

Chlorophyll and Metal Porphyrins in Photocatalytic Redox Reactions of Hydrogen Peroxide

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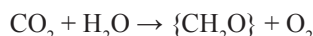
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The photocatalytic decomposition of H₂O₂ in the presence of chlorophyll and metal complexes of tetraphenylporphyrin and phthalocyanine immobilized on silica was studied. The value of adsorption of porphyrins is shown to influence kinetics of H₂O₂ decomposition. Processes of reduction of some electron acceptors photocatalyzed by chlorophyll in H₂O₂ solution are demonstrated.

Keywords: Chlorophyll, metal porphyrins, hydrogen peroxide, photocatalysis, electron acceptors

Introduction

Photosynthesis is a complex biological process. It consists of a large number of redox reactions, some of them are photocatalyzed by chlorophyll. Common equation of photosynthesis is:^[1]



At present time a nature of inorganic electron donor and a mechanism of its oxidation are opened to question. It is proposed that water molecules are oxidized to O₂, and hydrogen peroxide is an intermediate of water oxidation.^[2-7] Moreover it is assumed that H₂O₂ is a source of photosynthetic oxygen.^[8] In that way H₂O₂ is electron donor in photosynthesis. The presence of H₂O₂ in natural water (10⁻⁵-10⁻⁶ mol/l) and intracellular liquids makes possible to presume a biological activity of H₂O₂.^[2] Furthermore H₂O₂ oxidation is less endothermic than water one.^[6]

The study of chemistry and molecular organization of photosynthesis is very important for creation of artificial photosynthetic systems. Thus the investigation of electron transfer from H₂O₂ to acceptor molecules photocatalyzed by chlorophyll or its synthetic analogues is very interesting. It is known that Fe, Ni, Co, Mn and platinum metals complexes with porphyrins are effective catalysts of H₂O₂ decomposition.^[9-11] In this work a photocatalytic activity of chlorophyll, Chl (**1**), and metal complexes of tetraphenylporphyrin, MTPP (M = Cr (**2**), Cu (**3**), Sn (**4**), Zn (**5**), Cd (**6**), and phthalocyanine MPc (M = Al (**7**), Zn (**8**)) in the reaction of H₂O₂ decomposition was studied. In addition a possibility of reduction of nicotinamadeninucleotid phosphate, NADP, and methyl red dye, MR, connected with H₂O₂ decomposition photocatalyzed by chlorophyll was shown.

Experimental

Mixture of chlorophyll *a* and *b* was isolated and purified from dry nettle leaves using known methods.^[12,13] Chlorophyll

a (**1**) was separated from chlorophyll mix by chromatography on a column with powdered sugar heated-up at 100 °C within 4 h preliminary. Chlorophyll mixture was dissolved in hexane-ether system (3:7) and put on a column. Elution was realized by the same solvent system to distribute of pigments on the column fully. A fraction painted by chlorophyll **1** was mechanically taken, and then it was washed off by ether. Individuality and concentration of chlorophyll **1** were determined by UV-vis spectroscopy in quartz cells (1 cm) on spectrophotometer HACH DR/4000V (Sweden) to be identical to the literature data.^[14]

Chlorophyll a, 1. UV-vis λ_{max} (ether) nm (lgε): 662 (4.96), 615 (4.14), 578 (3.88), 533.5 (3.57), 430 (5.08), 410 (4.88).

Porphyrins **2-6** and phthalocyanines **7-8** were synthesized and purified in Ivanovo State University of Chemistry and Technology (Ivanovo, Russia).

Adsorption of complexes **1-8** on silica L 40/100 (Chemapol) was realized by addition of silica (1 g) to the solutions of chlorophyll **1** in acetone, complexes **2-6** in chloroform and phthalocyanines **7-8** in DMF. Concentration of solutions was varied for preparing of samples with different value of adsorption. Suspensions were kept in the darkness for 12 h. Samples were filtered on vacuum, repeatedly washed out with distilled water and dried to constant weight in vacuum-exicator over CaCl₂. Recorded optical density of solutions before and after adsorption was used for determination of complexes quantity per 1 g silica.

For kinetic experiments 10 ml bicarbonate buffers (pH 8.5) containing 0.2 mol/l H₂O₂ («Reakhim», Russia) and 200 mg of silica with one of the supported complexes **1-8** were placed in the photochemical reactor. The obtained suspensions were irradiated by visible light using halogen lamp (150 W) with condenser and system of lenses at constant stirring. Concentration of H₂O₂ was determined by titration method in 0.2 M H₂SO₄ medium using KMnO₄. All experiments were carried out at 20 °C. In experiments on reduction of electron acceptors the solutions of NADP (0.7·10⁻⁴ mol/l) or MR (8.1·10⁻⁴ mol/l) were added to water suspension of supported chlorophyll **1**. In the experiments with MR ethanol was added into reaction system. For determination of reduced forms of acceptors their spectral characteristics were used. UV-vis λ_{max} (water) nm (lgε): 320 (3.77) for reduced NADP and λ_{max} (ethanol) nm (lgε): 498 (2.68) for reduced MR.^[14]

Results and Discussion

Hydrogen Peroxide Photodecomposition in the Presence of Chlorophyll and Metal Complexes of Tetraphenylporphyrin and Phthalocyanine

Chlorophyll **1**, porphyrins **2-6** and phthalocyanines **7-8** were used in the adsorbed form as they are more considerably stable on silica surface, and solid catalysts do not interfere with the analysis of H_2O_2 concentration. It has appeared that in the presence of all complexes there was H_2O_2 decomposition accelerating under the visible light irradiation. Kinetics of H_2O_2 decomposition photocatalyzed by Cu tetraphenylporphyrin **3** is presented in Figure 1 as an example. It is possible to express the rate of catalytic H_2O_2 decomposition as:

$$w = k[\text{Cat}]^n[\text{H}_2\text{O}_2]^m,$$

where k – rate constant, $[\text{Cat}]$ – the quantity of the supported catalyst per 1 litre of a solution. If $[\text{Cat}] = \text{const}$ it is possible to designate $k[\text{Cat}]^n$ as k_{obs} . Then equation of rate will be:

$$w = k_{\text{obs}}[\text{H}_2\text{O}_2]^m.$$

In all cases for all considered complexes **1-8** kinetic curves of H_2O_2 decomposition was well straightened in coordinates $\ln[\text{H}_2\text{O}_2] - t$ (Figure 2). Thus $m = 1$ it is allowed to accept the (pseudo)first order of reaction of decomposition by H_2O_2 .

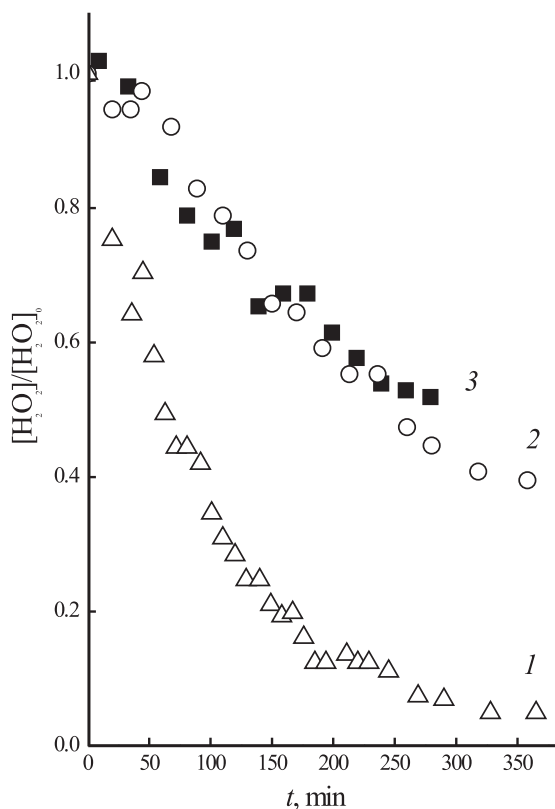


Figure 1. Kinetics of H_2O_2 decomposition photocatalyzed by complex **3**. The value of adsorption is 0.93 (**1**) 2.3 (**2**) 7.73 $\mu\text{mol/g}$ (**3**). Initial concentration of hydrogen peroxide is $[\text{H}_2\text{O}_2]_0 = 0.2 \text{ mol/l}$.

The data of catalytic and photocatalytic activities of complexes **1-8** in H_2O_2 decomposition are presented in Table 1. Values N correspond to number of mol H_2O_2 per 1 mol (photo)catalyst at 1 h. The parameter η shows an acceleration of H_2O_2 decomposition under the influence of light irradiation. The acceleration is observed for Mg, Zn and Al complexes (compounds **1**, **5**, **7**, **8**). These are metals of intransitive group. The main advantage of these complexes is ability to generate long-living (to 1 ms) triplet excited states with a high quantum yield (60-90%)^[15] under the visible light irradiation that is very important for photodependent processes. From thermodynamics it is known that photodependent reactions are more favourable, than dark ones because a pigment molecule absorbing light quantum passes in excited state, thereby lowering an energy barrier of reactions.^[16]

In the case when the reaction of H_2O_2 decomposition proceeds in the darkness the greatest catalytic activity is characteristic for porphyrins **1**, **2**, **4**, **6** containing Mg, Cr, Zn and Sn. Without irradiation one of the H_2O_2 molecules is oxidised, and another one is reduced. Use of the adsorbed forms of porphyrins gives rise to their various behaviour in dark and light-induced processes too. The organization of surface layers influences on kinetic parameters of process.

The properties of copper porphyrin **3** for which $\eta = 18.5$ were unexpected. Probably, it is a result of influence of structure of the adsorbed layer obtained in experiment, or coordination with surface OH-groups of silica. Besides, a number of interesting properties of cupric ions is given by features of filling of its electronic shell.^[17] Photocatalytic activity of the adsorbed metal complexes in each case depends on the redox potential and photophysical properties of the complex and its associates.^[18]

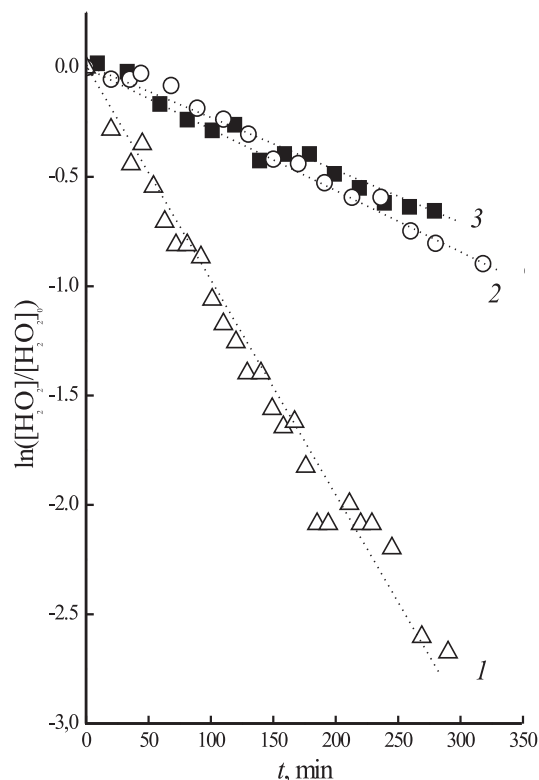


Figure 2. Semi-logarithmic linear anamorphoses of kinetic curves presented in Figure 1 with corresponding numbers.

Table 1. Catalytic properties of chlorophyll **1**, porphyrins **2-6** and phthalocyanines **7-8** supported on silica in H₂O₂ decomposition in bicarbonate buffer (pH 8.5) in darkness and under the visible light irradiation.

Complex	[Cat]·10 ⁵ , mol/l	$k_{\text{obs}} \cdot 10^5, \text{ s}^{-1}$	$k \cdot 10^2, \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	$N, \text{ h}^{-1}$	$k_{\text{obs}} \cdot 10^5, \text{ s}^{-1}$	$k \cdot 10^2, \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	$N, \text{ h}^{-1}$	η
		In darkness			Under the visible light irradiation			
1	1.0	0.62	62.0	2232	1.18	118	4248	1.9
2	132	1.50	1.14	41	2.27	1.72	62	1.5
3	111	0.13	0.12	4	2.27	2.05	74	18.5
4	110	3.87	3.52	126	4.35	3.95	142	1.1
5	103	0.39	0.38	13	0.60	0.58	21	1.6
6	103	0.97	0.94	34	1.11	1.08	38	1.1
7	1.5	0.24	16.0	576	4.25	283	10188	17.7
8	1.5	0.26	17.3	622	5.25	350	12600	20.2

The photocatalytic activity of immobilized complexes **1-3**, **7** with different values of adsorption (a) in the reaction of H₂O₂ decomposition was investigated. The obtained data show that the greatest activity of Cu porphyrin **3** is characteristic for $a = 0.93 \mu\text{mol/g}$ (Table 2). However, at $a \geq 2.3 \mu\text{mol/g}$ activity of the complex **3** decreases. The further increase of quantity of complex **3** on silica surface does not affect on kinetics of the process. Apparently, inactive associates of porphyrin are formed. An example of formation of active associates is Cr porphyrin **2** (Table 2). Its photocatalytic activity is growing as a values increase. So the maximum effective constant of the reaction rate of H₂O₂ decomposition is $6.1 \cdot 10^{-5} \text{ s}^{-1}$ at $a = 7.87 \mu\text{mol/g}$. It should be noted that porphyrin association is observed even at rather small values of adsorption.^[7]

Table 2. Dependence of photocatalytic activity of supported complexes **1-3**, **7** in the reaction of H₂O₂ decomposition on adsorption value.

Complex	a , $\mu\text{mol/g}$	$k_{\text{obs}} \cdot 10^5$, s ⁻¹
1	0.23	3.1±0.2
	0.57	2.8±0.1
	1.92	2.1±0.1
2	0.95	4.3±0.1
	2.3	2.0±0.1
	7.87	6.1±0.4
3	0.93	16±2
	2.3	4.5±0.2
	7.73	4.2±0.2
7	0.45	1.1±0.1
	0.95	1.5±0.1
	2.34	3.3±0.2

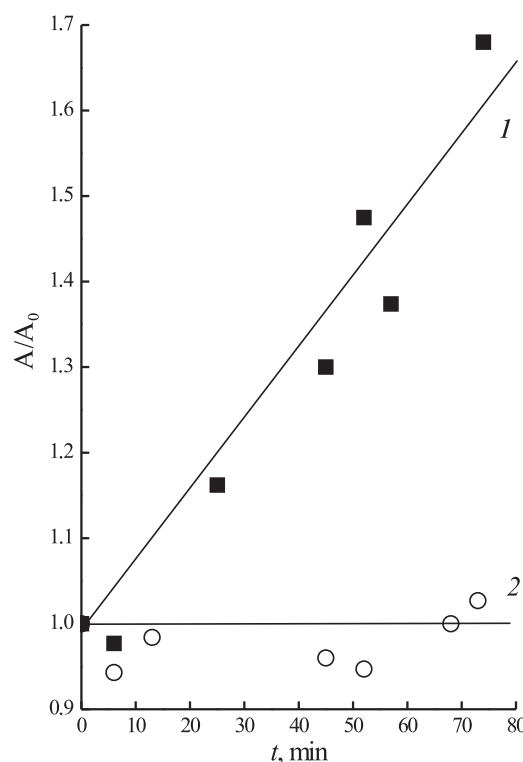
The photocatalytic activity of phthalocyanine **7** in the dependence on adsorption values is analogous to that of complex **2** (Table 2). The activity is growing as a values increase from 0.45 to 2.34 $\mu\text{mol/g}$. Recorded BET-type isotherm of adsorption of phthalocyanine **7** on silica shows that $a = 0.95 \mu\text{mol/g}$ corresponds to monomolecular surface layer.

Thus association of porphyrins and phthalocyanines results in both the increase and decrease of photocatalytic activity in dependence on type of metallocomplex. Association influences on steric parameters and photophysical properties of the supported complexes.^[17]

Electron Transfer in H₂O₂ – Chlorophyll – Electron Acceptor Systems under the Light Irradiation

To prove a possibility of light energy storage in the form of chemical potential an electron transfer from H₂O₂ to acceptor molecules with chlorophyll participation was investigated. Sodium salt of NADP and MR dye (*p*-dimetilaminoazobenzol-2-carboxylic acid) were used as acceptors. NADP is photosynthetic electron acceptor and MR is well studied, widely applied synthetic acceptor.^[19,20]

Kinetics of NADP reduction was studied spectrophotometrically in visible spectrum range. At the irradiation during *ca.* 80 min the supported chlorophyll **1** ($a = 0.015 \mu\text{mol/g}$) was proved to be active in NADP reduction (Figure 3). However in the absence of H₂O₂ in the system chlorophyll possesses no activity in accumulation of

**Figure 3.** NADP reduction induced by chlorophyll under the visible light irradiation in the presence of H₂O₂ (**1**) and without H₂O₂ (**2**).

reduced form of NADP. The reduction reaction of MR was investigated spectrophotometrically observing the decrease of the intensity of absorption band of the initial oxidized form. The obtained data confirm the photocatalytic activity of supported chlorophyll **1** ($a = 0.063 \mu\text{mol/g}$) in reduction of methyl red (Figure 4). In the presence of hydrogen peroxide activity of chlorophyll accelerates at conditions of photocatalysis.

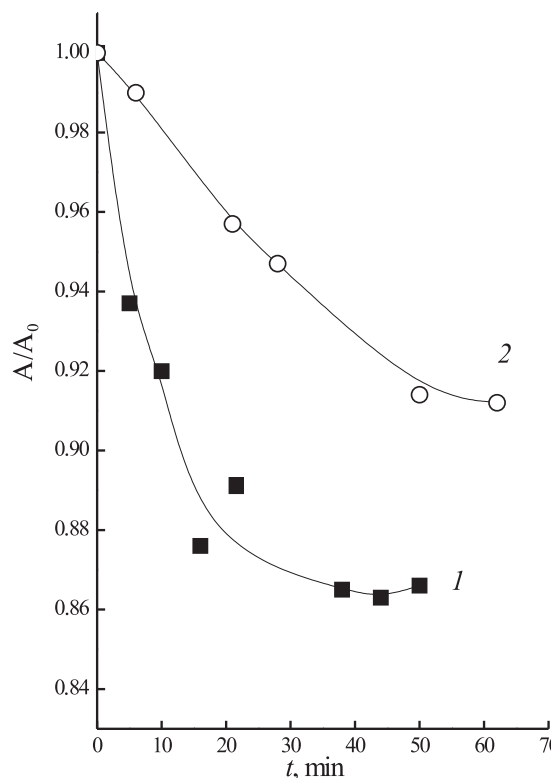


Figure 4. MR reduction induced by chlorophyll under the visible light irradiation in the presence of H_2O_2 (1) and without H_2O_2 (2).

Thus in threefold systems H_2O_2 -chlorophyll-acceptor under the visible light irradiation the reduction of electron acceptors (NADP and MR) takes place what proves the ability of H_2O_2 to function as an electron donor in these conditions.

Conclusions

The artificial photosynthetic systems with hydrogen peroxide participation were prepared. It was shown that immobilized chlorophyll and a number of its synthetic analogues such as metal complexes of tetraphenylporphyrin and phthalocyanine possess a catalytic activity in the reaction of H_2O_2 decomposition. The photocatalytic activity depends

on values of adsorption differently. It was demonstrated that electron transfer from H_2O_2 to acceptor molecules is possible. The obtained results expand knowledge about the photosynthesis mechanism.

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References

- Hall D.O., Rao K.K. *Fotosintez* [Photosynthesis] (eng. transl.). Moscow: Mir, **1983**, 134 p. (in Russ).
- Komissarov G.G. *Zh. Khim. Fiz.* **2003**, *1*, 24 (in Russ).
- Wydrzynski T., Renger G. *Photosynthetica* **1990**, *2*, 320.
- Bader K.P. *Biochim. Biophys. Acta* **1994**, *1188*, 213.
- Miyake C., Asada K. *Res. Photosynthesis* **1992**, *2*, 563.
- Lobanov A.V., Safina Yu.A., Nevrova O.V., Komissarov G.G. Interaction of O_2 and H_2O_2 under Irradiation of Chlorophyll-Silica-Water Suspensions Saturated with Air. In: *Problems of Origin and Evolution of Biosphere* (Galimov E.M., Ed.). Moscow: Librokom, **2008**, 195 p.
- Nagata T., Nagasawa T., Zharmukhamedov S.K., Klimov V.V., Allakhverdiev S.I. *Photosynthesis Research* **2008**, *93*, 1-3, 133.
- Komissarov G.G. *Fotosintez: Fiziko-Khimicheskiy Podkhod* [Photosynthesis: Physique-Chemical Approach]. Moscow: URSS, **2003**, 224 p. (in Russ).
- Berezin B.D. *Koordinatsionnye Soedineniya Porfirinov i Ftalozianina* [Coordination Compounds of Porphyrins and Phthalocyanine]. Moscow: Nauka, 1978. 280 p. (in Russ.).
- Govorov A.G., Korzhenevsky A.B., Koifman O.I., Shikova T.G. *Zh. Fiz. Khim.* **1995**, *10*, 1776 (in Russ).
- Cheremenskaya O.V., Solovieva A.B., Ponomarev G.V., Timashev S.F. *Zh. Fiz. Khim.* **2001**, *10*, 1787 (in Russ.).
- Komissarov G.G. Diss. Dr. Chem. Sci. Moscow, Semenov Institute of Chemical Physics of Russian Academy of Sciences, 1973. (in Russ).
- Iriyama K., Ogura N., Takamiya A. *J. Biochem.* **1974**, *4*, 901-904.
- Doson R., Elliot D. *Spravochnik Biokhimiya* [Biochemist's Handbook] (eng. transl.). Moscow: Mir, **1991**, 544 p. (in Russ).
- Parmon V.N. Molecular Systems for Water Decomposition. In: *Photocatalytic Transformation of Solar Energy. Part 2*. Novosibirsk: Nauka, **1985**, 248 p. (in Russ).
- Rubin A.B. *Biofizika* [Biophysics]. Vol. 2. Moscow: MSU, **2004**, 469 p. (in Russ.).
- Stepin B.D., Tsvetkov A.A. *Neorganicheskaya Khimiya* [Inorganic Chemistry]. Moscow: Vysshaya shkola, **1994**, 608 p. (in Russ).
- Berezin B.D., Enikolopian N.S. *Metalloporfiriny* [Metalloporphyrins]. Moscow: Nauka, 1988. 160 p. (in Russ).
- Boardman N.K. *Annual Review of Plant Physiology* **1970**, *21*, 115-140.
- Liu G., Zhou J., Wang J., Yan B., Li J., Lu H., Qu Y., Jin R. *Biotechnology Letters* **2008**, *5*, 869-875.

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