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Coordination and Photocatalytic Properties of Metal Porphyrins in Hydrogen Peroxide Decomposition

Anton V. Lobanov,[a@] Olga V. Nevrova,[a] Vladimir A. Ilatovskii,[a] Gennady V. Sin'ko,[b] and Gennady G. Komissarov[a]

[a]Semenov Institute of Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russia
[b]Russian Federal Nuclear Center – E.I. Zababakhin All-Russian Research Institute of Technical Physics, 456770 Snezhinsk, Russia
[@]Corresponding author E-mail: avlobanov@mail.ru

The coordination interaction between metal complexes of porphyrins, including chlorophyll, and hydrogen peroxide was detected. The kinetic parameters of photocatalytic decomposition of H_2O_2 in the presence of chlorophyll and metal porphyrins immobilized on silica were studied. Photocatalytic activity of a number of non-transition metal tetraphenylporphyrins is shown to correlate with their ability to generate photopotential.

Keywords: Metal porphyrins, chlorophyll, hydrogen peroxide, coordination, photocatalysis

Introduction

Many medical and biological processes consist of photosensitive redox stages that occur with the participation of metal porphyrins and hydrogen peroxide. For instance photosynthesis consists of redox reactions photocatalyzed by chlorophyll. During photosynthesis the interaction of electron donor and carbon dioxide leads to the formation of energy-intensive organic compounds and generation of oxygen.[1] At present time it is proposed that water molecules are oxidized to O_2, and hydrogen peroxide is an intermediate of water oxidation.[2,3] However it is also possible that probably H_2O_2 is a primary electron donor.[2] It is important that H_2O_2 oxidation is less endothermic than water one.[4] In photodynamic therapy of cancer and other pathologies metal porphyrins produce singlet oxygen,[5] which is converted into hydrogen peroxide in aqueous media.[3] Thus, *in vivo* the pharmacologically active porphyrins interact with H_2O_2 also.

Creation of artificial photosensitive systems is useful for the study of coordination and photochemical interaction of metal complexes of porphyrins and reactive oxygen species. It is known that some metal complexes with porphyrins and phthalocyanines are effective catalysts of H_2O_2 decomposition in dark.[6] In this work a photocatalytic activity of chlorophyll *a* (Chl) and metal (Cr, Cu, Sn, Zn, Cd, Mg) complexes of tetraphenylporphyrin (TPP) in the reaction of H_2O_2 decomposition was studied. Special attention is paid to the coordination of metal porphyrins and hydrogen peroxide.

Experimental

Chlorophyll *a* was separated by known method.[4] Individuality and concentration of Chl were determined by UV-vis spectroscopy in quartz cells (1 cm) on spectrophotometer DR/4000V (HACH-Lange, USA). Metal complexes of tetraphenylporphyrin were synthesized and purified in Ivanovo State University of Chemistry and Technology (Ivanovo, Russia). Hydrogen peroxide and sodium bicarbonate («Reakhim», Russia) were used without additional purification.

Immobilization of metal complexes on silica L 40/100 (Chemapol) was realized by addition of silica (1 g) to the solutions of Chl in acetone and complexes of tetraphenylporphyrin in chloroform. Suspensions were kept in the darkness to evaporate the solvent. Samples were repeatedly washed out with distilled water and dried to a constant weight in vacuum-exicator over $CaCl_2$.

For kinetic experiments 10 ml of bicarbonate buffers (p*H* 8.5) containing 0.2 M H_2O_2 and 200 mg of silica with one of the supported complexes were placed into 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 H_2O_2 was determined by titration method in 0.2 M H_2SO_4 medium using 0.01 N $KMnO_4$ solution. All experiments were carried out at 20 ^{0}C.

Quantum chemical calculations of complexes of O_2 and H_2O_2 were performed using the procedure 6-31G** in the DFT-approximation with the exchange-correlation functional PBE1PBE in the program Gaussian 03.[7]

Results and Discussion

Chlorophyll and metal complexes of tetraphenylporphyrin coordinate hydrogen peroxide according to the electron adsorption spectra (Figure 1). Solutions of H_2O_2 were sequentially added to TPP metal complex solutions (10^{-5} mol/l) to concentrations from 10^{-7} to 10^{-3} mol/l. One can see that changes in the electronic spectra are concerned with only increase or decrease of the extinction in the bands and the of isosbestic point observation. All visible bands correspond to $\pi \rightarrow \pi^*$ transitions. At addition of H_2O_2 energy parameters of the bands do not change. This means that the place of coordination of hydrogen peroxide molecule is magnesium ion, but not the porphyrin macrocycle, since the frontier orbitals of d^0- and d^{10}-metal complexes are localized on the ligand and they are very sensitive to outer-coordination.

Quantum chemical calculations show that although there are many local energy minima for binary systems of metal complexes and hydrogen peroxide, arrangement of these small molecules near the metal ions shows to be the most energetically favourable. Figure 2 illustrates the structure of the coordination complex $Chl\cdots H_2O_2$ as an example.

Photocatalytic activity in the reaction of H_2O_2 decomposition is shown to be demonstrated for chlorophyll and different metal complexes of tetraphenylporphyrin immobilized on silica. Kinetic parameters of their catalytic and photocatalytic activities are given in the Table 1.

Under the visible light irradiation decomposition of H_2O_2 accelerates in the cases of all the metal complexes studied, except highly active complex with Fe^{III}. Complexes of TPP with magnesium, zinc and chlorophyll are the most active in the process of H_2O_2 decomposition. It should be noted that the surface amount of metal complexes was much higher than monolayer. Thus, the experimental kinetic data describe the collective activity of associated molecular ensembles of metal porphyrins. It is important that aggregation of chlorophyll and porphyrins, in particular, their dimerization facilitate the coordination of hydrogen peroxide and the rate of its decomposition.[8]

Recently, in experiments on the effect of Becquerel on photoelectrodes modified with various metal complexes of porphyrins their activity in the generation photopotential was determined.[9] In this paper, a comparative analysis shows that there is a linear correlation between the photoelectrochemical and photocatalytic properties of d^0- and d^{10}-metal complexes of TPP (Figure 3). No similar correlation was observed for the TPP complexes with transition metals. Thus, the analogy in photovoltaic and photocatalytic properties of metal porphyrins exists only in the case of metal complexes which are capable to generate long-lived triplet excited states with high quantum yield. Consequently, these properties are interrelated and could be used to estimate and predict each
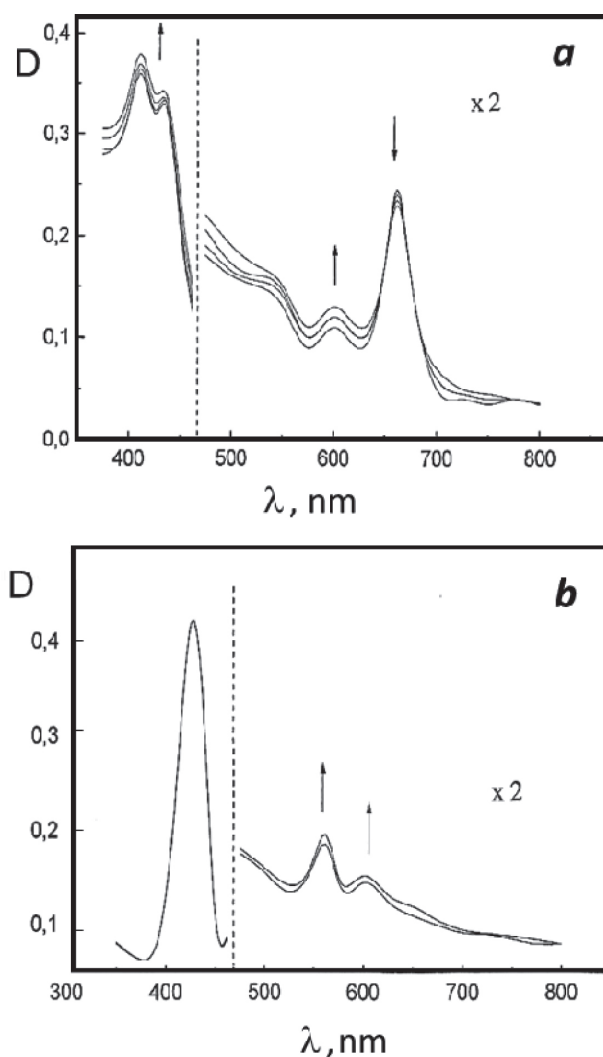

Figure 1. Electronic absorption spectra of Chl in ethanol (50%) and ZnTPP in 0.05% surfactant Tween-20 at addition of H_2O_2.

Table 1. Kinetic parameters of catalytic and photocatalytic activities of Chl and metal complexes of tetraphenylporphyrin immobilized on silica in H_2O_2 decomposition (pH 8.5)[a].

Metal complex	v_{im}[d], µmol/g	$(N/V)\cdot10^5$, mol/l	$k_{ob}\cdot10^5$, s⁻¹	k_{ef}, l·mol⁻¹ s⁻¹	TN, h⁻¹	$k_{ob}\cdot10^5$, s⁻¹	k_{ef}, l·mol⁻¹ s⁻¹	TN, h⁻¹	η, %
			In darkness			Under irradiation			
Chl	5.5	11.0	0.36	0.033	120	0.74	0.067	240	50
CrTPP	66	132	1.50	0.011	40	2.27	0.018	65	38
CuTPP	56	111	0.13	0.001	4	2.27	0.020	72	94
ZnTPP	55	110	3.87	0.035	130	4.35	0.040	145	10
CdTPP	52	103	0.39	0.004	14	0.60	0.006	22	36
SnTPP[b]	52	103	0.97	0.009	32	1.11	0.011	40	20
FeTPP[b]	21	41	17.9	0.438	1580	18.0	0.439	1580	0
MgTPP	49	98	–	–	–	5.0	0.051	185	–
PdTPP	55	110	7.79	0.071	255	–	–	–	–
YbTPP[c]	57	114	–	–	–	1.82	0.016	60	–

[a]In the Table k_{ef} is the effective rate constant, N is the number of moles of (photo)catalyst, V is the volume of the reaction solution, k_{ob} is the observed rate constant that could be expressed as $k_{ef}(N/V)^n$ because the rate of H_2O_2 decomposition $w = k_{ef}(N/V)^n [H_2O_2]^m$, where N/V, n and m = 1 do not change.[4] The catalyst turnover number (TN) corresponds to the number of moles H_2O_2 per a mole catalyst per an hour. Parameter η shows the percentage difference of k_{ef} for dark and light reactions.
[b]The coordination sphere of the metal ion also includes one (for Fe^{III}) or two (for Sn^{IV}) chloride anion.
[c]Ytterbium ion additionally contains one molecule of acetylacetone as extraligand on the third valence.
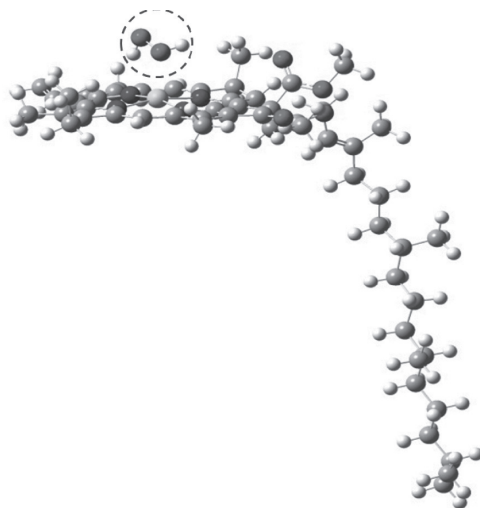[d]Amount of metal complex deposited per 1 g of silica.

Figure 2. The most energetically favorable structure of the coordination complex $Chl \cdots H_2O_2$ according to the quantum chemical calculations.

Figure 3. The linear correlation between the photocatalytic activity of d^0- and d^{10}-metal complexes of tetraphenylporphirin (shown by asterisks) and their ability to generate photopotential.

other. For example, difference between rates of dark and light-induced decomposition of H_2O_2 could be a test parameter in the development of molecular solar energy converters.

Conclusions

The model photosensitive systems with hydrogen peroxide participation were prepared. Immobilized metal complexes of porphyrins and chlorophyll possess the catalytic activity in the reaction of H_2O_2 decomposition. Linear correlation between the photovoltaic and photocatalytic properties of non-transition metal complexes of TPP was found. Decomposition of hydrogen peroxide photocatalyzed by metal complexes of porphyrins in the certain cases is able to provide energy storage reaction with increase of the chemical potential. On the one hand, it is important for the development of processes of utilization of solar energy. On the other hand, it is of interest to study the energy of intracellular biochemical processes involving pharmacologically active metal complexes.

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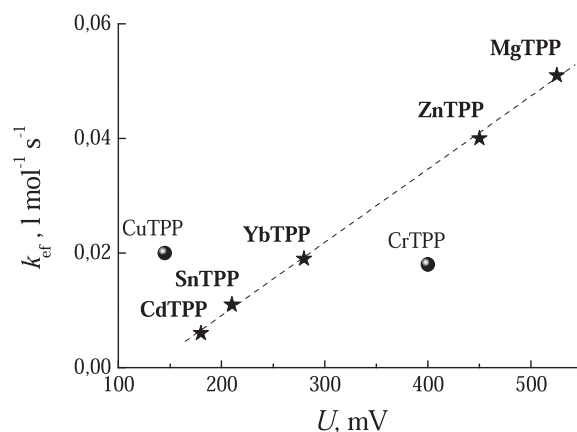
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