

### Could Hydrogen Peroxide Photolysis Occur in the Absence of Transition Metals?

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Z. Naturforsch. **36b**, 654–655 (1981);  
received February 25, 1981

Hydrogen Peroxide, Photocatalysis,  
Trace Metals

Quantum yields of hydrogen peroxide photolysis increase with the square root of concentration of added Cu(II). The cupric ions are photocatalytically active already at trace concentrations ( $10^{-7}$  M), *i.e.*, at the concentrations present in any real reaction system. Hydrogen peroxide photolysis is completely suppressed on addition of complexing agents such as EDTA. It is believed that no hydrogen peroxide photolysis would occur in complete absence of photocatalytically active transition metal ions.

Although the catalytic effects of Fe(III) and Cu(II) on hydrogen peroxide photolysis have long been known [1–3], no one so far has addressed the question of whether any  $H_2O_2$  photolysis can take place without the photocatalytically active transition metal ions participating in it. This is not surprising since the universally accepted Haber-Weiss mechanism [4] does not envisage such effects to be involved. We have shown recently that the high quantum yields of the photoinitiated sulphite oxidation arise as a result of photochemical generation of a catalyst of thermal reaction [5], and that no photooxidation will occur in the absence of photocatalytically active transition metal ions [6, 7]. The results induced us to raise the title question.

We carried out two series of experiments. In the first one, we examined the effect of photocatalyst ( $CuSO_4$ ) additions, seeking the smallest addition upon which the rate of photolysis would just measurably be increased. In the second series, we studied the decrease in the rate brought about by additions of ethylenediamine tetracetic acid (EDTA) as a complexing agent. Since the rate of thermal decomposition was low compared with the rate of photolysis under the applied experimental conditions, the observed effects could exclusively be related to the photoinitiated reaction.

Table I lists the results obtained in examining the effect of Cu(II) additions on  $H_2O_2$  photolysis

Table I. Quantum yields,  $\Phi$  (molecules  $O_2/h\nu$ ), of hydrogen peroxide photolysis at various concentrations of added  $CuSO_4$ . Initiation radiation 313 nm (HBO 200 (Osram) – UVKSIF filter (Zeiss)), intensity  $7.3 \times 10^{15}$   $h\nu/s$ ,  $[H_2O_2]_0 = 7.3$  M, 20 °C. The rate of hydrogen peroxide thermal decomposition ranged, under the applied conditions, from  $5.6 \times 10^{-5}$  ml  $O_2/s$  for a blank to  $7.0 \times 10^{-3}$  ml  $O_2/s$  at Cu(II) addition of  $9.1 \times 10^{-4}$  M, *i.e.* it constituted about 10% of the overall rate at irradiation.

Cu(II) addition (mol/l)	Rate of photolysis (ml $O_2/s$ )	Quantum yields (molecules $O_2/h\nu$ )
0	$6.28 \times 10^{-4}$	2.31
$9.1 \times 10^{-8}$	$1.06 \times 10^{-3}$	3.90
$9.1 \times 10^{-7}$	$3.16 \times 10^{-3}$	11.6
$9.1 \times 10^{-6}$	$9.78 \times 10^{-3}$	35.9
$9.1 \times 10^{-5}$	$2.76 \times 10^{-2}$	101
$9.1 \times 10^{-4}$	$7.13 \times 10^{-2}$	262

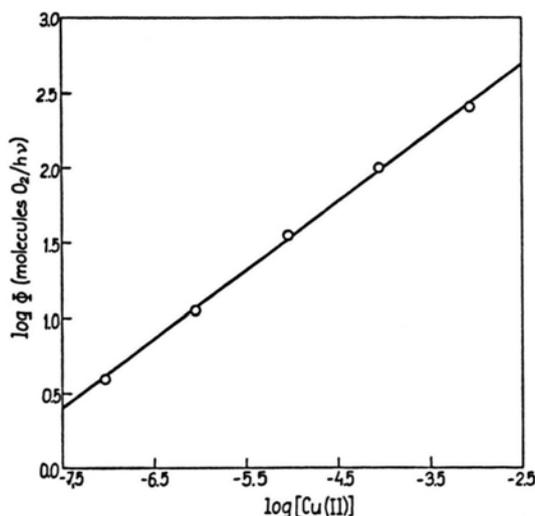


Fig. 1. Quantum yields  $\Phi$  (molecules  $O_2/h\nu$ ) as a function of the concentration of added  $CuSO_4$ . Initiated by light of 313 nm (HBO 200 high-pressure mercury arc (Osram) combined with a UVKSIF 313 interference filter (Zeiss)), intensity  $7.3 \times 10^{15}$   $h\nu/s$ , 20 °C.

initiated by 313 nm. It can be seen that the rate of photolysis is markedly enhanced by an addition of as little as  $9 \times 10^{-8}$  M Cu(II). This implies that hydrogen peroxide photolysis is affected by transition metal ions at such minute concentrations as can be expected to be present as a background in any real reaction system. The dependence of the quantum yields of photolysis,  $\Phi$  (*i.e.* the number of  $O_2$  molecules per  $h\nu$ ), on the concentration of added Cu(II) is represented in Fig. 1, and may be expressed by the equation:

$$\Phi = 6.76 \times 10^3 \times [Cu(II)]^{0.46}$$

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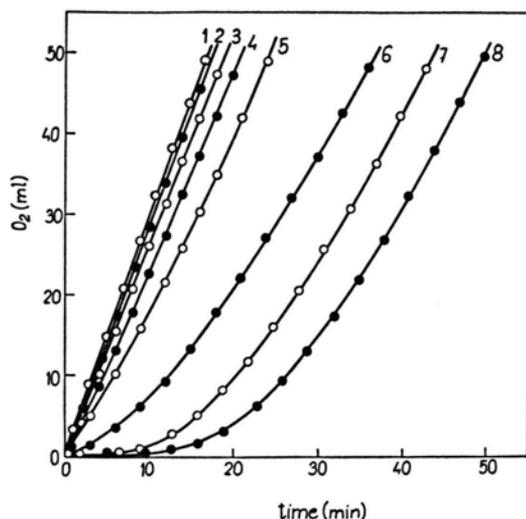


Fig. 2. Effect of EDTA on hydrogen peroxide photolysis. Initiated by the whole spectrum of a HBO 200 high-pressure mercury arc (Osram), 20 °C.

$[\text{H}_2\text{O}_2]_0 = 7.3 \text{ M}$ ,  $[\text{CuSO}_4] = 4.2 \times 10^{-6} \text{ M}$ .

$[\text{EDTA}]$ : 1—0, 2— $8.4 \times 10^{-7} \text{ M}$ , 3— $1.7 \times 10^{-6} \text{ M}$ , 4— $2.5 \times 10^{-6} \text{ M}$ , 5— $3.4 \times 10^{-6} \text{ M}$ , 6— $4.2 \times 10^{-6} \text{ M}$ , 7— $5.0 \times 10^{-6} \text{ M}$ , 8— $5.9 \times 10^{-6} \text{ M}$ .

The amount of oxygen evolved in thermal decomposition was maximum under the conditions of experiment 1 (without EDTA addition), amounting to 0.7 ml O<sub>2</sub> in 30 min.

Fig. 2 shows the results of the second series of experiments in which the effect of varying EDTA concentration was studied at a constant addition of photocatalytically active CuSO<sub>4</sub> ( $4.2 \times 10^{-6} \text{ M}$ ). At  $[\text{EDTA}] \geq [\text{Cu(II)}]$ , a sharp fall was observed in the initial rate of photolysis. The feature was further verified at a larger CuSO<sub>4</sub> addition ( $4.2 \times 10^{-5} \text{ M}$ ). The pronounced drop of the initial rate of photolysis is unequivocally in line with the picture of EDTA functioning by binding the photocatalytically active metal ions into inactive complexes. With  $[\text{EDTA}] > [\text{Cu(II)}]$ , nearly no photolysis occurs at the beginning; only after a time interval, which is proportional to the concentration difference ( $[\text{EDTA}] - [\text{Cu(II)}]$ ), does the rate of photolysis increase gradually up to values comparable with those observed in the absence of EDTA. This fact may be explained in terms of photolysis of a Cu(II)EDTA complex, associated with oxidative destruction of EDTA in the coordination sphere. Similar photoinitiated aerobic degradation has been reported for Fe(III)EDTA complexes [8].

The results of both series of experiments indicate that hydrogen peroxide photolysis would not occur in complete absence of photocatalytically active transition metal ions, and that the rate and quantum yields of the so-called non-catalyzed photolysis are, in fact, determined by a concentration level of the transition metal ions constituting a background of the reaction system.

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