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SPECIFIC FEATURES OF THE KINETICS OF DESTRUCTIVE DEGRADATION OF PORPHINE AND PHTHALOCYANINE DERIVATIVES IN OXIDISING MEDIA[1]

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Keywords:
tetrapyrrolemacroheterocyclic compounds; porphyrins; phthalocyanines; oxidative degradation, redox potentials

Abstract. *The paper presents the analysis on chemical, thermal and electrochemical stability of some aromatic macroheterocycles (MHC) of porphyrin (H_2P) class as well as their benzo- and aza-analogues, establishes electronic and structural factors determining the rate of pigment destruction in the presence of oxidant. The values of redox potentials of porphyrin-, tetraaz-, tetrabenzo-porphyrin- and phthalocyanine-type MHCs correlate with the temperatures at which their thermo-oxidative degradation starts and the decomposition rates in oxidizing media. The combined benzo- and azamer substitution in H_2P molecules leads to their destabilisation with respect to oxidants, the situation depending strongly on the nature of the oxidant (H_2O_2, $S_2O_8^{2-}$ and NO_3^-), the solvent (H_2SO_4, HOAc) as well as the nature of the metal in the molecule. The polymer state or spatial distortion of the MHC has a significant influence on the resistance to oxidising agents. The reaction mechanisms of oxidation of label-free porphyrins and phthalocyanines by hydrogen peroxide are shown to be identical. In both cases, the reaction centres of MHCs are N-H-bonds, either in the meso-position (H_2Ps) or in the coordination cavity of the H_2N_4 molecule (H_2P), and the pigments are cleaved to colourless products.*

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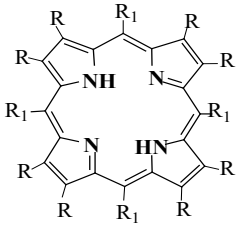
Introduction

The stability of porphyrins (H_2P) and their complexes in redox environments is among the practically important issues. This fact is related to the fact that natural porphyrins, such as

[1] *In memory of my father and teacher, a talented scientist and great optimist, academician of the Russian Academy of Natural Sciences, Boris Dmitrievich Berezin (1929-2012)*

chlorophyll in the structure of green leaves, haem in haemoglobin as well as cytochromes, catalases and peroxidases, are constantly in contact with oxidants (O_2, H_2O_2, HO_2^-,NO_2^-, NO_3^- etc.) under conditions of their biogenesis and functioning in a living cell [1-4]. Synthetic H_2Ps and their metal complexes (MPs) such as porphin (I) and its derivatives (compounds II-IV, X), as well as benzo- and aza-analogs (compounds V-IX), in particular, various phthalocyanines (H_2Pc and MPc), are used as catalysts in oxidation reactions of organic compounds [5-10], photosensitizers for technical and biomedical applications, are used in photodynamic therapy (PDT) for cancer and infectious diseases [11-21] and are also constantly in contact with oxidants. Because of their particular importance, issues related to the stability of H_2P and H_2Pc in oxidizing environments have been investigated and discussed in a number of monographs, reviews and original papers [2-5, 13, 14, 22].



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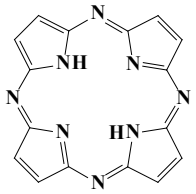

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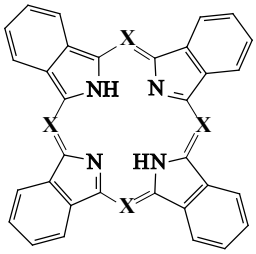

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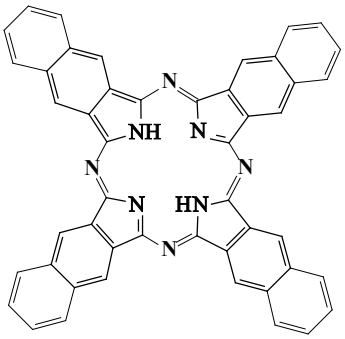

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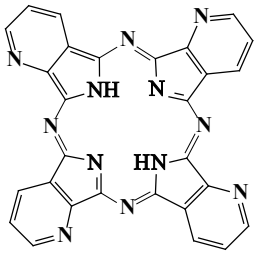

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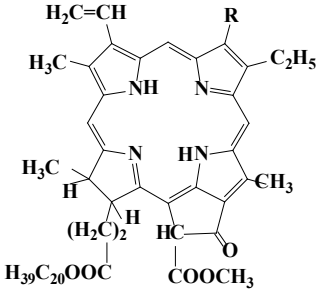


X.

Porphyrins and phthalocyanines have low values of normal redox potentials [2, 23, 24], therefore they are thermodynamically unstable systems in oxidizing environments [3-6, 22]. As a result, they are easily subjected to chemical, photochemical and electrochemical redox transformations [25-29]. The ease of occurrence of these transformations essentially depends on a number of factors, including features of the structure of the macroheterocycle itself, donor-acceptor characteristics of the functional substituents on the periphery of its molecule, the nature of the oxidizing environment, etc. [22, 26, 27]. The structure-dependent processes under study are the basis of the light stage of photosynthesis, the functioning of haemoglobin and H_2P-based enzymes [1, 4, 25].

When porphyrins lack functional groups capable of redox processes, the oxidation rate of their molecules can serve as a characteristic of their boundary molecular orbitals. The magnitude of the energy gap NVMO-VZMO macrocycles with predominantly planar structure

(compounds I-III) and their complexes with metals obtained from the ESP, consistent not only with the results of quantum-chemical calculations, but also with electrochemical data presented in Table 1, according to which the difference between the first potential oxidation and reduction of porphyrins proper is usually (2.25±0.15) V [3].

Table 1. Half-wave potentials ($E_{1/2}$) of the oxidation of porphyrins, their aza- and benzo-analogues [24, 29]

Compound	Solvent	Comparison electrode	$E_{1/2}^{Ox1}$, B	$E_{1/2}^{Ox2}$, B	ΔE^{Ox-Red}, B
H_2P, **I**	-	-	0.91	-	-
$H_2(\beta\text{-Et})_8P$, **II**	DMF	SCE	0.96	1.19	2.30
$Zn(\beta\text{-Et})_8P$	CH_2Cl_2	SCE	0.63	1.02	2.24
$H_2(\beta\text{-Et})_8Chl$	*n*-PrCN	-	0.64	1.18	-
$H_2(ms\text{-Ph})_4P$, **III**	DMF	SCE	1.11	-	2.19
$Zn(ms\text{-Ph})_4P$	DMF	SCE	0.86	1.04	2.21
$H_2(ms\text{-4-Tol})_4Chl$	CH_2Cl_2	SCE	0.74	0.98	-
H_2TAP, **V**	*o*-DCB	QRE (Fc^-/Fc)	0.82	-	2.52
H_2TAChl	*o*-DCB	QRE (Fc^-/Fc)	0.64	-	1.77
H_2Pc, **VII**	CH_2Cl_2	SCE	0.93	1.14	1.71
H_2TBP, **VI**	DMSO	SCE	0.55	-	1.68
ZnTBP	DMF	SCE	0.38	-	1.86
$Zn(\beta\text{-Et})_8(ms\text{-Ph})_4P$	-	-	0.47	-	-
$H(N\text{-Me})(ms\text{-4-Tol})_4P$	CH_2Cl_2	SCE	0.70	1.10	-

SCE and QRE (Fc^-/Fc) are saturated calomel electrode and ferrocene electrode, respectively.

Most H_2Ps generally undergo a reversible two-step electrochemical oxidation and reduction of the macrocyclic system [3, 23, 24]. The reduction potentials β ($E_{1/2}$) averaged for predominantly planar - (in particularβ -octaethylporphyrin or ethioporphyrin **II**) and *meso*-substituted porphyrins (for example *meso*-tetraphenylporphyrin **III**) are -(1.3±0.3) V and -(1.7±0.3) V, and oxidation potentials +(0.7±0.3) V and +(1.1±0.3) V (see Table 1) [23]. In [28] full electrochemical characterization of a number of aza- and benz-substitution products of porphyrins - phthalocyanine ligands (H_2Pc, in particular, unsubstituted compound **VII**) and tetraazaporphyrins (H_2TAP, **V**) is given and it is found that all these compounds are able to give two, and take up to four electrons. It can be said that expansion of the aromatic π-system of MHC, e.g. due to tetrabenzo- or tetranaphtho-substitution in molecules **VI**-**IX**, for example in the series H_2TAP (**V**) - H_2Pc (**VII**) - H_2NPc (**VIII**, naphthalocyanine) results in a significant decrease of the first oxidation potential. This tendency to change the value of $E_{1/2}^{Ox1}$, so as sligtly increase $E_{1/2}^{Red1}$ in the case of tetra-*tret*-butyl-substituted compounds: $H_2(\beta\text{-}tert\text{-Bu})_4TAP$ (1.31; -0.74) – $H_2(\beta\text{-}tert\text{-Bu})_4Pc$ (0.95; -0.80) – $H_2(\beta\text{-}tert\text{-Bu})_4NPc$ (0.65; -0.89). A gradual decrease of the oxidation potentials also occurs in the series: porphyrins (0.9÷1.1) < porphyrazines (0.7÷0.8) < tetrabenzoporphyrins (H_2TBP, 0.5÷0.7) [29] (see Table 1). Conversion to metal complexes, in particular to complex compounds of H_2P with Zn(II) (see Table 1), also markedly reduces the oxidation potentials of MHC, usually by (0.25-0.30) B at the first step.

The values of redox potentials of porphyrin-, tetraaz-, tetrabenzo-porphyrin- and phthalocyanine-type MHCs correlate with the temperatures at which their thermo-oxidative degradation starts and the decomposition rates in oxidizing media. Thus, according to the data of [27], the oxidation rate constant for the ethioporphyrin ligand (H_2(β-Alk)$_8$ P, **II**) alkylated at all eight $^{\beta}$-positions of the molecule is only (3.05-10-4) c^{-1} with benzoyl peroxide. The $E_{1/2}$ value of the H_2P ligand depends not only on the type of the aromatic molecule and the nature of the substituents, but also on the nature of the coordinated metal and the extraligands in the complex. In [30] the kinetics of oxidation of pheophytin*a* (label-free chlorophyll *a*, compound **X**) and its complexes with Cu(II), Co(II), Ni(II) and Fe(II) in ice-cold acetic acid (HOAc) in the presence of potassium nitrate was studied. The oxidation reaction proceedsmonomolecularly, regardless of the nitrate concentration, and the introduction of the metal into the MHC catalyses the pheophytin oxidation process.

Table 2. Kinetics of oxidative degradation by hydrogen peroxide and potassium nitrate of nitrogenous macroheterocycles [22, 30, 36]

Macroheterocycle	Solvent	Concentration H_2O_2, mol·l^{-1}	effective rate constant k_{ef}^{298}, $c^{-1}\cdot10^3$	Reaction order $n_{H_2O_2}$
H_2Pc, **VII**	17M H_2SO_4	0.12	1.77	1
	17M H_2SO_4	KNO_3 ($6.65\cdot10^{-4}$ mol l^{-1})	very rapidly	-
ZnPc	17M H_2SO_4	KNO_3 ($7.77\cdot10^{-3}$ mol/l^{-1})	0.30	-
H_2Chl, **X**	17.3M HOAc	KNO_3 ($6.83\cdot10^{-3}$ mol/l^{-1})	0.02	0
Chlorophyll (MgChl)	17.3M HOAc	KNO_3 ($6.83\cdot10^{-3}$ mol/l^{-1})	0.02	0
Polymer phthalocyanine* $(H_2Pc)_{i=6-12}$	17M H_2SO_4	0.281 KNO_3 ($4.91\cdot10^{-2}$mol/l^{-1}) $(NH_4)_2S_2O_8$ ($5.00\cdot10^{-2}$mol/l^{-1})	2.90 very rapidly 4.70	1 - 1
H_2Pc, **VII**	17M H_2SO_4	$(NH_4)_2S_2O_8$ ($5.00\cdot10^{-2}$mol/l^{-1})	1.30	1
H_2TPyPA, **IX**	17M H_2SO_4	0.302	0.17	0.7

* The first rate constants are given (*i* is maximum).

The combined benzo- and aza-substitution in porphyrin molecules leads to their destabilization towards oxidants [22, 27]. However, the situation strongly depends on the nature of the specific oxidant, the environment, and the nature of the metal in the MR composition. Thus, the localization of the oxidation reaction centre and the mechanisms of the process proved to be fundamentally different for phthalocyanine **VII** and its complexes when reacted in the presence of peroxides in nitrobenzene [27] and in sulphuric acid [30]. In sulphuric acid, the localization site is a single target protonated *meso*-nitrogen atom. Moreover, due to changes in the environment, those MRs that were passive may end up among the active ones, and vice versa. In [31] oxidative degradation of tetrabenzoporphine (H_2TBP, tetrabenzocondensedporphyrin **VI**), as well as its sulfo-, nitro-, amino- and other derivatives by potassium persulfate in acetic and

sulfuric acids was studied. All benzoporphyrins were less oxidation stable than phthalocyanine except $H_2TBP(SO_3H)_4$, which was an order of magnitude more stable than H_2Pc. These facts are in agreement with the data on the oxidation potentials of compounds **VI** and **VII** (see Table 1).

The authors [32] studied the kinetics of oxidative degradation of π-electron-deficient tetra-2,3-pyridinoporphyrazine (H_2TRura, **IX**, a product of additional tetraazazamenation) and its complexes with hydrogen peroxide in 17M H_2SO_4. The order of reaction on H_2O_2 is unity, and value of true constant (k_v, l-mol^{-1}-s^{-1}) varies from 1.72-10^{-4} at H_2TPyPA to 0.126 at PdTPyPA, that is these compounds are 10-100 times more stable in comparison with appropriate phthalocyanines [22].

The paper [27] shows that the oxidation rate of ethioporphyrin (**II**, $k = 3.05 \cdot 10^{-4}$ s^{-1}), tetrabenzoporfine (**VI**, $k = 15 \cdot 10^{-2}$ s^{-1}), tetraazaporphine (**V**, $k = 3.9 \cdot 10^{-6}$ s^{-1}) and phthalocyanine (**VII**, $k = 2.43 \cdot 10^{-2}$ s^{-1}) benzoyl peroxide correlate as 1 ÷ 500 ÷ 0.01 ÷ 80 [27]. Thus, tetrabenzosubstitution leading to an expansion of the aromatic π-system of H_2P and a lowering of the oxidation potential of the macroheterocycle dramatically decreases its resistance to oxidizing agents, whereas the electron acceptor tetraase substitution, on the contrary, decreases the oxidation rates. The combined effect of tetrabenzo- and tetrasubstitution in phthalocyanine leads to a slightly lower oxidant resistance compared to H_2P.

Another option for conducting oxidative processes is the degradation of MHCs by oxygen at elevated temperatures [29, 33-35]. The tendency of the macroheterocycles under study to thermo-oxidative degradation in the presence of air oxygen increases with the decrease of the initial temperature of mass loss process (t_n, °C) in the series of ligands (1) and their metal complexes (2) [29, 33].

$$H_2Pc\ (\mathbf{VII}, 460) > H_2(ms\text{-}Ph)_4P\ (\mathbf{III}, 407) > H_2(\beta\text{-}Et_4Bu_4)P\ (\mathbf{II}, 400) > H(N\text{-}Me)(ms\text{-}Ph)_4P\ (240) \sim H_2(\beta\text{-}Ph)_8(ms\text{-}Ph)_4P\ (\mathbf{IV}, 244) \quad (1)$$

$$ZnTBP\ (345) > Zn(ms\text{-}Ph)_4P\ (340) > Zn(\beta\text{-}Et_4Bu_4)P\ (325) > (AcO)Zn(N\text{-}Me)(ms\text{-}Ph)_4P\ (230) > Zn(\beta\text{-}Ph)_8(ms\text{-}Ph)_4P\ (211) \quad (2)$$

These data allow us to note a decrease in the thermal stability of MHCs both in the series of ligands and their zinc complexes as the aromaticity of the molecules decreases and the nonplanarity increases in the transition to strongly nonplanar multiply substituted compounds, e.g. **IV**. The highly aromatic H_2Pc (**VII**) and the zinc metal complex with H_2TBP (**VI**) are the most thermostable in the case under study. The metal complexes are always 30-80 degrees less stable to thermal oxidation than the ligands, which is consistent with their oxidation potentials shown in Table 1.

The analysis of the literature allows to define the trends in the oxidative stability of porphyrins and their more aromatic aza- and benzo-analogues. In case of numerous H_2Ps, which have a highly loose macrocycle structure due to multiple functional substitution and other reasons [37-40], there is no clarity on this issue. Therefore, this paper presents and discusses the oxidation of one of the most spatially distorted porphyrins, dodecaphenylporphine {$H_2(\beta\text{-}Ph)_8(ms\text{-}Ph)_4P$, **IV**} and its predominantly flat analogue *meso*-tetraphenylporphine {$H_2\ (ms\text{-}Ph)_4P$, **III**} by hydrogen peroxide. An analysis of the literature on the oxidation processes of non-planar H_2P as well as possible mechanisms of oxidation processes is carried out.

Experimental part

Macroheterocycles H_2(*ms*-Ph)$_4$P (**III**) и H_2(*β*-Ph)$_8$(*ms*-Ph)$_4$P (**IV**) are synthesised according to the methodology [41]. The acetic acid and hydrogen peroxide were labelled 'p'. HOAc was subjected to double freezing followed by Fischer water content control.

The kinetics of the oxidation of MHC **III** and **IV** with hydrogen peroxide in ice-cold HOAc medium was monitored spectrophotometrically by decreasing the optical density in the 724 nm band of the electron absorption spectrum (EAS). The benchmark of comparison was chosen as *meso*-tetraphenylporphine {H_2(*ms*-Ph)$_4$P, **III**}.

In the coordinates $\lg\frac{A_o - A_\infty}{A_\tau - A_\infty} - t$, where A_o, A_τ and $A\infty$ are the optical densities at the beginning, during and at the end of the experiment a characteristic dependence is observed (Fig. 1, *left*), indicating the first order of the porphyrin reaction. The effective rate constants of the oxidation reaction (3) are shown in Table 3.

$$-\frac{dC_{H_2P}}{dt} = k_{eff} \cdot C_{H_2P}. \quad (3)$$

Fig. 1 (*right*) shows a feature of the kinetic dependence of the polymer oxidation process, i.e. the effect of the polymer state of the phthalocyanine on its stability [36].

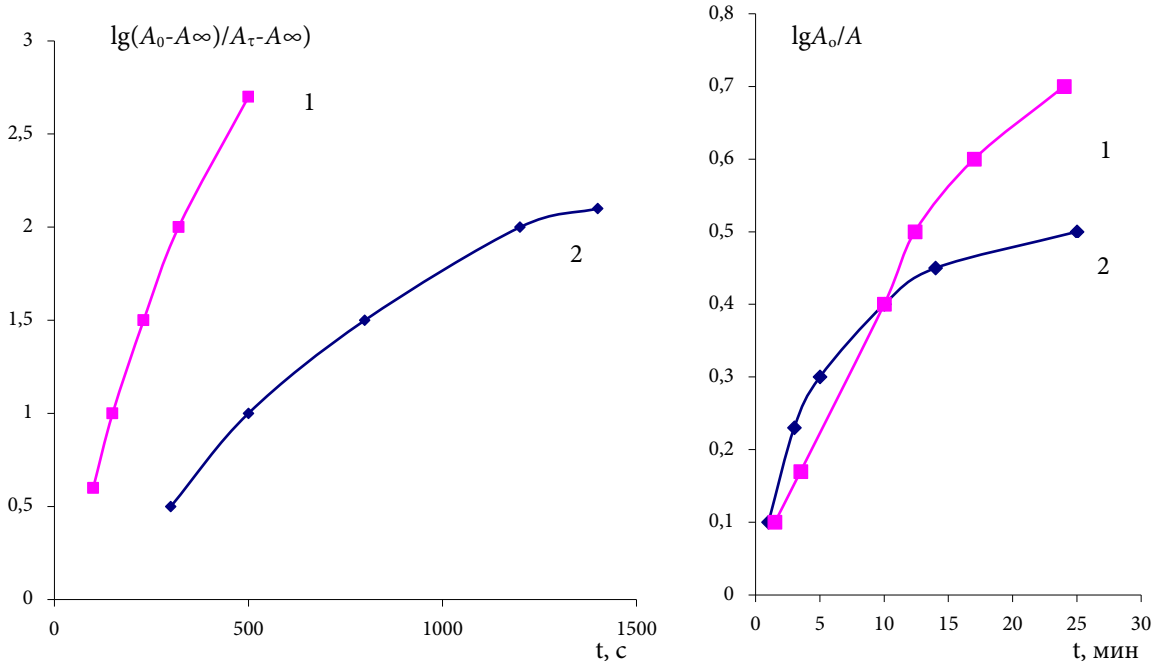


Fig. 1. Oxidation reaction rate of dodecaphenylporphine (**IV**, C_{H_2P} = 10^{-5} mol·l^{-1}) hydrogen peroxide ($C_{H_2O_2}$ = 0.353 mol·l^{-1}) in a solution of ice-cold HOAc (*left*) and oxidation of polymer phthalocyanine $(H_2Pc)_i$ linear structure (i = 12) ($C_{H_2O_2}$ = 0.281 m/l) in solution 17M H_2SO_4 (*right*) at 308 (1) и 298 (2) K

Results and Discussion

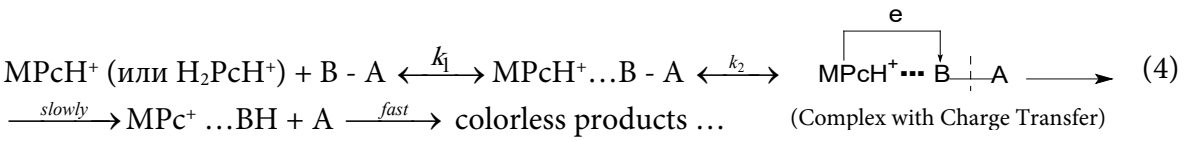
We compare the kinetic data on the oxidative degradation of tetrapyrrole and tetraisoindolemacrocycles in acid solutions obtained and available [2, 22, 27, 29-32] and clarify the

electronic and structural factors determining the rate of aromatic macrocycle destruction. Chemical, electrochemical and photochemical oxidation of metalloporphyrins, metallophthalocyanines and their analogues is accompanied by oxidation of the central metal atom, redistribution of spin density between the central metal atom and the macrocyclic π-ligand. In this case, cationic radicals of porphyrins are formed [3, 23, 25], which greatly complicate the picture of oxidative transformations of compounds of this type.

We consider possible oxidation mechanisms based on label-free macrocycles (ligands) based on H_2P (**I**), H_2Pc (**VII**) and their derivatives. The first studies were conducted on phthalocyanine (**VII**) and its numerous complexes (Fig. 2) [22, 30]. Table 2 shows the kinetic data for the oxidation reactions of nitrogenous macrocycles with hydrogen peroxide, potassium nitrate and persulfate in acidic media.

The values of standard redox potentials of MHC **VII** (see Table 1) and its complexes (from 0.342 V for ZnPc to 0.725 V for PtPc) are small, so they react easily with strong oxidants [22]. Many of them are titrated in sulphuric acid solutions with salts of Ce(IV). Ligand **VII** is rapidly oxidised by potassium nitrate (see Table 2).

In [22, 30, 36] the reaction mechanism of the oxidation of phthalocyanines was discussed in detail, the scheme of which can be schematically and in generalised form represented as



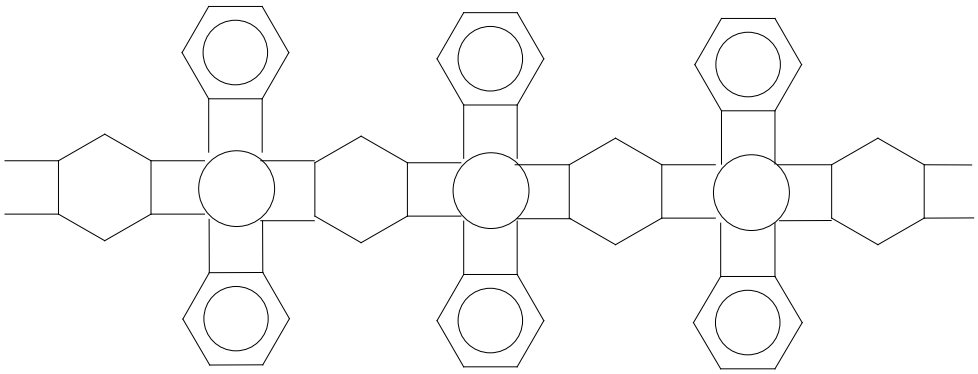


Fig. 2. Chain polymer phthalocyanine based on pyromellitictetranitrile

At the first stage, a H-complex of protonated phthalocyanine with the main centre (B:) of the oxidant B: - A is formed relatively rapidly. The oxidising agent can be H_2O_2, ONO_2^-, $^-O_3S\text{-}O\text{-}O\text{-}SO_3^-$ and others. In the second stage, H_2Ps transfers a proton and then an electron to the opening orbital of the oxidant to form a charge transfer complex (CDC). The latter decomposes in the limiting stage into the radical cation MRs^+ and fragments of the oxidant molecule.

The introduction of pyridine residues instead of benzene nuclei into structure **VII** (H_2TRuPA, compound **VIII**) strongly stabilises H_2Ps towards oxidants (see Table 2). The reason for the stabilisation of **VIII** is the decrease of the VZMO energy of the macrocyclicchromophore C_8N_8 due to the strong electron acceptor effect of the pyridine nuclei. This electronic effect in process (4) hinders the formation of KPZ and its decomposition to the radical cation H_2TRuPA^+ mainly by increasing the activation energy. Besides this energetic reason, a kinetic one is also possible - oxidant binding at the four protonated pyridine nitrogen atoms, which

cannot lead to oxidation of the macrocycle. In general, the oxidation rate constant of **VIII** is reduced by more than an order of magnitude in compare to **VII** (see Table 2).

We expect a strong decrease of the oxidative capacity of the aromatic macrocycles for porphyrins due to the absence of such unique reaction centres of oxidant localisation as H_2Ps have in the periphery of the macrocycle (*meso*-nitrogen atoms). Significant decrease of the VZMO energy for porphyrins leads to an increase of half-wave potentials in electrochemical oxidation processes [23, 24, 29] (see Table 1).

Aromaticity of porphyrins is larger than the same for phthalocyanines in [3, 29]. Therefore, they are more reactive by πvia -bonding of the conjugated system (hydrogenation, oxidative addition, etc.) [3, 29]. For the same reason, the oxidation of H_2P can be accompanied by the addition of hydrogen peroxide (2OH) elements at various π-system positions [3-6, 23]. This addition occurs more easily in neutral solvents and more difficult in acidic environments. Increased electron density at reaction centreslocalised at and near the *meso*-positions of the molecule is usually required. The bridging*meso*-positions are occupied by nitrogen atoms in porphyrazines (**V**) and phthalocyanines (**VII)**. For this reason, even at high concentrations of H_2O_2, hydrogen peroxide elements are not attached via π--bonds. H_2P molecules (compounds **I**-**IV**) attach H_2O_2 as reactive oxygen species, e.g. singlet $^1O_2$ [14, 15, 20, 42-44] is at *meso*- and adjacent positions. However, these issues have not been sufficiently investigated since the oxidation reactions of organic compounds are among the most complex, especially when polyfunctional molecules are oxidised [26].

In compare with the ordinaryporphyrin **III**, dodecaphenylporphyrin **IV** has a predominantly planar macrocycle and belongs to H_2P with a strongly non-planar, spatially distorted structure [29, 37]. A significant bathochromic shift of the long wavelength band in the absorption spectra is typical of this kind of MHC.

In compare with H_2Pc and the most of H_2P dodecaphenylporphyrin {$H_2(\beta$-Ph$)_8$(*ms*-Ph$)_4$P, **IV**} is not soluble nor in H_2SO_4, nor in monohydrate. It is slightly soluble in ice-cold acetic acid (λ_1 = 724.0 nm), dichloromethane (λ_1 = 721.0 nm), in HCOOH (λ_1 = 717.5 nm), CF_3COOH (λ_1 = 768 nm), in mixture of HOAc–H_2SO_4 (λ_1 = 711.5 nm), in acetone (λ_1 = 736.0 nm), but in mixture of acetone–NH_3 (λ_1 = 714.5 the solution is not stable. For most of the above media tetraphenylporphyrin {H_2(*ms*-Ph$)_4$P, **III**} exhibits values of λ_1 in the 640-655 nm, i.e. 75-100 nm hypsochromic as compared with distorted MHC **IV**.

Another characteristic feature of nonplanar H_2P compounds, not containing distinct electron-donor or acceptor substituents, in comparison with classical porphyrins [4, 13, 29, 35, 37-41] is a decrease of oxidation potentials ($E_{1/2}{}^{Ox}{}_i$) with increasing nonplanarity and, practically, invariability of reduction potentials ($E_{1/2}{}^{Red}{}_i$). It corresponds to the convergence of the boundary orbitals (VZMO-NVMO) and is consistent with the bathochromic shift of the long wavelength Q_x band in the ESP of these compounds. For example, this kind of regularity is observed for predeconvertedporphyrins such as compound **IV** and their complexes [29, 37], Ni(II) complexes with *meso*substituted H_2P [39], in porphyrins and their complexes {e.g. Fe(III) and Zn(II)} as their β,β- hydrogenation of π-systems is sequential [3, 38] and to a lesser extent in N-substituted ligands [29, 40]. The presence of substituents of different electronic nature in the H_2P molecule (MP) also leads to characteristic changes in potentials. For example, if the

substituents are in the phenyl rings, the changes in potentials will be small (no more than 0.1 V) If the functional group (usually the electron acceptor of Cl, Br, NO_2) enters directly into the *β*- or *meso*-position of the main macrocycle, this leads to a strong positive shift of redox potentials, which in non-flat H_2 P can compensate the decrease of value $E_{1/2}^{Ox_i}$ caused by distortion of the molecule.

Like other structural types of porphyrins, non-planar H_2P and their complexes can be easily oxidised by air oxygen in the presence of hydrogen peroxide, salts of Tl(III) or Ce(IV) aan undergo reduction by light quanta and ascorbic acid or hydrazine [29, 37]. Complexes of the dodecaphenylporphine (**IV)** under study are extremely unstable with the most metals in acidic media and dissociate immediately to ligands [29, 37], therefore we excludethe analysis of their oxidative stability to H_2O_2 and other oxidants in these conditions [30, 32, 36].

By Table 3, compound **IV** in ice-cold acetic acid solutions at high concentrations of H_2O_2 (0.35-0.45 M) is oxidized at a rate k_{ef}^{298} = (1.9-6. 4)·10^{-3}s $^{-1}$, whereas *meso*-tetraphenylporphine **III** at higher concentrations of $_H$ $2O_2$ (0.66-0.79 M) at a rate several times lower (k_{ef}^{298} = 1.4-2.1)·10^{-3} s^{-1}. Already at a 1.29·10^{-5} M solution of MHC **IV** in the presence of 0.449· M H_2O_2 in ice-cold HOAc medium the oxidation reaction at 298 K ends in 10 minutes. In these conditions the porphyrinmacrocycles under study decompose to colourless products.

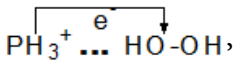
Table 3. Oxidation reaction rate constants H_2(*ms*-Ph)$_4$P (**III)** и H_2(*β*-Ph)$_8$(*ms*-Ph)$_4$P **(IV)** hydrogen peroxide in NOAS solutions

Compound					
H_2(*ms*-Ph)$_4$P (III, C_{H2P} = 2.0·10^{-6}mol·l^{-1})			**H_2(*β*-Ph)$_8$(*ms*-Ph)$_4$P (IV, C_{H2P} = 6.4·10^{-6}mol·l^{-1})**		
C_{H2O2}, mol·l^{-1}	**T, K**	**k_{ef}·10^{-3} c^{-1}**	**C_{H2O2}, mol·l^{-1}**	**T, K**	**k_{ef}·10^{-3} c^{-1}**
0.663	298	1.4±0.2	0.353	296	1.4±0.1
	308	3.1±0.3		298	1.3±0.2
0.750	298	2.0±0.3		308	6.4±0.2
	308	3.2±0.2		318	13.8±1.1
0.794	298	2.1±0.3	0.449	296	5.2±0.4
	308	3.5±0.3		298	6.4±0.3
				308	11.3±1.0

By Table 3 it is possible to approximate the order of the oxidation reaction of porphyrins **III** and **IV** by $C_{H_2O_2}$. For H_2(*ms*-Ph)$_4$P it is close to one, whereas in the strongly non-flat H_2(*β*-Ph)$_8$(*ms*-Ph)$_4$P is a significantly lower value. Thus, the maximal peripheral phenylation of the H_2P molecule in case of compound **IV** leads to weighting of the molecule, to the appearance of low-energy vibrational states and to the expected loss of thermal (see series 1 and 2) or photochemical [45] stability, surprisingly little destabilizes the **IV** molecule in the presence of H_2O_2. Meanwhile, the steric tension in the macrocycle created by the *β*- and *meso*-phenyl rings of the **IV** molecule favours the oxidation reaction. The reason seems to be the higher basicity of compound **IV** [46-48], which, unlike MHC **III**, is target protonated in ice cold HOAc, slightly reducing its oxidation capacity.

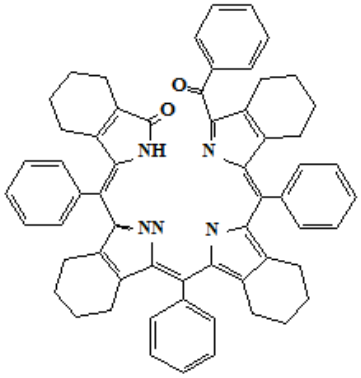
The similarity of hydrogen peroxide oxidation rates of H_2Ps (see Table 2) in H_2SO_4 solutions (1.77·10^{-3}) $^{s-1}$ and H_2P (phthalocyanines and porphyrins with inactive functional groups C_6H_5, etc.) confirms the reaction redox centre of molecules is in their N-H^+ bonds for both cases.

In the first case, they are in the *meso*-position at the periphery of the MHC, while in the second, they are at the central nitrogen atoms of the reaction centre $H_4N_4^{2+}$. At the first step, as in the case of H_2Ps (4), the H-associate $PH_4^{2+}...H_2O_2$is formed in porphyrins, which causes KPZ in the second step:



and then the cation radical $PH_2^{(+)}...OH^-$ and $OH^{\cdot}$ through further transformations quickly form colourless degradation products. The mechanisms of oxidative degradation of porphyrins with active functional groups (cyclopentanone ring and vinyl group of chlorophyll and its analogues (compound **X**), their ligands; vinyl groups of protoporphyrins and hemes) are more intricate, as follows from data in Table 2.

Most studies on oxidation processes have not analysed H_2P (MP) products [3, 29]. An exception is the work [49], which gives an example of oxidation of the predeco-substituted analogue of compound **IV** {H_2*[β,β*-$(CH_2)_4$*]*(*ms*-Ph)$_4$P} and its phenyl-substituted derivatives with sodium nitrite in trifluoroacetic acid, with benzoyl-biliverdines (compound **XI**) as a selective product of 70% yield.



XI.

Thus, the paper presents the analysis on chemical, thermal and electrochemical stability of some aromatic macroheterocyclesof porphyrin class as well as their benzo- and aza-analogues, establishes electronic and structural factors determining the rate of pigment destruction in the presence of oxidant. The values of redox potentials of porphyrin-, tetraaz-, tetrabenzoporphyrin- and phthalocyanine-type MHCs correlate with the temperatures at which their thermo-oxidative degradation starts and the decomposition rates in oxidizing media. The combined benzo- and azamer substitution in H_2P molecules leads to their destabilisation with respect to oxidants, the situation depending strongly on the nature of the oxidant (H_2O_2, $S_2O_8^{2-}$ and NO_3^-), the solvent (H_2SO_4, HOAc) as well as the nature of the metal in the molecule. The polymer state or spatial distortion of the MHC has a significant influence on the resistance to oxidising agents. The reaction mechanisms of oxidation of label-free porphyrins and phthalocyanines by hydrogen peroxide are shown to be identical. In both cases, the reaction centres of MHCs are N-H$^+$ bonds, either in the *meso*-position (H_2Ps) or in the coordination cavity of the H_2N_4 molecule and the pigments are cleaved to colourless products.

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