetic chain length in a free radical chain mechanism).

The total quantum yield of hydrogen peroxide photolysis catalyzed by ferrioxalate increases from an initial value of 8 molecules $O_2/h\nu$ to 18 molecules $O_2/h\nu$ after 60 min irradiation. Since the quantum yield of the photoionitiated reduction of ferrioxalate⁶ is approximately 1, the average length of a catalytic cycle $\nu_c = 8 - 18$.

Reaction Mechanism

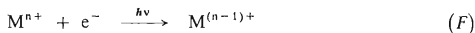
It is evident that the Haber-Weiss mechanism of hydrogen peroxide photolysis must be reformulated, since it is unable to account for the established fact that the reaction does not occur at a measurable rate in the absence of transition metals.

The decomposition of hydrogen peroxide (equation (G)), *i.e.* a reaction in which a triplet molecule (dioxygen) is formed from a singlet molecule, is spin-forbidden. As other spin-forbidden reactions, it is markedly catalyzed by transition metal compounds, even when these are present in trace concentrations. The activation energy for the non-catalyzed reaction is so high that there is practically no reaction if transition metal ions are entirely absent. Trace amounts of transition metals are, however, sufficient to trigger the thermal reaction⁷.

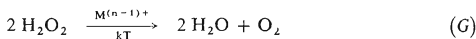
All authors^{1,4,7} are united in the conclusion that the catalytic activity of metal ions in the thermal reaction depends on the oxidation state of the ions. Fe(II) ions, for instance, are catalytically more active than Fe(III). It cannot be ruled out that certain catalytic activity which has been observed for Fe(III) is merely a consequence of its reduction to Fe(II). Based on these facts and the results of the present study, the following mechanism may be proposed for hydrogen peroxide photolysis.

The catalytically poorly active or inactive transition metal ions, which are present in the reaction system as impurities in trace concentrations or have been added to the system, are reduced by the effect of light to catalytically active ions of lower oxidation states. (For a discussion of the photochemical reduction of metal ions, see ref.¹⁰.) The latter ions catalyze the thermal decomposition of hydrogen peroxide, undergoing gradual oxidation to catalytically inactive ions of the higher oxidation state. The mechanism may be represented by the following reaction scheme.

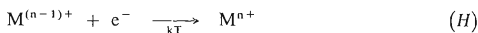
Photochemical generation of catalyst



Catalyzed thermal reaction



Catalyst deactivation



The mechanisms of steps (F) to (H) of the photolysis remain to be elucidated. There is, however, some evidence⁷ allowing consideration of the mechanism of the catalyzed thermal decomposition of hydrogen peroxide (reaction (G)). Recently, several authors¹¹⁻¹³ have advanced the view that the hydrogen peroxide decomposition occurs in the coordination sphere of the catalyzing ion. This proposition is consistent with results of isotopic experiments^{14,15} indicating that all of the molecular oxygen formed by hydrogen peroxide decomposition originates from the peroxide whose O-O bond remains intact.

The proposed mechanism (equations (F) to (H)) accounts for all characteristic features of hydrogen peroxide photolysis. The high quantum yields are due to catalytic cycles, and not to a free radical chain mechanism. The observation that hydrogen peroxide decomposition is initiated by wavelengths that are not absorbed by hydrogen peroxide is associated with the mechanism of the initiation step (reaction (F)). The inhibiting effects of nucleophilic compounds are a result of their ability to combine with the photocatalytically active M^{n+} ions or the catalytically active $M^{(n-1)+}$ ions to form unreactive complexes.

The evidence of this study and the proposed mechanism of hydrogen peroxide photolysis give an impulse to check the validity of mechanisms accepted for other reactions of hydrogen peroxide.

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