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Oxidative Degradation of Porphyrins and Metalloporphyrins under Polythermal Conditions

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Abstract—Influence of structure on the thermal properties of a large group of natural and synthetic porphyrins (H_2P) and metalloporphyrins (MP) was analyzed on the ground of thermogravimetric studies. The initial stage of thermal degradation of "classical" porphyrin containing a flat or pseudo-planar macrocycle is a result of oxidative degradation of the macrocyclic structure with the formation of linear tetrapyrrols. The negative effect on the thermal stability of porphyrins exerts the violation of the planar structure of the macrocycle, and the presence of bulky alkyl and polar pseudoalkyl substituents. In many cases, the general trend in the decrease in the stability of metalloporphyrins (MP) in comparison with the corresponding H_2P is a consequence of intramolecular metal ↔ ligand redox processes.

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The most characteristic feature of the molecular structure of porphyrins is the presence of a large number of double σ,π-bonds, united in an extended macrocyclic π-system. Thanks to the macrocyclic effect, the porphyrins and their derivatives are characterized by a low reactivity in the oxidation-reduction reactions in comparison with nonaromatic unsaturated hydrocarbons [1, 2]. Nevertheless, in the presence of atmospheric oxygen, H_2O_2, and other redox reagents proceeds an irreversible degradation process of porphyrins, the rate of which increases with increasing temperature and in the light. Therefore, for the study of behavior of the porphyrin-containing systems in polythermal conditions by different methods (DSC, DTA, MTA, UGS, TGA, densimetery, viscometry, solubility measurement, etc.) it is necessary to obtain an information on the impact of structural factors on the thermal stability of these compounds. Such data is of equal practical importance at both the optimization of the synthesis conditions, treatment, and storage, and use of the porphyrins as dyes, catalysts, components of redox system, drugs, etc. In this regard, the fundamental question of the influence of molecular structure on the thermal stability and redox properties of porphyrins is of particular significance.

The analysis of accumulated so far significant data bank of thermogravimetric investigations of the oxidative degradation of synthetic and natural porphyrins with different structures [3–15] has already allowed revealing the pattern of the structure–thermostability relations. The results of thermogravimetric studies of H_2P, MP, and their analogs are shown in Tables 1–4. The general laws of thermooxidative transformations of crystalline H_2P and MP are reflected in typical derivatograms in Figs. 1–3.

Patterns of thermooxidative degradation of ligands and metallocomplexes of "classical" porphyrins. The molecular structure of most ligands investigated by thermogravimetric method are shown below. The unique thermal properties of the tetrapyrrole macrocycles in comparison with the organic compounds belonging to many other classes [16] has been proved previously by mass spectrometry and thermogravimetry [3–15]. It was shown that many macrocyclic tetrapyrrols can sublimate without decomposition at high temperatures under reduced pressure. For example, phthalocyanine (H_2Pc) and its complexes (MPc) sublimate at 10^{-3}–10^{-5} mm Hg, 500–550ºC without changing their molecular structure [15]. On this property is based an effective method of porphyrazines purification by sublimation [13, 14].

Table 1. Thermooxidative degradation of porphyrins and metalloporphyrins [4–7][a]

Compound	mp, °C	T_s, °C	T_{max}, °C	T_{end}, °C	Compound	mp, °C	T_s, °C	T_{max}, °C	T_{end}, °C
Porphin [15]	250	–	–	–	ZnDP (d.m.e.)	210	365	510	550
H_2Pc [15]	–	460	520	600	ZnMP (d.m.e.)	–	350	525	590
CuPc [15]	–	380	430	630	ZnPP (d.m.e.)	–	305	505	540
MgPc [15]	–	370	450	600	ZnGP (t.m.e.)	–	247	432	475
FePc [15]	–	320	350	540	NiDP (d.m.e.)	230	340	460	520
H_2TPhP	290	407	478	530	NiMP (d.m.e.)	250	320	460	510
NiTPhP	–	375	455	495	NiPP (d.m.e.)	200	300	430	520
(Cl)FeTPhP	–	370	405	435	NiGP (t.m.e.)	190	290	410	460
CoTPhP [15]	–	340	445	680	(Cl)FePP	–	240	470	560
ZnTPhP	–	340	520	540	$H_2(Bu)_4(Me)_4P$	–	400	530	620
H_2DP (d.m.e.)	219	375	560	650	$Cu(Bu)_4(Me)_4P$	–	280	325	500
H_2MP (d.m.e.)	215	370	525	650	$H_2TAP(C_6H_5)_8$	–	220	505	550
H_2PP (d.m.e.)	228	360	540	630	ZnTBTPhP	–	470	630	690
H_2GP (t.m.e.)	235	300	440	570	ZnTBP	–	345	520	760

[a] mp is the melting point, T_s is the start of degradation, T_{max} is the peak temperature of exotermic effect, T_{end} is the temperature of the end of the degradation process, H_2DP (d.m.e.), H_2MP (d.m.e.), H_2PP (d.m.e.) are dimethyl deutero-, meso- and protoporphyrinates, respectively. H_2GP (t.m.e) is tetramethyl hematoporphyrinate. $H_2TAP(C_6H_5)_8$ is octaphenyltetraazaporphyn. H_2TPhP is tetrabenzoporphin H_2TbTPhP is tetrabenzotetraphenylporphin.

Table 2. Thermooxidative degradation of the ligand H_2T(3,5-di-*t*-BuPh) P and its complexes with Cu(II), Ni(II), Cd(II), Zn(II), Ag(II), Pd(II), Hg(II) , Mn(III), and Fe(III) [5–7][a]

Process	T_s, °C	T_{max}, °C	T_{end}, °C	Δ^{theor}	Δ^{exp}
H_2T(3,5-di-Bu^{t}Ph)P → N_2 + Ox	390	438	600	–	–
NiT(3,5-di-Bu^{t}Ph)P → Ni_2O_3 + N_2 + Ox	385	445	520	7.38	7.5
ZnT(3,5-di-Bu^{t}Ph)P → ZnO + N_2 + Ox	375	440	538	7.22	7.12
CdT(3,5-di-Bu^{t}Ph)P → CdO + N_2 + Ox	360	460	500	10.94	10.56
CuT(3,5-di-Bu^{t}Ph)P → CuO + N_2 + Ox	340	390	473	7.07	6.97
PdT(3,5-di-Bu^{t}Ph)P → PdO + N_2 + Ox	290	460	515	10.48	10.23
AgT(3,5-di-Bu^{t}Ph)P → Ag_2O + N_2 + Ox	270	460	560	9.91	9.85
HgT(3,5-di-Bu^{t}Ph)P → Hg(пар) + N_2 + Ox	202	429	615	–	–
(Ac)MnT(3,5-di-Bu^{t}Ph)P → Mn_2O_3 + N_2 + Ox	190	440	560	13.43	13.33
(Cl)T(3,5-di-Bu^{t}Ph)P → Fe_2O_3 + N_2 + Ox	230	373	480	13.85	13.92
[FeT(3,5-di-Bu^{t}Ph)P]$_2$ → Fe_2O_3 + N_2 + Ox	200	460	515	7.10	7.01

[a] Δ^{theor}, Δ^{exp} are theoretical and experimental values of the mass of metal oxide, %; Ox are oxides of C, H.

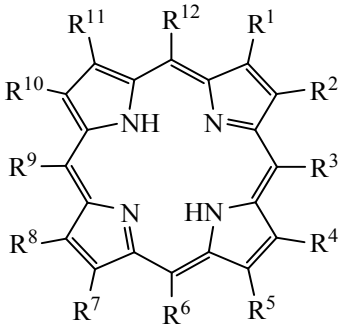
As has been proved [15, 17], the initial stage of the catabolism of natural metalloporphirins is associated with rupture of the macrocycle at the double bond (–CH=C<) of one methine bridge through oxidative elimination of the carbon atom to CO.

The identity of the initial stages of the catabolism and the termooxidative degradation of porphyrins [15] has been now confirmed experimentally by an example of H_2T(3,5-di-*t*-BuPh)P [18]. The degradation of H_2T·(3,5-di-*t*-BuPh)P starts at T_s = 390ºC (Fig. 1a, Table 2).

Table 3. Thermooxidative degradation of N-methylated porphyrins and zinc(II) porphyrins [8–10]

Process	T_s, °C	T_{max}, °C	T_{end}, °C	Δ^{theor}	Δ^{exp}
H(N–Me)TPhP → N_2 + Ox	260	625	682	–	–
H(N–Me)OetP → N_2 + Ox	310	478	600	–	–
(AcO)Zn(N–Me)TPhP → ZnO + N_2 + Ox	230	476	598	10.82	10.5
(AcO)Zn(N–Me)OetP → ZnO + N_2 + Ox	212	534	592	12.11	11.92

"Classical" porphyrins with flat or pseudo-planar macrocycle



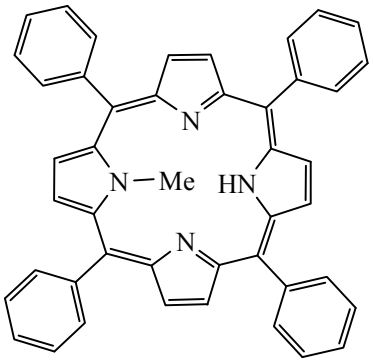
$H_2(Bu)_4(Me)_4P$: $R^1 = R^5 = R^7 = R^{11}$ =Bu; $R^2 = R^4 = R^8 = R^{10}$ = Me; $R^3 = R^6 = R^9 = R^{12}$ = H; H_2TPhP: $R^1 = R^2 = R^4 = R^5 = R^7 = R^8 = R^{10} = R^{11}$ = H; $R^3 = R^6 = R^9 = R^{12}$ = PhH_2T·(3,5-di-Bu^{t}Ph)P: $R^1 = R^2 = R^4 = R^5 = R^7 = R^8 = R^{10} = R^{11}$ = H; $R^3 = R^6 = R^9 = R^{12}$ = 3,5-di-*t*-BuPh; H_2T(3,5-Bu^t-4-OHPh)P: $R^1 = R^2 = R^4 = R^5 = R^7 = R^8 = R^{10} = R^{11}$ = H; $R^3 = R^6 = R^9 = R^{12}$ = 3,5-*t*-Bu-4-OHPh; H_2T(4-Bu^{t}Ph): $R^1 = R^2 = R^4 = R^5 = R^7 = R^8 = R^{10} = R^{11}$ = H; $R^3 = R^6 = R^9 = R^{12}$ = 4-*t*-BuPh.

Table 4. The initial steps of termooxidative degradation of water-soluble derivatives of tetrapyridylporphin [12]

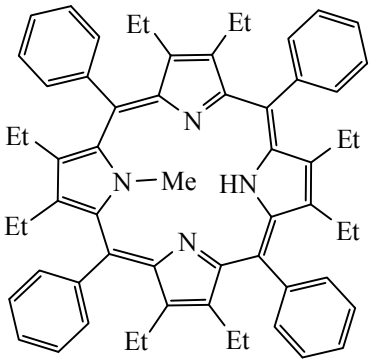
Comp. no.	Step I		Step II
	T_{endo}, °C	$\Delta^{theor}/\Delta^{exp}$, %	T_{exo}, °C
I	200	38.92/37.42	261
II	200	47.31/45.86	250
III	200	47.84/48.23	260
IV	195	44.21/40.35	227

[a] T_{endo}, T_{exo} the initial temperature of endothermic and exothermic stages, respectively; Δ^{theor}, Δ^{exp} are theoretical and experimental values of mass loss of the sample in the first stage.

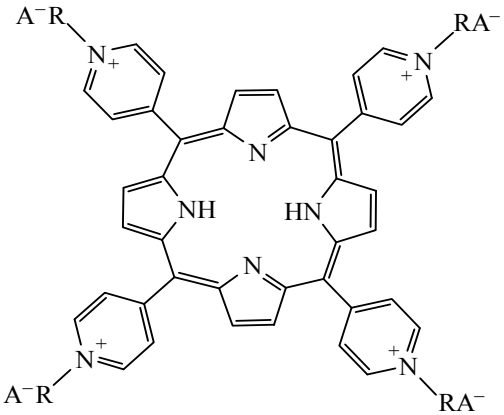
"Sterically strained" porphyrins with "deformed" macrocycle



H(N–Me)TPhP



H(N–Me)OEP



H_2TPyP: RA = –CH–COOHCl (**I**), –CH–COOHBr (**II**), $–CH_3I$ (**III**), $–CH_2COOC_2H_5Cl$ (**IV**).

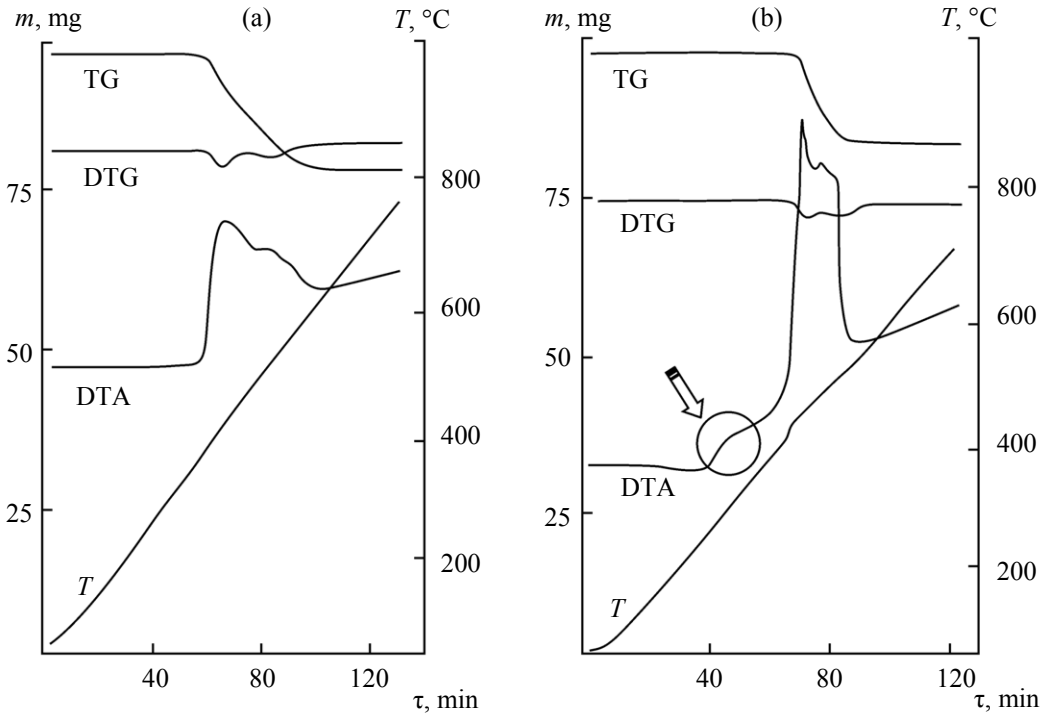


Fig. 1. Derivatograms of the ligand (a) $H_2T(3,5\text{-di-}t\text{-BuPh})P$ and (b) its complex with Ag(II). The arrow shows the stage of degradation due to the process of intramolecular oxidation of the ligand by the metal ion.

The spectrophotometric monitoring of the products of some stages of the process of thermooxidative degradation of the $H_2T(3,5\text{-di-}t\text{-BuPh})P$ ligand showed that in the EAS of chloroform solutions of samples obtained at heating the compounds to 390–450ºC the Soret band is absent, and the typical for the long-wavelength region four-band spectrum of porphyrin is transformed into a two-band pattern with λ_{max} 480 and 650 nm, which is typical for EAS of bilatriene [19]. Further stages of degradation are apparently related to the oxidation of the remaining bridge (=CH–) groups, peripheral substituents and pyrrole fragments. The maximum exothermic peak in DTA curve, obviously, was due to the oxidation of the organic part of the molecule to gaseous products. The distortion of macrocyclic structure of tetrapyrrols dramatically lowers the thermal stability of product of decyclization, and ever light heating of the sample above the temperature of degradation onset (T_s) results in effective oxidation of organic and inorganic components of the porphyrin and metalloporphyrin molecule with the formation of oxides of the elements composing them which are stable in these environmental and temperature conditions. These processes are manifested as one or several (separated or combined) stages of mass loss of the sample with exo-peaks in the DTA curve at temperatures with the corresponding maxima (T_{max}). In the case of the porphyrin ligands the process ends (T_{end}) in full weight loss of the sample. Residual solid product of the metalloporphirin decomposition is the corresponding metal oxide (Table 2), stable at a temperature of the experiment in an atmosphere of oxygen [20].

The "classical" porphyrins (H_2P) and their derivatives with insignificant deviation from the planar structure of the macrocycle are the most thermally stable. According to Table 1, the largest values of T_s show the phthalocyanines and other ligands belonging to "classical" porphyrins with a planar or pseudo-planar structure of the macrocycle: the porphyrins of proto-group and the porphin alkyl- and aryl-derivatives, including $H_2(Bu)_4(Me)_4P$, H_2TPhP, $H_2T(3,5\text{-di-}t\text{-BuPh})P$.

The expansion of the aromatic π-system of the macrocycle [1] increased appreciably the thermal stability of compound: The values of T_s in a series of porphirinates ZnTPhP, ZnTBP, and ZnTBTPhP increased by 130°C.

The negative effect on the tetraphenylporphin stability against thermooxidative degradation provides the

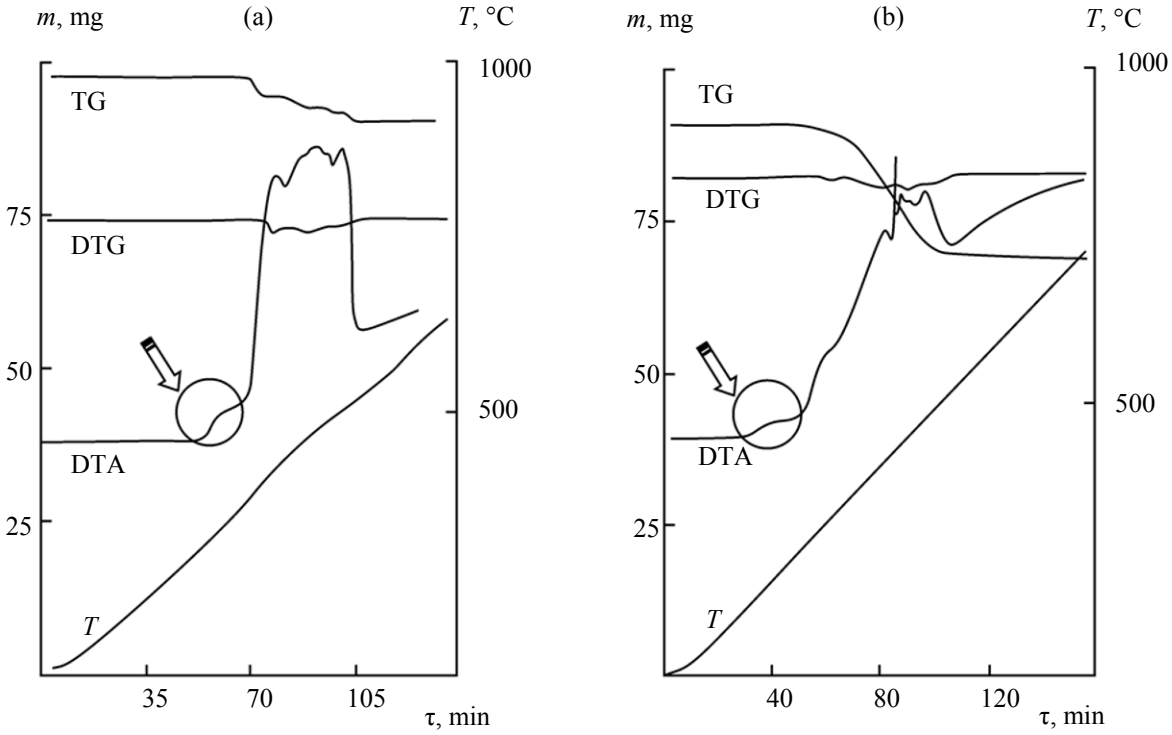


Fig. 2. Derivatograms of the complexes $H_2T(3,5\text{-di-}t\text{-BuPh})P$ with (a) Pd(II) and (b) Mn(III). The arrow shows the stage of degradation due to the process of intramolecular ligand oxidation by the metal ion.

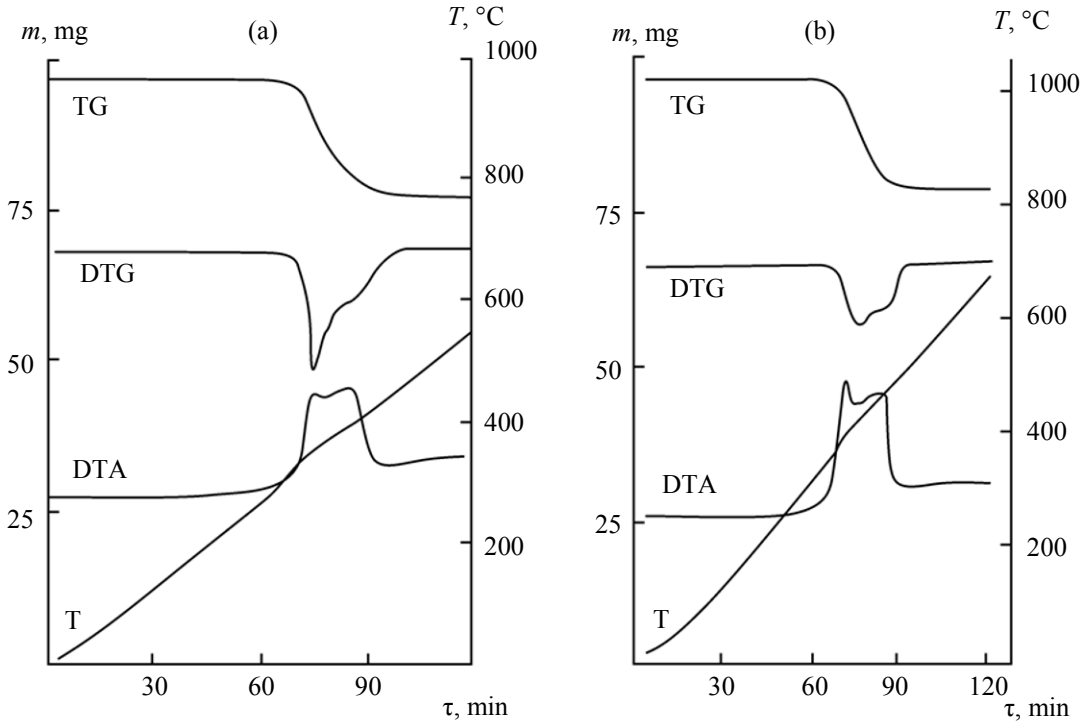


Fig. 3. Derivatograms of the complexes $H_2T(3,5\text{-di-}t\text{-BuPh})P$ with (a) Cd(II) and (b) Zn(II).

introduction of bulky alkyl substituents to the phenyl fragments. Thus, the presence of eight *tert*-butyl residues lowers stability of H_2T(3,5-di-*t*-BuPh)P compared with H_2TRhR by 17°C. A similar pattern can be traced in the case of the complexes NiTPhP, ZnTPhP, (Cl)FeTPhP and relevant *tert*-butyl-substituted analogs (Tables 1, 2).

Symmetrically substituted synthetic porphyrins are more thermally stable than natural compounds, for example, the porphyrins of blood group, containing alkyl or pseudoalkyl substituents in the pyrrole ring (Table 1). So the value T_s for H_2T(3,5-di-*t*-BuPh)P is by 15–90ºC higher than for the ligands of the protogroup (H_2DP, H_2MP, H_2PP, H_2GP). It is noteworthy that the substitution of hydrogen (deuterium) atoms in 2,4-positions of pyrrole fragments by methyl, vinyl, and oxygen-containing substituents leads to a marked (75°C) decrease in T_s in the series of ligands H_2DP > H_2MP > H_2PP > H_2GP.

But the most significant decrease in resistance to termooxidation is observed in the case of the "sterically strained" macrocycles, H(NMe)OEtP, H(NMe)TPhP, $H_2TAP(C_6H_5)_8$ (Tables 1, 3). Thus, the distortion of planar structure of the tetraphenylporphin macrocycle by N-methylation leads to a decrease in thermal stability of H(NMe)TPhP and its complex with zinc(II) by 147°C and 110°C respectively. The lowest resistance among the studied so far synthetic porphyrins show $H_2TAP(C_6H_5)_8$ (Table 1) and water-soluble porphyrins **I–IV** (Table 4).

Thermal stability of an MP, as a rule, is lower than that of the corresponding ligand H_2P (Table 1–3). This is defined by the changes in the aromaticity and π-polarization of the macrocyclic system, and in the chemical activity of the interpyrrole bridging groups as a result of complexation [1, 15].

Analysis of the data of the porphyrins of protogroup shows that the complexation does not change the general pattern of influence of the nature of peripheral substituents on the stability of the compounds toward thermal oxidation: the sequence of decrease in T_s remains the same in going from the ligands (see above) to the related complexes: MDP > MMP > MPP > MGP.

The influence of structural factors (including electronic structure of the complexing metal ion and the conformation of macrocycle) on the stability and the features of the processes of thermal degradation of MP has been studied by the example of a sufficiently large group of metal complexes on the basis of H_2T(3,5-di-*t*-BuPh)P, a number of "sterically strained" N-methylated derivatives of porphin, and water-soluble porphyrins.

Features of thermooxidative degradation of the ligand and metal complexes of tetra(3,5-di-*tert*-butylphenyl)porphin. The thermal stability of H_2T(3,5-di-*t*-BuPh)P [6, 7, 18] is higher than that of its metallocomplexes, which is consistent with the general pattern for MP and H_2P (Tables 1, 2). In the derivatograms of the studied complexes of tetra(3,5-di-*tert*-butylphenyl)porphin (Figs. 1b, 2, 3) the phases with a maximum decrease in the mass of the sample (TG curve) are accompanied by the greatest exothermic effect due to the combustion of organic part of the molecule and the oxidation of the metal with oxygen. Except for HgP, the process of the complexes degradation ended by the formation of the corresponding metal oxide (Table 2); the composition of the latter was confirmed by analytical methods [20, 21].

Despite the persistence of general patterns, the specific features of the initial stage of degradation of the complexes affecting significantly the quantitative characteristics of the thermal stability of porphyrinates are clearly seen. They depend on the electronic structure of the complexing metal ion. Among the considered porphyrinates, an increase in the T_s from 190 to 390°C is observed in the following series of compounds: (AcO)MnP < $(FeP)_2O$ ≈ HgP < (Cl)FeP < AgP < PdP < CuP < CdP < ZnP < NiP < H_2P. A higher thermal stability among the porphyrinates have the complexes M(II)P, formed by double charged metal ions with electronic configuration $(n–1)d^{10}ns^0$ (Zn^{2+}, Cd^{2+}) and $3d^84s^2$ (Ni^{2+}), that in this degree of oxidation do not show pronounced oxidative properties. Moreover, by the value of T_s the complex NiP approaches the ligand H_2T(3,5-di-*t*-BuPh)P. Note that among the most high thermally stable tetraphenylporphirinates the highest thermal stability is observed in NiTPhP (Table 1).

The complexes H_2T(3,5-di-*t*-BuPh)P formed by the metals Ag(II), Pd(II), Hg(II), Cu(II), Mn(III), and Fe(III) with a strong oxidizing activity in an appropriate degree of oxidation, show lower thermal stability. Moreover, the T_s values of the complexes fall in the subgroups of *d*-elements (NiP > PdP; CuP > AgP; ZnP > CdP > HgP). The least resistance shows the complex HgP. In general, this may be due to the increased oxidative properties of the complexing ion of the complex and the inconsistency of the size of the ion and the coordination cavity of the macrocycle [1, 15]. A distinctive feature of the processes of

decomposition of complexes AgP, PdP, HgP, CoP, CuP, (AcO)MnP, $(FeP)_2O$, and (Cl)FeP [where H_2P is H_2T(3,5-di-*t*-BuPh)P] is the presence of the initial stage, which is manifested as the small exo-peaks in the DTA curve (Fig. 1b, Fig. 2), but is not accompanied by appreciable weight loss of the sample (TG and DTG curves). This stage is not seen in the thermograms of NiP, CdP, and ZnP (Fig. 3). The spectrophotometric control of the samples at this stage showed [6, 7] that in the EAS of the solution in chloroform of HgP the degradation product retains the Soret band and four bands in the visible region, indicating the destruction of the complex, but the preservation of porphyrin structure, although the quantitative characterictics (λ_{max} and log ε) of the spectrum differ from those of the spectrum of the original H_2T (3,5-di-*t*-BuPh) P. The electronic spectrum of the product solutions at the initial stage of the complexes (AcO)MnP, $(FeP)_2O$, and (Cl)FeP degradation while containing the characteristic bands shows a red shift and intensity change, indicating the rearrangements of the molecular structure of the complex due to the processes of intramolecular metal↔ligand oxidation-reduction. The nature of the EAS of solution of the samples of AgP, PdP, CuP and (ASO)MnP heated to the temperature slightly above the temperature of the start of the intramolecular oxidation indicates the destruction of the porphyrin macrocycle to a linear tetrapyrrole. A similar transformation occurs with the porphyrinates of Ni(II), Zn(II), and Cd(II) at the temperatures slightly above T_s.

Structuraly strained N-methylated porphyrins and metalloporphyrins. Among the variety of porphyrins with the distortion of the macrocycle planar structure particularly distinguished are mono-NH-substituted (or NR-substituted, where R is alkyl group) [8, 9, 11] porphyrins and their metallocomplexes with the structure $(X)M(R)N_4$ (X is inorganic anion or hydrocarbon residue), most of which are unstable. Therefore the results of investigations of thermooxidative degradation of these compounds by the example of two most stable ligands, N-methyl-substituted of octaethylporphin [H(NMe)OEtP] and tetraphenylporphin [H(NMe)TPhP], as well as their complexes with zinc(II), may find application in different areas of the use of N-substituted porphyrins in polythermal conditions.

The changes in the thermograms of the samples of H(NMe)OEtP and H(NMe)TPhP illustrate the conservation of the general pattern characteristic for processes of thermooxidative degradation of synthetic and natural porphyrins [8]. However, N-methylation leads to a significant decrease in T_s of degradation of the ligands H(NMe)OEtP, H(NMe)TPhP and their complexes (Table 3) in comparison with "classical" counterparts (Tables 1, 2). For example, the destruction T_s of the complex (AcO)Zn(NMe)TPhP is by 110°C lower than that of ZnTPhP, and the stability of the methylated ligand H(NMe)TPhP is by 147°C lower than that of "classical" H_2TRhR.

Specificity of the processes of destruction of complexes (AcO)Zn(NMe)OEtP and (AcO)Zn(NMe)TPhP consists in the removal of CH_3 group in the first stage which is facilitated by the enhanced deviation from the plane of the molecule of the metalloporphyrin as compared with the original ligand. Further intramolecular rearrangement leads to the formation of structurally undistorted ZnTPhP and ZnOEtR complexes where the ion Zn^{2+} is tetracoordinated by the nitrogen atoms of reaction center of the porphyrin ligand. Such structural rearrangement initiates the subsequent stage of removing acido-anion. By an example of the complex (AcO)Zn(NMe)TPhP the initial chemical transformations can be schematically represented by the following equation:

$$(AcO)Zn(NMe)TPhP + 1/2O_2 \rightarrow ZnTPhP + CH_2O + AcOH.$$

The process of further oxidation and destruction of the chromophore occurs along the classical scheme described above.

Thermal analysis of water-soluble derivatives of tetrapyridylporphin. Since recent years the water-soluble porphyrins are of particular interest [22–27] in connection with the possibility of their use in analytical chemistry and for creation of new drugs, like photosensitizers for the treatment of malignant tumors and in the process of inactivation of bacteria and germs. The increased use of water-soluble porphyrins necessitates studying the stability of the compounds under the influence of various factors, including oxidizers at elevated temperatures. Table 4 shows the results of termogravimetric analysis of some water-soluble tetrapyridylporphins [12].

Thermooxidative degradation of water-soluble porphyrins is characterized by three main stages of the weight loss of sample. The first stage is accompanied by the endoeffects, two subsequent stages, by exothermic effects on the DTA curve. The experimentally registered mass loss of the sample in the first phase is close to the theoretical decrease in mass due to

the deletion of four molecules of the hydrohalide. The total weight loss in the two initial stages corresponds to the theoretical loss due to removal of four pseudoalkyl substituents in the pyridyl fragments. The analysis of the samples obtained after the first two stages shows that in all cases the macrocyclic structure is preserved, therewith the porphyrin loses its solubility in water but becomes soluble in organic solvents. The nature of the spectra of solutions in benzene indicates the retained porphyrin structure [1]. Obviously, in the two initial stages the "burning out" of functional substitutes occurs. The high intensity of exo-processes in the subsequent high-temperature stage testifies to the active oxidation and combustion of the main part of the chromophore molecule.

In line with these findings, the increase in temperature above 195–200ºC leads to irreversible changes in the molecular structure of the tetrapyridylporphin water-soluble derivatives. Among the studied synthetic and natural porphyrins, the water-soluble derivatives are less thermostabile even than the structurally strained porphyrins, including $H_2TAP(C_6H_5)_8$ and N-methylated derivatives of synthetic porphyrins (Tables 1–4).

Thus, porphyrins and metalloporphyrins are characterized by increased resistance to termooxidative destruction in comparison with many other classes of organic compounds. The initial stage of the processes of thermooxidative destruction of the ligands and metallocomplexes of "classical" porphyrins is associated with oxidative degradation of macrocyclic tetrapyrrole structure into linear oligopyrroles through elimination of one of the carbon atoms of methine bridges. Further stages are due to conjugate processes of oxidation of organic fragments of molecules and the atom the complexing metal with the formation of chemical forms that are stable under the conditions of the experiment. The negative impact on the stability of macrocyclic oligopyrroles exert the violation of the planar structure of the macrocycle and the introduction of bulky alkyl and pseudoalkyl polar substituents. The overall downward trend in the stability of metalloporphyrins in comparison with H_2P in many cases is the result of intramolecular metal ↔ ligand redox reactions.

EXPERIMENTAL

Thermogravimetric studies were performed on a 1000D derivatograph (MOM Company, Hungary) in atmospheric oxygen (~20–40 mg samples, heating rate 2.5 deg min^{-1}, temperature range 17–800°C). Characteristics of synthesis, identification, and thermogravimetric analysis of the compounds considered are listed in the cited sources [3–12, 18].

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