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Kinetics of Reaction between Nickel Porphyrinates and Dicumene Peroxide

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Abstract—Reaction of nickel 5,15-di(*o*-methoxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrinate and 5,10,15,20-tetraphenylporphyrinate with dicumene peroxide in benzene at 295 K was investigated by spectrophotometric method. Kinetic parameters of the reaction were determined, and mechanism of the studied process was suggested. Comparative analysis of the oxidative and reductive properties of nickel porphyrinates in reaction with dicumene peroxide was accomplished. Effect of the electronic and conformation factors on the reaction kinetics was shown. The theoretical calculation of the geometric parameters of the reagents and intermediates of the reaction was performed by PM3 quantum-chemical method.

Keywords: nickel porphyrinates, dicumene peroxide, oxidation-reduction properties, kinetics, macrocycles

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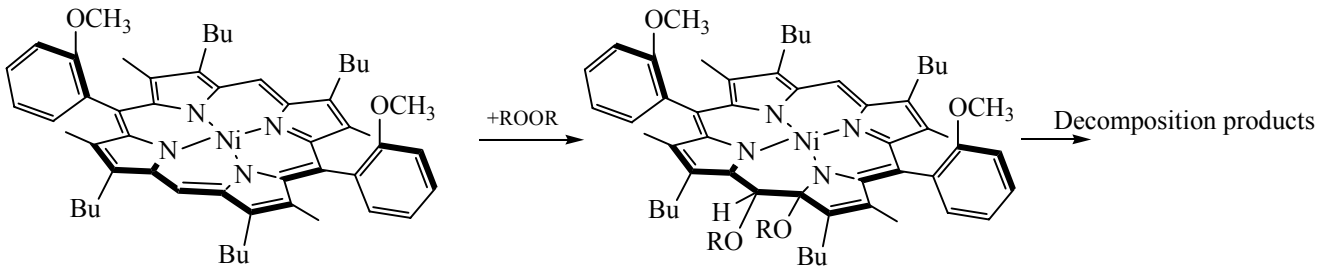
Metal porphyrinates being active components of hemoglobin, myoglobin, chlorophyll and some enzymes play important role in a number of redox reactions in biological systems. Preparation of synthetic analogs of such compounds and modelling the reactions with their participation are topical issues of contemporary chemistry. Besides that metal porphyrinates possess specific optic, magnetic, conductive, and catalytic properties that allow application of the compounds for preparation of new multifunctional materials for engineering processes [1–5].

Investigation of the redox properties of macrocyclic complexes in reactions with compounds containing active oxygen is important for better understanding of the mechanisms of catalytic and enzymatic processes [6–8]. In extension of the research on metaloporphyrins chemistry [9–11] in the present work the reaction of nickel 5,15-di(*o*-methoxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrinate (NiP) and nickel 5,10,15,20-tetraphenylporphyrinate (NiTPP) with dicumene peroxide in benzene at 295 K was investigated.

The reaction of nickel porphyrinates (NiP, NiTPP) with dicumene peroxide proceeded at the macrocycle periphery with addition of the aryloxy groups at *meso*- and α-positions with the formation of sterically strained and unstable compound **A** (Scheme 1).

In the course of the reaction in the electron absorption spectrum a decrease in the intensity of the principal absorption bands was observed up to their almost complete disappearance (Fig. 1). The formation of π-cation-radical of nickel porphyrinate was not

Scheme 1.



noticed as proved by the appearance view of the electronic spectrum (the absence of the characteristic wide bands in the long-wave region [12, 13]).

Reactions of the nickel porphyrinates (c_{NiP} 3.2 × 10^{-5} mol/L, c_{NiTPP} 8.0 × 10^{-6} mol/L) with dicumene peroxide ($c_{peroxide}$ 2.3 × 10^{-5}–2.3 mol/L) proceeded sufficiently slowly to permit us kinetic measurements. Thus, the reaction was of the first order with respect to nickel porphyrinate that was concluded from the linear dependence log $(c_0/c\tau)=f(\tau)$ and satisfactory constancy of values k_{eff} (Fig. 2 and the table).

$$-dc_{NiP(NiTPP)}/d\tau = kc_{NiP(NiTPP)}. \quad (1)$$

Effective rate constants k_{eff} increased with the growth of the dicumene peroxide concentration.

$$\log k_{eff} = \log k_v + n\log [ROOR]. \quad (2)$$

From Eq. (2) values of the rate constant (k_v) were determined (see table) together with the order of the reaction with respect to the peroxide, n = 1. Considering the reaction orders with respect to the reagents, the rate equation for the reaction NiP with dicumene peroxide is as follows:

$$-dc_{NiP}/d\tau = k_v[NiP][ROOR]. \quad (3).$$

In the case of NiTPP the reaction rate was described with the same equation.

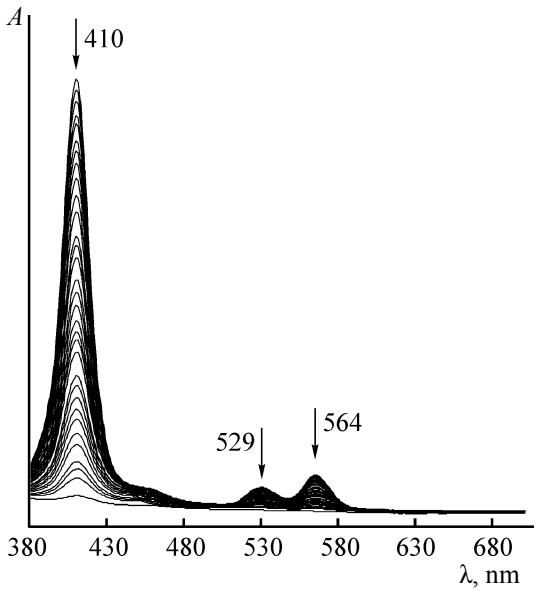


Fig. 1. Change of the electron absorption spectrum of NiP in the course of the reaction with dicumene peroxide ($c_{peroxide}$ 2.3 × 10^{-1} mol/L, c_{NiP} 3.2 × 10^{-5} mol/L).

The introduction of imidazole (Im) to the working solution of NiP did not affect the general view of the electron absorption spectrum of the complex that evidenced the absence of coordination of the base with

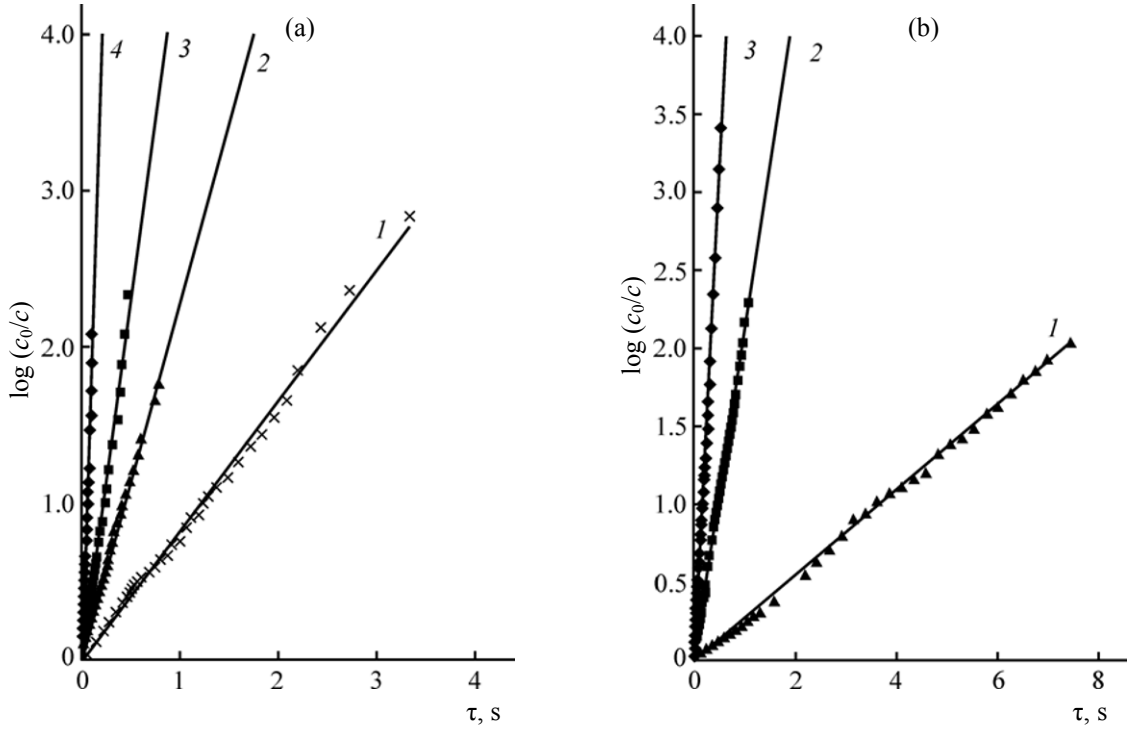


Fig. 2. Dependence of log (c_0/c_τ) on τ (a) NiP and (b) NiTPP at 295 K. c_{NiP} 3.2 × 10^{-5} mol/L, $c_{peroxide}$ 2.3 × 10^{-5} (*1*), 1.60 × 10^{-4} (*2*), 2.3 × 10^{-4} (*3*), 2.3 × 10^{-3} mol/L (*4*); c_{NiTPP} 8.0 × 10^{-6} mol/L, $c_{peroxide}$ 2.3 × 10^{-3} (*1*), 2.3 × 10^{-2} (*2*), 2.3 × 10^{-1} mol/L (*3*).

the metal cation. The absence of electron-withdrawing substituents and the presence of a distortion of the macrocycle led to the increase in its basicity and consequently to the low probability of its axial coordination [14]. Imidazole presence reduced the reaction rate due to the deactivation of dicumene peroxide with the base [15]. At the addition of imidazole to the solution of NiTPP, a shift of the absorption band from 414 to 416 was observed together with the change in its intensity and the isosbestic point retention (Fig. 3a). Such spectral alterations proved the coordination of the base with the metal atom [14, 16]. The composition of the molecular complex was determined by means of ESI mass spectroscopy. The presence of the signal of molecular ion *m/z* 807.5 indicates the presence of complex $(Im)_2$NiTPP in the system.

The reaction of the axial coordination proceeded in time followed by the oxidation of the molecular complex macrocycle with the peroxide (Fig. 3b). Accounting for the spectral changes we believed that the reaction of NiTPP with dicumene peroxide proceeded in two steps. The first step was the equilibrium process of complex (Im)NiTPP formation [Eq. (4)]:

$$\text{NiTPP} + \text{Im} \underset{}{\overset{K\text{p}_1\cdot k_1}{\rightleftharpoons}} \text{(Im)NiTPP, slow.} \qquad (4)$$

The direct reaction was of the first order by nickel porphyrinate and imidazole (Fig. 4). The rate equation for the direct reaction in the first step was as follows [Eq. (5)]:

$$-dc_{\text{NiTPP}}/d\tau = k_1[\text{NiTPP}][\text{Im}]. \qquad (5)$$

The spectral changes in the second step consisted in the red shift of the absorption band from 416 nm by 2 nm followed by the gradual reduction of the intensity of the absorption bands without retention of the isosbestic point up to their complete disappearance (Fig. 3b). Such alterations characterized the process of the second molecule of imidazole coordination to the macrocycle and oxidation of the formed complex $(Im)_2$NiTPP. In this case the experimentally found reactions orders with respect to reagents were also equal to 1 (Fig. 4). The values of the rate constants for the reaction are presented in the Table. Accounting to the spectral changes and the reaction orders with respect to the complex, imidazole, and peroxide, the experimental equation for the rate of the second step of the process may be expressed as [Eq. (6)]:

$$-dc[(\text{Im})_2\text{NiTPP}]/d\tau = k_v'[(\text{Im})\text{NiTPP}][\text{Im}][\text{ROOR}]. \qquad (6)$$

Based on the obtained kinetic characteristics the mechanism of the second step of the reaction of nickel porphyrinate with dicumene peroxide consisted in a quasi-equilibrium [Eqs. (7), (8)]:

$$(\text{Im})\text{NiTPP} + \text{Im} \underset{}{\overset{K\text{p}_2\cdot k_2}{\rightleftharpoons}} (\text{Im})_2\text{NiTPP},$$
$$\text{fast, } k_2 >> k_3, \qquad (7)$$

$$(\text{Im})_2\text{NiTPP} + \text{ROOR} \overset{k_3}{\longrightarrow} \text{Decay products},$$
$$\text{slow, } k_3 << k_1. \qquad (8)$$

Kinetic parameters of nickel porphyrinates oxidation with dicumene peroxide at 295 K

$c_{\text{peroxide}}\,10^3$, mol/L	$k_{\text{eff}} \times 10^4$, s^{-1}
c_{NiP} 2.3×10^{-5} mol/L	
2.3	1.975
0.23	0.417
0.16	0.255
0.023	0.081
k_v 0.013 L mol^{-1} s^{-1}	
c_{NiTPP} 8.0×10^{-6} mol/L	
230	6.11
23.0	2.16
2.3	0.268
k_v 0.002 L mol^{-1} s^{-1}	
$c_{\text{Im}}\,10^3$, mol/L	$k_{\text{eff}} \times 10^4$, s^{-1}
c_{NiTPP} 8.0×10^{-6} mol/L, c_{peroxide} 2.3×10^{-4} mol/L	
20.0	18.39
11.5	7.89
7.75	5.11
k_v[a] 0.372 L mol^{-1} s^{-1}	
20.0	1.23
11.5	0.70
7.75	0.48
k_v 0.006 L mol^{-1} s^{-1}	
$c_{\text{peroxide}}\,10^2$, mol/L	$k_{\text{eff}} \times 10^4$, s^{-1}
230	77.69
2.3	2.46
0.23	3.95
k_v 0.0054 L mol^{-1} s^{-1}	

[a] Rate constant of the axial coordination.

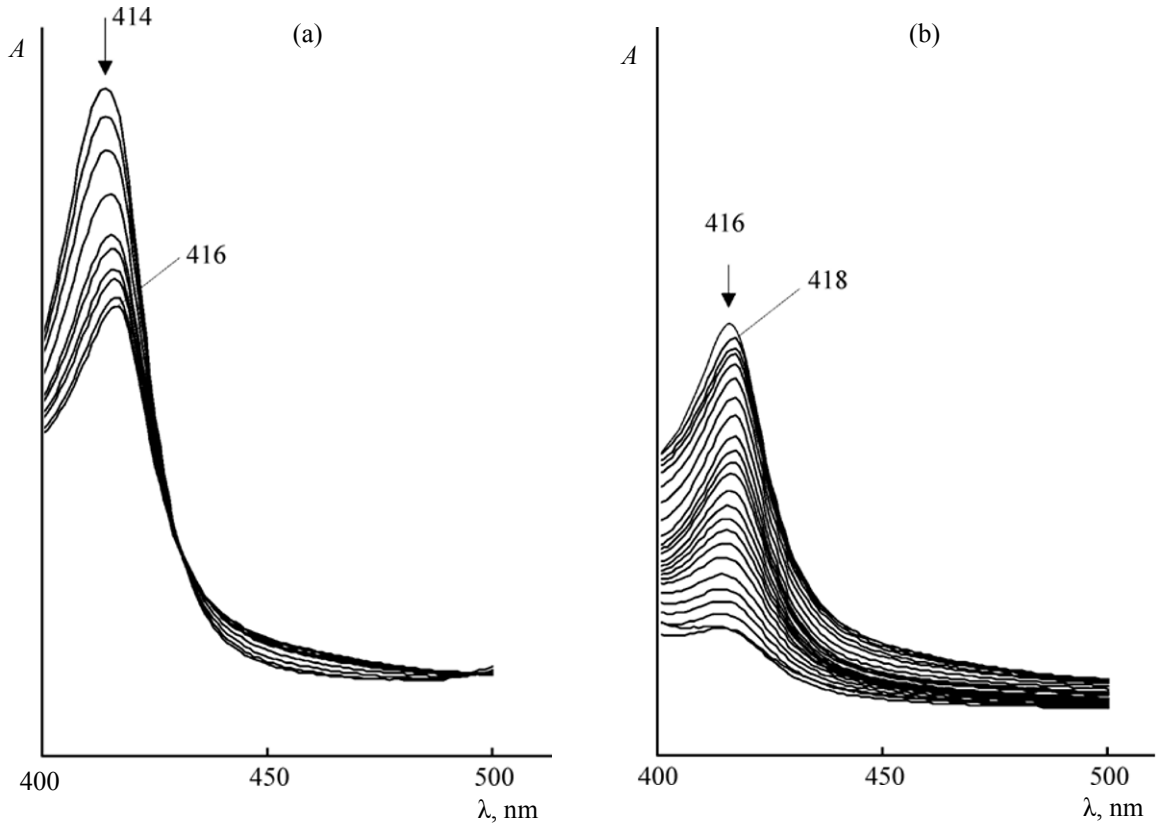


Fig. 3. Change of the electron absorption spectrum of NiTPP in the course of the reaction with dicumene peroxide in the presence of imidazole (c_{NiTPP} 8.0 × 10^{-6} mol/L, c_{Im} 1.15 × 10^{-2} mol/L, $c_{peroxide}$ 2.3 × 10^{-4} mol/L). (a) Step of imidazole coordination and (b) oxidation step.

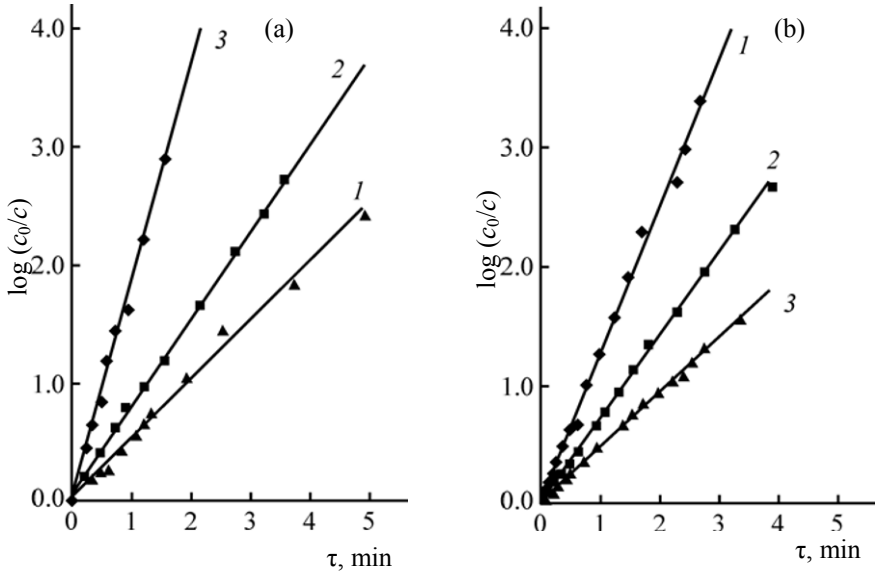


Fig. 4. Dependence of log (c_0/c_τ) on τ at 295 K (a) in the step of coordination and (b) in the oxidation step. c_{NiTPP} 8.0 × 10^{-6} mol/L, $c_{peroxide}$ 2.3 × 10^{-4} mol/L, c_{Im} 7.75 × 10^{-3} (*1*), 1.15 × 10^{-2} (*2*), 2.0 × 10^{-2} mol/L (*3*).

The reaction rate of the limiting stage for the theoretical scheme of the process may be written as the following [Eq. (9)]:

$$-dc[(Im)_2NiTPP]/d\tau = k_3[(Im)_2NiTPP][ROOR]. \quad (9)$$

The concentration $[(Im)_2NiTPP]$ may be expressed through the equilibrium constant and concentrations of the starting compounds of the reaction (7) by Eq. (10):

$$[(Im)_2NiTPP] = K_{p2}[(Im)NiTPP]\,[Im]. \quad (10)$$

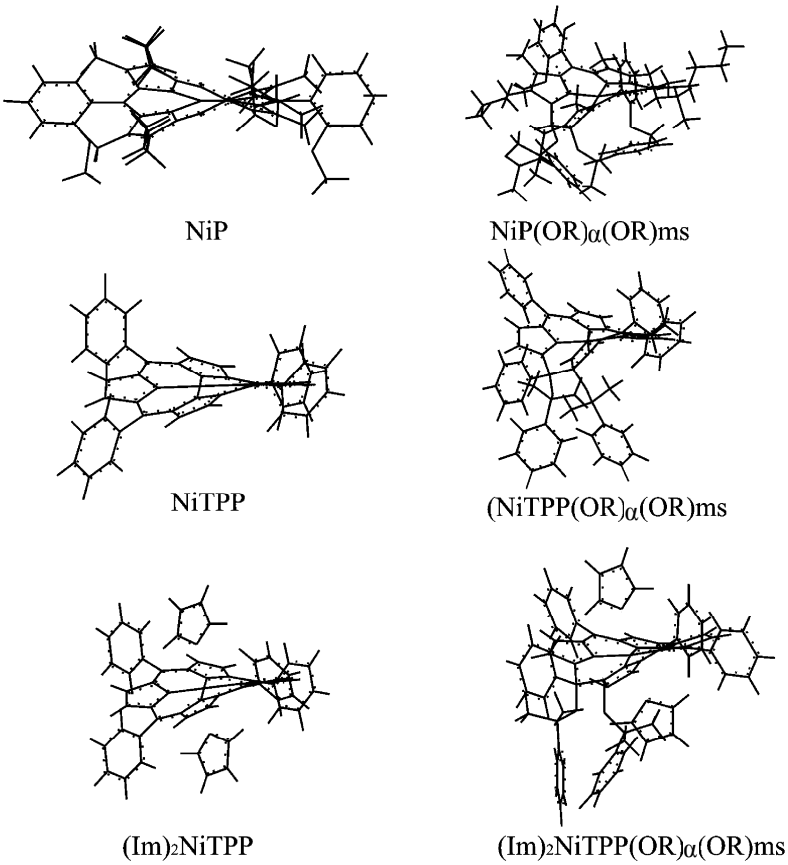


Fig. 5. Optimized structures of the nickel porphyrinates and some intermediates in the oxidation reaction calculated by PM3 quantum-chemical method.

Combining Eqs. (10) and (9) the final view for the rate equation of the second stage of the reaction was obtained Eq. (11):

$$-dc[(\mathrm{Im})_2\mathrm{NiTPP}]/d\tau = k_3K_{p2}[(\mathrm{Im})\mathrm{NiTPP}][\mathrm{Im}][\mathrm{ROOR}]. \quad (11)$$

Theoretical Eq. (11) where $k_3K_{p2} = k_v'$ is well proved by the experimentally obtained kinetic Eq. (6) and confirmed the established reaction orders with respect to the compounds participating in the reaction.

Imidazole presence in the system caused a change in the reagents content; the formed axial complex reacted with the peroxide three times faster than the nickel tetraphenylporphyrinate (see table).

Comparing the kinetic characteristics of the reactions with participation of NiP and NiTPP it is necessary to emphasize that the rate of oxidation of the latter was substantially lower (see table) due to the influence of the electronic and conformation factors of the nickel porphyrinate macrocycle. Thus, the presence of four electron-withdrawing substituents and slight degree of NiTPP molecule deformation as distinct from NiP did not led to significant increase in the macrocycle basicity and promoted the increase in the nickel tetraphenylporphyrinate stability in reaction with the peroxide.

Earlier the reactions of magnesium 5,15-di(*o*-methoxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrinate with organic peroxides were investigated [17]. The analysis of the kinetic parameters of the reaction demonstrated that the reaction with magnesium porphyrinate was faster by four orders of magnitude than the same reaction of nickel porphyrinate (see table). It may be ascribed to the influence of the metal nature on the redox properties of the complex. As all transition metals, nickel forms complexes through the dative covalent bonding. The presence of the dative bond caused redistribution of the electron density in the macrocycle unlike that in magnesium porphyrinate and therefore providing stabilization of nickel porphyrinate in a variety of reactions.

The geometric structure of the reagents and intermediates of the reaction was calculated by quantum-chemical method PM3 [18–20]. Nickel porphyrinates molecules showed nonplanar structure and were charac-

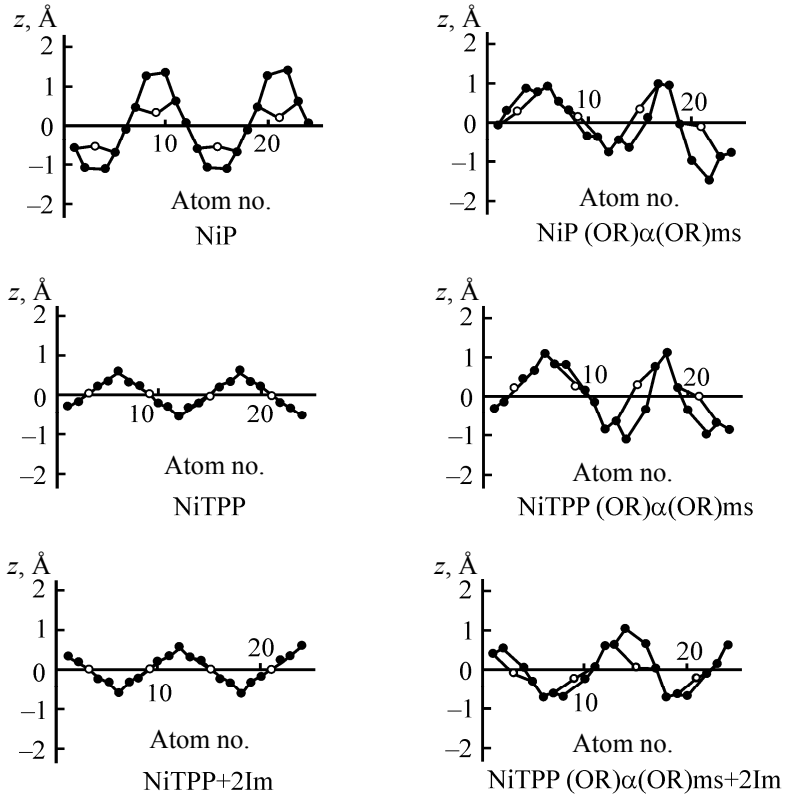


Fig. 6. Deviations from the average plane of the tetrapyrrole macrocycle of its skeleton atoms at *z* axis for the nickel porphyrinates and the reaction intermediates according to the data of quantum-chemical calculations by PM3 method. (Light circles) nitrogen atoms and (dark circles) carbon atoms.

terized by D_{4h} symmetry, saddle-like deformation type for NiP and corrugation for NiTPP (Figs. 5 and 6). The degree of the macrocycle deformation in the case of NiP was higher (Fig. 6). The formation of C_α–OR and C_m–OR bonds caused significant distortion of the macrocycle. The steric strain in both complexes was so substantial that allowed a suggestion of a distortion of the conjugated π-system of the macrocycle. Instability of the chromophore was also proven by the experimental data.

In summary, the electronic and conformation factors of the macrocyclic compound together with the nature and coordination environment of the metal cation allow an effective control of the oxidation reaction of nickel porphyrinates with organic peroxides.

EXPERIMENTAL

Electron absorption spectra were registered on Cary 50 apparatus at 295 K. ^{1}H NMR spectra were recorded on Bruker AVANCE-500 spectrometer. ESI mass spectra were obtained on Bruker microTOF spectrometer.

Irradiation of the reaction mixture was performed with the use of the medium pressure mercury lamp of TUNGSRAM 20W F33 type.

Kinetic parameters of the investigated reaction were obtained according to the known procedure [21]. Effective rate constants (k_{eff}) were determined by the change in the solution optical density on working wave lengths (λ 410–418 nm) after definite time intervals by the equation of formally first order [Eq. (12)] provided dicumene peroxide and imidazole were in excess.

$$K_{eff} = 1/\tau \log (c_0/c_\tau), \quad (12)$$

where c_0, c_τ are concentrations of the complex at start of the process and at time τ.

Values k_v, k_{eff} and determination of average deviations were optimized with the help of Microsoft Excel and ggh.exe (QB-45) by the Guggenheim method. Relative error was ~6–12%.

Quantum-chemical calculations were performed on approximation level CNDO [22] by PM3 method [18–

20] with complete optimization of the geometry up to specified gradient 0.0004 kJ mol^{-1} $Å^{-1}$).

Nickel 5,15-di(*o*-methoxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrinate was synthesized by the known procedure [22]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 10.20 s (2H, *ms*-H), 7.67 d (2H, *o*-H, phenyl, *J* 6.9 Hz), 7.62 t (2H, *m*-H, phenyl, *J* 7.9 Hz), 7.21 t (2H, *p*-H, phenyl, *J* 7.9 Hz), 7.10 d (2H, *m*-H, phenyl, *J* 7.9 Hz), 3.98 t (8H, CH_2, butyl, *J* 8.2 Hz), 3.82 s (6H, OCH_3), 2.56 s (12H, CH_3), 2.18 m (8H, CH_2, butyl), 1.65 m (8H, CH_2, butyl), 1.09 t (12H, CH_3, butyl, *J* 8.1 Hz), –2.36 s (2H, NH). Electron absorption spectrum (benzene), λ_{max}, nm (log ε): 564 (3.47), 529 (3.68), 410 (4.68).

Nickel 5,10,15,20-tetraphenylporphyrinate was synthesized by the known procedure [22]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.70 s (8H, β-H), 8.07 d (8H, *o*-H, phenyl, *J* 5.6 Hz), 7.60 t (12H, *m,p*-H, phenyl, *J* 8.2 Hz), –2.81 s (4H, NH). Electron absorption spectrum (benzene), λ_{max}, nm (log ε): 577 (4.49), 538 (4.67), 414 (5.01).

^{1}H NMR spectra were obtained in the Centre of Joint Use of Verkhnevolzhskii Regional Centre of physical and chemical research.

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