Electronic and Steric Effects of Substituents on the Coordinating Properties of Porphyrins

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Abstract—Kinetics of the formation of zinc complexes of porphyrin with various substituents was studied in acetic acid and pyridine. The introduction of strong electron-withdrawing substituents (nitro groups) to the *meso*-positions of the porphyrin macrocycle was shown to change the reaction rate by an order of magnitude or less compared to the phenyl-substituted analogs. However, the introduction of a large number of bulky substituents leads to the deformation of the porphyrin ligand and thus affects much stronger the coordination properties of porphyrins, decreasing or increasing the rate of the complexation reaction by several orders of magnitude.

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The deformation of the porphyrin macrocycle due to the introduction of a large number of bulky substituents affects greatly the basic properties of the porphyrin ligand and, depending on the solvent nature, increases (in basic solvents) or decreases (in the solvents of acidic nature) the reaction rate of complex formation by these ligands by several orders of magnitude [1, 2]. However, the substituents themselves can more or less affect the process rate as the electron donors or acceptors.

In this regard, the purpose of this study was to determine the ratio of the contributions of the substituents electronic and steric effects to the kinetic parameters of the formation of metalloporphyrins.

In this work we studied the kinetics of the reactions of the zinc complexes formation with porphyrins containing strong electron-withdrawing substituents in one or two *meso*-positions of the macrocycle: 10-nitro-5,15-diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphin (I), 10,20-dinitro-5,15-diphenyl-3,7,13,17tetramethyl-2,8,12,18-tetraethylporphin (II), compared with 5,10,15-triphenyl-2,3,7,8,12,13,17,18-octamethylporphin (III), 5,10,15,20-tetraphenyl-2,3,7,8,12,13,17,18-octaphenylporphin (IV), 2,3,7,8,12,13,17,18-octaphenylporphin (V), and 2,3,7,8,12,13,17,18-octamethylporphin (VI), in acetic acid and pyridine.



I, $R^1 = Et$, $R^2 = Me$, $R^3 = R^5 = Ph$, $R^4 = NO_2 R^6 = H$; **II**, $R^1 = Et$, $R^2 = Me$, $R^3 = R^5 = Ph$, $R^4 = R^6 = NO_2$; **III**, $R^1 = R^2 = Me$, $R^3 = R^4 = R^5 = Ph$, $R^6 = H$; **IV**, $R^1 = R^2 = Me$, $R^3 = R^4 = R^5 = R^6 = Ph$; **V**, $R^1 = R^2 = Ph$, $R^3 = R^4 = R^5 = R^6 = H$; **VI**, $R^1 = R^2 = Me$, $R^3 = R^4 = R^5 = R^6 = H$.

The following porphyrins were synthesized: 10nitro-5,15-diphenyl-3,7,13,17-tetramethyl-2,8,12,18tetraethylporphin (I) and 10,20-dinitro-5,15-diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphin (II) were obtained by nitration of 5,15-diphenyl-3,7,13,17tetramethyl-2,8,12,18-tetraethylporphin (VII) with a mixture of sodium nitrite and trifluoroacetic acid, according to [3]. Porphyrin VII was synthesized in 38% yield by the condensation of dipyrrolylmethane (VIII) with benzaldehyde under the influence of chloroacetic acid in methylene chloride in an inert atmosphere, followed by oxidation of the intermediate porphyrinogen with *p*-chloranil [3].



The nitration with sodium nitrite at the equimolar ratio of the reagents [reaction (2)] resulted in mononitroporphyrin (I) in 56% yield. Further nitration of I led to dinitroporphyrin (II) in 38% yield.



The formation of complexes of porphyrins with double-charged metal cations in nonaqueous solutions proceeds in accordance with Eq. (3).

$$H_2P + [MX_2(Solv)_{n-2}] \rightarrow MP + 2HX + (n-2)Solv.$$
(3)

Here X is acido ligand, *Solv* is a solvent molecule, n is the coordination number of the metal cation. Typically, reaction (3) obeys the first order kinetic Eq. (4) with respect to porphyrin [4, 5].

$$-dc(\mathrm{H}_{2}\mathrm{P})/dt = kc(\mathrm{H}_{2}\mathrm{P})c^{n}(\mathrm{M}\mathrm{X}_{2}), \qquad (4)$$

where k is the rate constant, $c^n(MX_2)$ is the salt concentration, $c(H_2P)$ is the concentration of porphyrin. The reaction order with respect to the salt is determined experimentally by measuring the dependence of the effective rate constant (k_{ef}) of reaction (3) on the salt concentration (c). In our case, the order of reaction (3) with respect to the zinc acetate both in pyridine and in acetic acid equal unity [6]. The value of k_{ef} is related to the true rate constant (k_v) according to equation (5).

$$k_{\rm ef} = k_{\rm v} c^n (\rm MX_2). \tag{5}$$

The kinetic data on the porphyrins I and II coordination with zinc acetate are listed in Tables 1 and 2, in comparison with previous results.

In non-aqueous media the reaction of the complex formation proceeds in one step by a bimolecular mechanism. The formation of the transition state includes, firstly, the restructuring and partial destruct-



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Porphyrin	$c[\text{Zn}(\text{OAc})_2] \times 10^3,$ M	$k^{298} \times 10^2$, 1 mol s ⁻¹	ΔE , kJ mol ⁻¹	ΔS^{\neq} , J mol ⁻¹ K ⁻¹
I	0.268	2.29±0.09	56±2	-96±9
II	0.268	0.75±0.04	84±2	-10±6
Ш	0.268	The reaction is very slow		
IV	0.268	The complex is not formed		
V	0.52	481±15	67±3	29±9
VI ^a	0.50	67±1	39±1	_
				163±3

 Table 1. Kinetic parameters of the porphyrins I–VI coordination by the zinc acetate in acetic acid

^a Data of [12].

Table 2. Kinetic parameters of the reaction of porphyrins I–

 VI coordination by the zinc acetate in pyridine

Porphyrin	$c[\text{Zn(OAc)}_2] \times 10^3, \text{ M}$	$k^{298} \times 10^2$, 1 mol s ⁻¹	ΔE , kJ mol ⁻¹	ΔS^{\neq} , J mol ⁻¹ K ⁻¹
I	2.53	13.4±0.5	91.0±1.0	36±3
II	2.53	43.5±0.5	93.6±1.5	54±5
$\mathbf{III}^{\mathrm{a}}$	5.00	88±2	54.6±0.4	-97±1
IV^a	5.00	150±3	47.0±0.9	-118±3
V	2.68	2.08±0.05	30.5±3.5	-208±5
VI ^a	5.00	0.632±0.005	103±1	9±3

^a Data of [8].

Table 3. Electron absorption spectra of porphyrins I, II, V–VII

yrin	Absorption bands maxima λ_{max} , nm (log ϵ)					
Porph	Ι	II	III	IV	Cope	
Ι	665 (3.41)	595 (3.78)	sh	524 (4.04)	418 (5.04)	
II	696 (3.78)	607 (3.91)	sh	541 (4.06)	447 (4.99)	
\mathbf{V}	635 (3.47)	583 (3.95)	550 (4.04)	518 (4.23)	423 (5.13)	
VI	620 (3.65)	568 (3.68)	535 (4.60)	500 (4.60)	400 (5.61)	
VII	625 (3.30)	574 (3.85)	542 (3.70)	508 (4.23)	409 (5.34)	

tion of the coordination sphere of the solvated metal, secondly, the formation of coordination bonds between the metal cation and tertiary nitrogen atoms of the porphyrin, and thirdly, extension and polarization of the ligand N–H bonds [4].

The substituents in the porphyrin macrocycle, depending on their electronic effect ($\pm C$ and $\pm I$), determine the distribution of the π -electron density and hence the degree of solvation in the ground state, as well as lead to a different protonation of the N–H bonds. Some bulky substituents force the porphyrin molecule to adopt the most energetically favorable conformation, even when it destroys the planar structure of the macrocycle.

Theoretical calculations [7–9] and our experimental studies [1] showed that the spectral changes of porphyrins with a sterically non-planar structures are very characteristic, so that the red shift of all bands in electron absorption spectra (EAS) of a porphyrin can be attributed to the deformation of its tetrapyrrole macrocycle with a high confidence.

Spectral characteristics of the studied porphyrins (Table 3) showed that replacement of methyl groups in the β -positions of the pyrrole fragments of macrocycle (porphyrin **VI**) by the phenyl (**V**) leads to ~15 nm red shift of the absorption bands. At the accumulation of substituents in the *meso*-positions of the macrocycle the red shift of the first absorption band in the EAS increases and reaches 70 nm in the spectrum of porphyrin **II** compared with **VII**.

Introduction of strong electron-withdrawing substituents to the *meso*-positions promote blue shift of the bands in the EAS. According to the four-orbital Simpson–Platt–Gouterman model [10], the blue shift is due to a decrease in the energy of the highest occupied molecular orbital (HOMO) owing to the greater electron density on the methine carbon atoms. Despite this, all absorption bands suffer the red shift. It is obvious that at the application of two opposite effects (deformation of the porphyrin framework and the -I, -C effects of nitrogroups) the structural factor dominates.

The electron-withdrawing substituents are known to increase the protonation of the N–H bond and, therefore, should increase the rate of reaction (3). At the same time, the acceptor groups reduce the electron density on the tertiary nitrogen atoms thus impeding the strengthening of N–M bonds in the transition state

and therefore reducing the reaction rate of the metalloporphyrin formation.

Data in Tables 1 and 2 show that the rate of the formation of the β -octaphenylporphyrin zinc complex V is approximately 3–7 times higher compared with β octamethylporphyrin VI. Calculations of the structural parameters of the porphyrin V [11] showed that the phenyl fragments are located at the angle of $\sim 75^{\circ}$ to the plane of the macrocycle and, consequently, may affect the state of the reaction center N⁴ only via the system of σ -bonds, showing -I effect. The eight phenyl substituents at the porphyrin macrocycle reduce the negative charge on the central nitrogen atoms, thus facilitating the N-H bonds breaking under the influence of polar solvent in the transition state. Methyl groups in the pyrrole β -positions in the pyrrole macrocycle VI exhibit the opposite effect (+I), which apparently reduces the reaction rate of the metalloporphyrin formation. However, these factors do not influence significantly the rate of the complexation reaction, the rate constant varies within the same order of magnitude.

When acetic acid is used instead of pyridine, the rate of reaction of metalloporphyrins with a flat structure of the macrocycle V, VI, as one would expect, is reduced due to stabilization of the salt solvation shell (Tables 1 and 2). In acetic acid, salts of transition metals form a relatively labile solvate complexes, easily decomposing at the interaction with porphyrin. Pyridine has a strong electron-donating properties, and therefore forms a stable coordination sphere of the metal cation. Its partial destruction upon complexation with porphyrin requires considerable energy expenditure, thus pyridine reduces the rate of the complexation [12].

Another situation occurs in the case of the porphyrins with nonplanar structure of the tetrapyrrole macrocycle. In the publications [1, 3, 11, 14] based on calculations of the geometric parameters and on spectral data (Table 3) it was shown that porphyrins **I**–**IV** have a nonplanar structure, the degree of the macrocycle deformation increasing with the number of substituents in *meso*-positions. The basicity of the spatially distorted porphyrins was found to increase significantly compared with the flat analog [14]. There is a certain relationship between the coordination and the acid–base properties: The protonation of porphyrin ligands is a reaction competing with the established laws: The reaction rate of coordination of spatially distorted

porphyrins I and II at the interaction with zinc acetate is significantly lower in acetic acid than in pyridine, and with the porphyrins III and IV the reaction in the same conditions proceeds much slower.

In pyridine, a sharp increase in the rate of the complex formation when β -octamethylporphyrin contains aryl *meso*-substituents in its structure (in going from the porphyrin **VI** to **IV**) cannot be caused only by the electronic effects of substituents, but is primarily associated with the changes in the geometry of the molecule (Table 2). However, the replacement of one phenyl *meso*-substituent in the sterically distorted porphyrins by the nitro group (porphyrins **I** and **III**, **II** and **IV**) leads to a decrease in the reaction rate 3.5 to 6 times. Obviously, this is due to the stronger electron-acceptor influence of the nitro group.

EXPERIMENTAL

The electron absorption spectra (EAS) and the rate of reactions of the porphyrin zinc complexes I-VI were measured on a Shimadzu UV-1800 and Hitachi U-2000 spectrophotometers. Measurements were performed in thermally-controlled polished glass cells in the temperature range from 288 to 348 K. Temperature fluctuations did not exceed ± 0.1 K. In all studied cases, the spectra of the reacting systems included a clear isosbestic point. A typical example is shown in the figure.

The ¹H NMR spectra were recorded on a Bruker-500 spectrometer at the operating frequency 500 MHz in CDCl₃, internal reference TMS.

The solvents used (acetic acid, pyridine) were purified by the methods described in the literature [15, 16].

5,15-Diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyrin (VII). To a solution of 1.2 g (5.2 mmol) of 3,3'-diethyl-4,4'-dimethylpyrrolylmethane [3] and 0.6 ml (5.9 mmol) of benzaldehyde in 400 ml of methylene chloride in an atmosphere of carbon dioxide was added while stirring a solution of 1.0 g (10.6 mmol) of monochloroacetic acid in 20 ml of methylene chloride. The mixture was stirred in the dark for 4 h, then 1.9 g (7.7 mmol) of *p*-chloranil was added, and the mixture was kept for 12 h at room temperature. The solvent was evaporated, and the residue was washed with 5% sodium hydroxide solution, then with water, and dried. The purification was performed by chromatography on Al_2O_3 (III



Changes in the EAS in the course of coordination at T = 298 K: (a) β -octaphenylporphyrin by the zinc acetate in acetic acid, (b) 10-nitro-5,15-diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyrin by zinc acetate in pyridine.

degree of activity by Brockmann), eluent chloroform. Yield 1.25 g (38%).

Individuality of the compound was monitored by TLC on Silufol plates with the layer thickness of 0.5 mm (Merck), eluent heptane–benzene 1:1, $R_f = 0.4$.

EAS (chloroform), λ_{max} , nm (log ε): 625 (3.30), 574 (3.85), 542 (3.70), 508 (4.23) 409 (5.34). ¹H NMR spectrum, δ , ppm: 10.22 s (2H, 10,20-H); 8.05 m (4H, O-H_{Ph}); 7.75 m (6H, *m*,*p*-H_{Ph}); 2.47 s (12H, 3,7,13,17-CH₃); 3.96 q (8H, CH₂CH₃), 1.75 t (12H, 2,8,12,18-CH₂CH₃), -2.43 (NH) (CDCl₃, int. TMS).

10-Nitro-5,15-diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetraethyl porphyrin (I). One equivalent (5.45 mg, 0.079 mmol) of sodium nitrite was added to a solution of 49.55 mg (0.079 mmol) of the porphyrin **VII** in 5 ml of trifluoroacetic acid. The mixture was stirred at room temperature for 10 min, then poured into 50 ml of water and neutralized with 25% solution of ammonia until its color changed from green to redbrown. The precipitate was filtered off, washed with water, and dried to constant weight. Porphyrin was dissolved in benzene and chromatographed on alumina of III degree activity by Brockmann eluting with benzene. Yield 29.83 mg (56.2%).

EAS (chloroform), λ_{max} , nm (log ε): 665 (3.41), 595 (3.78), 524 (4.04), 418 (5.04). ¹H NMR spectrum, δ , ppm: 9.84 s (1H, *meso*-H); 8.08 m (4H, *o*-H_{Ph}); 7.75 m (6H, *m*,*p*-H_{Ph}); 3.8 q (4H , C<u>H</u>₂CH₃); 3.35 q (4H, C<u>H</u>₂CH₃); 2.28 s (6H, CH₃); 2.16 s (6H, CH₃), 1.59 t (6H, CH₂C<u>H</u>₃); 1.27 t (6H, CH₂C<u>H</u>₃), 2.69 s (NH) (CDCl₃, int. TMS).

10,20-Dinitro-5,15-diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyrin (II) was obtained by nitration of 41.05 mg (0.079 mmol) of porphyrin **VII** with two equivalents (10.9 mg, 0.16 mmol) of sodium nitrite in 5 ml of TFA, during 90 min. The yield after purification by chromatographic method was 38 mg (65.2%).

EAS (chloroform), λ_{max} , nm (log ε) 696 (3.78), 607 (3.91), 541 (4.06), 447 (4.99). ¹H NMR spectrum, δ , ppm: 8.08 m (4H, *o*-H_{Ph}); 7.81 m (6H, *m*,*p*-H_{Ph}); 3.11 q (8H, 2,8,12,18-CH₂CH₃); 1.96 s (12H, 3,7,13,17-CH₃), 1.18 t (12H, 2,8,12,18-CH₂CH₂); (12H, CH₃); 1.59 t (6H, CH₂CH₃); -2.41 br.s (NH) (CDCl₃, int. TMS).

Spectral data of porphyrins I, II, and VII did not differ from those described in the literature [3].

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