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Special Features of Singlet Oxygen Generation Photosensitized by Magnesium Complexes of Tetrapyrrolic Macrocycles

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Kinetic and photochemical parameters of generation of $^1O_2$ photosensitized by magnesium tetrapyrrolic complexes and products of $^1O_2$ conversion were obtained. Metal type is demonstrated to be the most essential factor in $^1O_2$ deactivation. Photosensitizing activity of magnesium complexes decreases at aggregation.

Keywords: Magnesium tetrapyrrolic macrocycles, singlet oxygen, photosensitizing activity.

Introduction

Triplet excited states of photosensitive molecules play a special role in the photocatalytic and photosensitized processes.[1] Phosphorescence (most often, it is the radiative transition T_1-S_0) is unresolved and the lifetime of the triplet states is 10^{-3} s and above usually, whereas the characteristic lifetime of singlet states is estimated as 10^{-9}-10^{-8} s. In the case of tetrapyrrole photosensitizers (TPS), the generation of long-lived triplet excited states with high quantum yield is typical for metal-free porphyrins and related compounds, as well as their complexes with d^0- and d^{10}-metals, *i.e.* elements containing no unpaired *d*-electrons. The most photobiologically important example of TPS with d^0-metals is chlorophyll containing magnesium ion.

Under photoexcitation of chlorophyll *a* (Mg-Chl) generation of the first triplet state T_1 with a high quantum yield (60%) is observed.[2] Energy of excited state T_1 is 11325 cm^{-1} (1.37 eV) and it lies at 3775 cm^{-1} (0.50 eV) below than level S_1.[3] Lifetime of T_1 measured at 77 K was found to be 2.0-2.7 ms, and the quantum yield of phosphorescence of the T_1 state is extremely small even in low-temperature solid matrices of ethanol, ether, pyridine, liposomal solutions and not more than $(1\text{-}3)\cdot 10^{-5}$ (for comparison, the fluorescence quantum yields of Mg-Chl from the S_1-state are of 0.20-0.35 at 293 K and 0.55 at 77 K, depending on the microenvironment).[4] Thus, the radiative processes of the triplet states of Mg-Chl hardly compete with the photosensitized reactions in the presence of oxygen and leads to the generation of singlet oxygen $^1O_2$ with a quantum yield closed to one of formation of the T_1 state.[5]

However, according to the modern concepts a primary photochemical act of charge separation in natural photosynthesis involves the participation of Mg-Chl and its supramolecular complexes in the first singlet excited state S_1.[6-8] The photochemical role of the triplet states of chlorophyll is still not fully clear at present, and as a rule it is associated with pathological destructive-photosensitized reaction of $^1O_2$ and reactive oxygen species. At the same time, there are mechanisms for effective decontamination of $^1O_2$ by chlorins[2] and transformation of $^1O_2$ in a physiologically important hydrogen peroxide in the chloroplasts.[9]

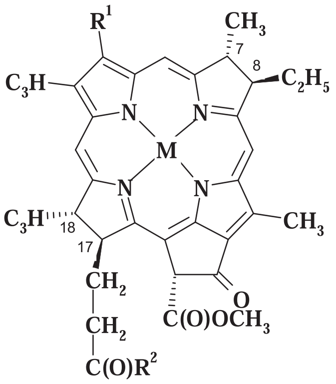
In this paper features of $^1O_2$ generation photosensitized by magnesium complexes of TPS and accumulation of products of $^1O_2$ transformation in organic (for example, anthracene) and aqueous phases were studied.

Experimental

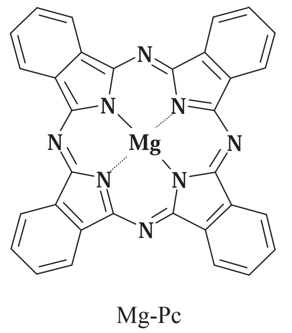
Chlorophyll *a* (Mg-Chl) and pheophytin (Pheo) were isolated from dry nettle leaves by known method.[10] Protochlorophyll (Mg-PChl) was isolated from ten-day maize seedlings by method already described.[11] Bacteriochlorophyll (Mg-BChl) of the biomass of phototrophic bacteria was obtained in Lomonosov Moscow Institute of Fine Chemical Technology (Technical University) (Moscow, Russia). Magnesium complex of phthalocyanine (Mg-Pc) was synthesized in Ivanovo State University of Chemistry and Technology (Ivanovo, Russia). The purity of the dyes was monitored by electronic absorption spectra with a spectrophotometer DR/4000V (HACH-Lange, USA) at wavelengths λ = 320-800 nm.

Experiments on generation of anthracene endoperoxide (AnO_2) and/or H_2O_2 was performed in standard quartz cuvettes (1 cm) under irradiation by halogen lamp (150 W) with lens, condenser and filter for cut-off radiation with $\lambda < 630$ nm. Light power was 10 mW/cm^2. Photolysis of anthracene (An) solutions ($8.9\cdot 10^{-4}$ mol/l) and Mg-Chl in CCl_4, CCl_4/H_2O mixture (1:1), $CHCl_3$, EtOH/H_2O (1:50), water-micellar system of 1% of Triton X-100 (TX-100) and not containing An suspension of silica (Sil) with deposited Mg-Chl, or Pheo ($1\cdot 10^{-8}$ mol pigment per 1 ml) in water (or D_2O) and in aqueous solutions of triethylamine (TEA), morpholine (Morf) and histidine (His) at concentrations of 0.1 mol/l was studied. In some of these systems Mg-BChl, Mg-PChl and Mg-Pc (in DMF/H_2O (1:50) also) were used. Amount of dye in all cases was $1\cdot 10^{-5}$ mol/l for solutions or $1\cdot 10^{-8}$ mol of dye per 1 ml of suspension. Value of p*H* (p*D*) of the aqueous was 12.4. Immobilization of TPS on Sil was performed as described earlier.[9] The kinetics of oxidation of anthracene (An), followed by loss of optical density of its solutions at the absorption bands of λ_{max} = 360 and 378 nm. The concentration of H_2O_2 formed was determined by iodometric titration in combination with spectrophotometry.[9] Quantum yields (Φ) of formation of AnO_2 and H_2O_2 were determined as the ratio of the number of formed molecules to the number of photons absorbed by the TPS in the initial fixed period of time.[12,13] The error of Φ determination was ±10%.

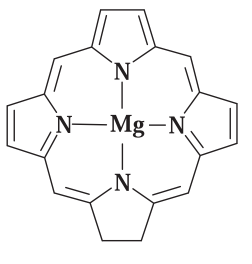
As a model of chlorophyll magnesium complex of chlorin was used (Mg-Chln). Calculations of Mg-Chln, O_2···Mg-Chln, O_2···Mg-Chln···His was based in part on the source code GAMESS (US).[14] Geometry optimization was carried out by density functional theory using the hybrid functional B3LYP in the restricted Hartree-Fock method for open shells. For the atoms of a molecule of oxygen used by the 6-31G (2d), for all the other atoms - the 6-31G.[15]



Mg-Chl: M = Mg, R^1 = –CH=CH_2,
$R^2 = –OCH_2CH=C(CH_3)(CH_2)_3[CH(CH_3)(CH_3)_3]_2CH(CH_3)_2$,
double bond C_7-C_8;
Mg-BChl: ; M = Mg, R^1 = –C(O)CH_3,
$R^2 = –OCH_2CH=C(CH_3)[(CH_2)_2CH=C(CH_3)]_2(CH_2)_2CH=C(CH_3)_2$;
Mg-PChl: as Mg-Chl with double bond C_{17}-C_{18};
Pheo: as Mg-Chl with M = 2H



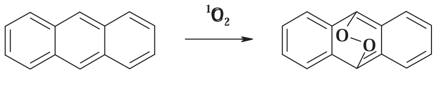
Mg-Pc



Mg-Chln

Results and Discussion

In many cases, for example, in heterogeneous systems, it is convenient to analyze the generation of $^1O_2$ by accumulation of stable oxidation products. For organic media test reaction of $^1O_2$ generation is the photooxidation of An to its endoperoxide:[16]



Absorption bands of An correspond to λ_{max} = 326, 340, 362 and 378 nm. Spectrum of solutions of An and TPS mixture is a simple superposition of individual spectra without changing of the position of the original bands and extinction. In this spectral range AnO_2 has no absorption bands. For photolysis An/TPS systems light with λ > 630 nm was used, so the light was absorbed by molecules of the TPS only. Under photolysis the optical density of solutions decreased. Absorption decrease allows to register the kinetics of AnO_2 accumulation. All TPS studied are active in $^1O_2$ generation. Use of photolysis light with λ > 630 nm does not lead to An oxidation in the absence of TPS, while a shorter wavelength light causes An oxidation by cycloaddition reactions[13] and $^1O_2$ formation probably (energy of triplet level of the An is 1.85 eV,[3] which is higher than the energy value of spin conversion $^3O_2 \rightarrow {}^1O_2$ which equals to 1 eV). Values of effective rate constant ($k_{ef}(AnO_2)$) were determined as the slope of the kinetic dependence of AnO_2 accumulation drawn in semi-logarithmic coordinates. Amount of AnO_2 per one of photon absorbed by TPS was defined by using the appropriate kinetic data. Similar plots were obtained for other TPS. The calculated values of $k_{ef}(AnO_2)$ and quantum yields of this reaction ($\Phi(AnO_2)$) are given in Table 1. One can see that parameters $k_{ef}(AnO_2)$ and $\Phi(AnO_2)$ correlate.

Process occurring after photoexcitation of TPS in systems containing anthracene and oxygen consists of the following steps:[16]

$$^1TPS_0 \xrightarrow{h\nu} {}^1TPS^* \qquad (1)$$
$$^1TPS^* \rightarrow {}^3TPS^*,\ k_{ST} \qquad (2)$$
$$^3TPS^* + {}^3O_2 \rightarrow {}^1TPS_0 + {}^1O_2,\ k_\Delta \qquad (3)$$
$$^1O_2 \rightarrow {}^3O_2,\ k_1 \qquad (4)$$
$$^1O_2 + An \rightarrow AnO_2,\ k_2 \qquad (5)$$

where k_{ST} is the intersystem conversion rate constant, k_Δ is rate constant of oxygen triplet state quenching, k_1 is the rate constant of $^1O_2$ deactivation (inverse magnitude to lifetime), k_2 is rate constant of reaction $^1O_2$ with anthracene. Quantum yield $\Phi(AnO_2)$ can be written as $\Phi(AnO_2) = \Phi_T\ \gamma_\Delta\ \gamma(AnO_2)$, where Φ_T is quantum yield of triplet state of the TPS, γ_Δ is the probability of $^1O_2$ formation at TPS triplet state quenching by molecular oxygen, $\gamma(AnO_2)$ is the probability of oxidation of anthracene to endoperoxide. The value of $\Phi_T \cdot \gamma_\Delta$ is an absolute quantum yield of singlet oxygen $\Phi(^1O_2)$.

Probability of formation of $^1O_2$, determined from kinetic analysis of oxygen quenching by $^3TPS^*$,[17] defined as $\gamma_\Delta = k_\Delta [O_2]\,\tau_T/(1 + k(O_2)\,[O_2]\,\tau_T)$, where τ_T is lifetime of $^3TPS^*$ in the presence of oxygen, $k(O_2)$ is the rate constant of quenching of triplet state TPS by molecular oxygen, including all types of quenching. For metal-free TPS, their complexes with magnesium and other non-transition metals it is well known that $\tau_T \geq 0.1$ ms, and $k(O_2) = (2 \pm 1)\cdot 10^9$ l/mol·s.[18-20]

The concentration of dissolved O_2 in aqueous solution is ~ $5\cdot10^{-4}$ mol/l, and in organic media it is higher in 5-20 times. Substitution of τ_T, $k(O_2)$ and $[O_2]$ values in the equation for γ_Δ leads to simplified expression $\gamma_\Delta = k_\Delta/\ k(O_2)$. However, it was found that for the monomer TPS generation of $^1O_2$ is the dominant process of $^3TPS^*$ quenching, and k_Δ and $k(O_2)$ constants do not differ more than in 0.7-1.26 times in practice.[26-30] This fact allows us to take $\Phi_T \approx \Phi(^1O_2)$. This condition was experimentally confirmed for Mg-Chl and a number of related compounds.[5] Thus, the quantum yields of the generation of TPS triplet excited states could be estimated with high accuracy in the case of direct determination of the quantum yield of photosensitized $^1O_2$ formation by time-

Table 1. Quantum yields and rate constants of photosensitized formation of AnO_2 and H_2O_2.

TPS	Solvent (support)	$\Phi(^1O_2)$	$\Phi(AnO_2)$	$\gamma(AnO_2)$	$k_{ef}(AnO_2)$, l/mol·s	$\Phi(H_2O_2)$	$k_{ef}(H_2O_2)$, l/mol s
Mg-Chl	CCl_4	0.57 [2]	0.012	0.021	68	–	–
Mg-Chl	CCl_4/H_2O	0.57 [2]	0.012	0.021	66	0.00011	12
Mg-Chl	$CHCl_3$	~0.60*	0.0021	–	12	–	–
Mg-Chl	$EtOH/H_2O$	<0.02*	<0.001	–	<0.1	$<10^{-5}$	<0.1
Mg-Chl	H_2O/Sil	–	–	–	–	0.00017	–
Mg-Chl	TEA/H_2O/Sil	–	–	–	–	0.00026	–
Mg-Chl	Morf/H_2O/Sil	–	–	–	–	0.00031	–
Mg-Chl	His/H_2O/Sil	–	–	–	–	0.00043	–
Mg-Chl	TX-100/H_2O	–	0.0021	–	10	0.00002	4.1
Mg-Chl	TX-100/D_2O	0.35 [2]	0.0072	0.020	36	0.00007	8.1
Mg-BChl	CCl_4	0.60 [2]	0.013	0.022	73	–	–
Mg-PChl	TX-100/D_2O	0.84 [5]	0.019	0.023	86	0.00016	18
Pheo	TX-100/D_2O	0.35 [2]	0.0024	0.007	94	–	–
Pheo	H_2O/Sil	–	–	–	–	0.00042	–
Mg-Pc	TX-100/D_2O	0.06-0.3**	0.0068	–	34	0.00008	10.2
Mg-Pc	DMF/H_2O	–	<0.001	–	<0.1	$<10^{-5}$	<0.1

*Approximate data based on the values of $\Phi(^1O_2)$ known for related compounds at similar conditions (*e.g.*, for Mg-Chl and Mg-BChl the values of $\Phi(^1O_2)$ are close in many solvents).[2,5,20,26-28]

**For Mg-Pc value of $\Phi(^1O_2)$, presumably, could be close to $\Phi(^1O_2)$ for complexes of phthalocyanines with aluminium or zinc.[29,30]

resolved measurements of its phosphorescence (at 1270 nm) with pulsed laser excitation. In cases where such measurement is difficult or impossible, application of specific compounds such as anthracene is useful. Equation $\gamma(AnO_2) = \Phi(AnO_2)/\Phi(^1O_2)$ was used for parameter $\gamma(AnO_2)$ determination. The values of $\gamma(AnO_2)$ are given in Table 1.

In accordance with the scheme of photosensitized oxidation of An the value of $\gamma(AnO_2)$ is defined as $\gamma(AnO_2) = k_2[O_2]/(k_1 + k_2[O_2])$.[16] Constant k_1 can be calculated from the data on $^1O_2$ lifetime, measured in many solvents. So, $^1O_2$ lifetime is 15 μs in EtOH, 67 μs in D_2O, 26 μs in mixture of EtOH/D_2O, 31 μs in benzene,[23] 60 μs in $CHCl_3$, 700 μs in CCl_4.[22] The value of k_2 constant was earlier determined from the known values of $\Phi(^1O_2)$, $\Phi(AnO_2)$ and k_1 for metal-free TPS in chloroform. For this type of complexes the value of k_2 was not dependent on the structure of porphyrin and equaled to $(6.1\text{-}6.3)\cdot 10^5$ l/mol·s.[16]

Comparison of the data presented in Table 1 shows that the values of $\gamma(AnO_2) = \Phi(^1O_2)/\Phi(AnO_2)$ are close for Mg-Chl, Mg-BChl and Mg-PChl in CCl_4, but different for Mg-Chl and Pheo in D_2O with the addition of detergent. However, the quantum yields of $\Phi(^1O_2)$ for Mg-Chl and Pheo in D_2O are similar, and one might assume similar values of $\Phi(AnO_2)$ too. The observed results are based on data on different deactivation $^1O_2$ by magnesium and metal-free complexes of TPS that were discussed earlier.[2] For bacteriochlorophylls and bacteriopheophytins it was shown that magnesium derivatives are more active in $^1O_2$ quenching compared with metal-free TPS. These data are in agreement with quantum-chemical calculations, which show that magnesium ion is the most advantageous binding site of the triplet and singlet oxygen with a model derived chlorophyll Mg-Chln. Thus, the $^1O_2$ quenching rate constants by Mg-BChl and BPheo (where BPheo – bacteriopheophytin *a*) k_q are $(9 \pm 2)\cdot 10^8$ and $(0.12 \pm 0.01)\cdot 10^8$ l/mol·s in CCl_4 or $(2.2 \pm 0.3)\cdot 10^8$ and $(0.3 \pm 0.1)\cdot 10^8$ l/mol·s in ether.[2] Consequently, the rate constant of interaction of $^1O_2$ and anthracene, as defined,[16] is an effective value and is determined by k_2 and k_q. Thus, the probability of $\gamma(AnO_2)$ to be approximately constant in the same solvent for complexes of the TPS with the same metal can be considered. But, for instance, for Mg-Chl and Pheo the values of $\gamma(AnO_2)$ are different (see Table 1).

In the cases of water system hydrogen peroxide could be considered as product of $^1O_2$ transformation. We have previously shown that Mg-Chl in the water systems photosensitizes formation of H_2O_2, and it was thermodynamically substantiated and experimentally confirmed that transformation of primary photogenerated $^1O_2$ is the advantageous channel for the synthesis of H_2O_2.[9,31] It was found $^1O_2$ transformation follows the formation of intermediate reactive oxygen species $^\bullet OH$, $O_2^{\bullet -}$ and $HO_2^\bullet$. Efficiency of H_2O_2 generation depends strongly on the p*H* of the solution. It is known that $^\bullet OH$ radicals in alkaline medium are the transients of H_2O_2 formation, as well as $O_2^{\bullet -}$ and $HO_2^\bullet$ in acidic medium.[32] In this case, the following diffusion controlled reactions with known rate constants take place:[24]

$$^\bullet OH + {}^\bullet OH \rightarrow H_2O_2,\ \ k_3 = 6\cdot 10^9 \text{ l/mol·s}, \tag{6}$$

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^\bullet,\ \ k_4 = 5\cdot 10^{10} \text{ l/mol·s}, \tag{7}$$

$$HO_2^\bullet + O_2^{\bullet -}\ (+H^+) \rightarrow H_2O_2 + O_2,\ \ k_5 = 9\cdot 10^7 \text{ l/mol·s}, \tag{8}$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2,\ \ k_6 = 2\cdot 10^6 \text{ l/mol·s}. \tag{9}$$

In the case of the determination of $^1O_2$ by H_2O_2 formation analysis in the aqueous phase the value of $\gamma(H_2O_2) = \Phi(^1O_2)/\Phi(H_2O_2)$, is determined by relation of the rate constants k_q, k_3, k_4, k_5, k_6 and the amount of radical and anion radical oxygen forms depending on p*H*. It should be noted that in addition to reactions (6) - (9) there is a number of other transformations of reactive oxygen species, which complicate the kinetic analysis. However, using TPS (or its metal complexes) as a standard with known directly measured value of $\Phi(^1O_2)$, and knowing $\Phi(H_2O_2)$, there is the possibility to determine the value of $\gamma(H_2O_2)$ which then could be used to determine $\Phi(^1O_2)$ in multiple aqueous systems, for example, in suspensions of silica gel with adsorbed TPS complexes with the same metal. As one can see from Table 1, a correlation between $\Phi(^1O_2)$ and $\Phi(H_2O_2)$ values is observed.

Generation of $^1O_2$ is also occurs under photoexcitation Mg-Chl immobilized on silica (Table 1). It is known that in the photosynthetic apparatus Mg-Chl and Mg-BChl are coordinated with aminoacid residues of the protein matrix. So, according to X-ray analysis of the reaction center of purple bacteria, Mg ions of all Mg-BChl are coordinated by nitrogen atoms of His residues located in the α-helical regions of protein subunits.[33] Experimental results show that the addition of nitrogen Lewis bases - triethylamine, morpholine, and in particular, histidine to immobilized Mg-Chl suspensions stimulates the generation of $^1O_2$. Apparently, the coordination Mg-N bond facilitates the interaction of Mg-Chl and oxygen. This conclusion is consistent with the results of quantum chemical calculations. More efficient generation of singlet oxygen in complex Mg-Chl with His associated with a decrease in the energy decay of states, including the formation of singlet oxygen.

Photosensitizing activity of aggregated TPS in $^1O_2$ generation decreases by more than an order of the reaction of both AnO_2 and H_2O_2 formation. The decrease of $^1O_2$ generation is observed in ethanol/water, where Mg-Chl is aggregated,[2] and in DMF/water solution of Mg-Pc. Most likely that triplet-triplet annihilation takes place in the molecular associates of Mg-TPS, and $^1O_2$ is practically not formed:

$$^3TPS^* + {}^3TPS^* \rightarrow {}^1TPS + {}^1TPS_0 \qquad (10)$$

Dependence of photosensitizing activity of TPS on the degree of their aggregation, on the one hand, could be a basis for directional receiving the photosensitive material with predetermined luminescent and photochemical properties. On the other hand, these features allow to consider the important role of various associates and supramolecular forms of TPS in generation or quenching of singlet oxygen in biological and pharmacological processes.

Conclusions

Thus, the analysis of the stable products of $^1O_2$ conversion such as anthracene endoperoxide and hydrogen peroxide are useful for confirmation of $^1O_2$ generation. Kinetic and photochemical study of $^1O_2$ generation photosensitized by magnesium tetrapyrrolic complexes shows that the process depends on the presence of magnesium ion in macrocycle because of magnesium complexes of TPS are more active in $^1O_2$ quenching compared with metal-free macrocycles.

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