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Study of Intermolecular Interaction of Mg-5,15-Di(*o*-methoxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphin with *o*-Xylene Organic Peroxides. Effect of Imidazole on the Reaction Kinetics

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Abstract—Using the method of spectrophotometric titration a reaction of magnesium porphyrinate with the *o*-xylene organic peroxides was investigated, the reaction mechanism and kinetic parameters were determined. The effect of imidazole on the rate of the reaction under investigation was demonstrated. The presence of steric strain in the magnesium porphyrinate macrocycle and its increase in the course of formation of intermediates was observed.

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One of the major trends in the development of supramolecular chemistry is the creation of biomimetic systems for biological and technical processes. In this regard, it remains relevant to study the effect of structure and composition of an artificial system on its catalytic properties and possible transformation in the chemical process. In this paper in continuation of earlier research a study is initiated of redox properties of sterically strained metal porphyrinates by an example of the reaction of organic *o*-xylene peroxides and Mg-5,15-di(*ortho*-methyloxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporfirin (MgP). We performed a search of the ways to control the reactivity of MgP. The reaction of a macrocyclic compound with organic peroxides was studied at T = 295K by spectrophotometry [1] and by computer simulation [2–4].

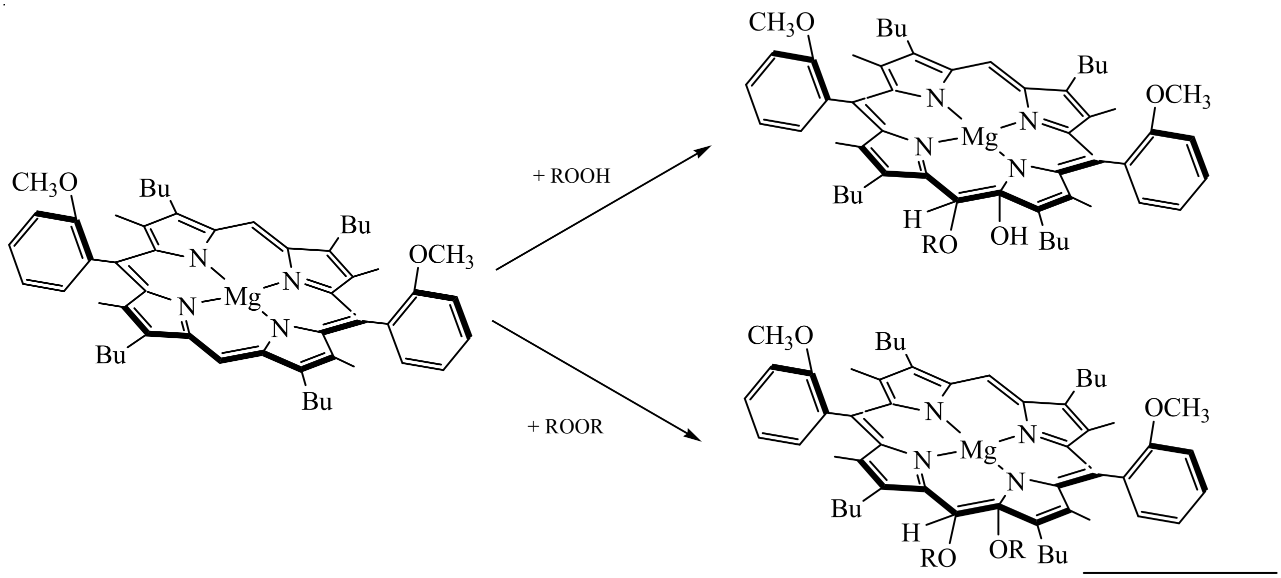
The oxidation of MgP with organic peroxides occurs at the periphery of the macrocycle [5–7] with the formation of a sterically strained unstable compound, which subsequently collapses to a colorless reaction products (Fig. 1). The reaction can proceed by two previously described mechanisms [8–10]: (1) addition of hydroxy and aryloxy groups at the meso- and α-position (represented by the reaction scheme); (2) a free radical mechanism with the formation of extremely unstable radicals MgP•(RO), MgP•(NO), and MgP•(Im), MgP•(RO), (Im)MgP•(HO), and (Im)MgP• (the latter in the presence of base in the reaction mixture) with a high degree of deformation.

Limiting stage is the formation of intermediates, the subsequent stage of degradation of the macrocycle is faster.

The oxidation of MgR (c_{MgR} = 0.93×10^{-5}–2.11×10^{-5} M) with organic peroxides of *o*-xylene ($c_{\mathrm{perox.}}$ = 0.23×10^{-6} M) in either absence or presence of a base (c_{Im} = 7.0×10^{-7}–4.50×10^{-3} M) was carried out under strong illumination at T = 295K. The reaction is a pseudo-first order (n = 1) with respect to the peroxide, as follows from the linearity of the dependence ln (c_0/c_τ) = f (t) and a satisfactory constancy of k_{ef} (Fig. 2, Table 1).

$$-dc_{\mathrm{perox}}/d\tau = kc^{n}_{\mathrm{perox}}. \quad (1)$$

Effective rate constants k_{ef} increase in direct proportion to the concentration of the complex. The reaction order on the metal porphyrinate (m) and the true value of the rate constant (k_{v}) (Fig. 3) were determined from the relation (2) by the least-squares method. The reaction order m = 1.



$$\log k_{ef} = \log k_v + m\log [\mathrm{MgP}]. \quad (2)$$

Thus, the equation of the rate of oxidation is as follows:

$$-dc_{\mathrm{MgP}}/dt = k_v[\mathrm{MgP}][\text{peroxide}]. \quad (3)$$

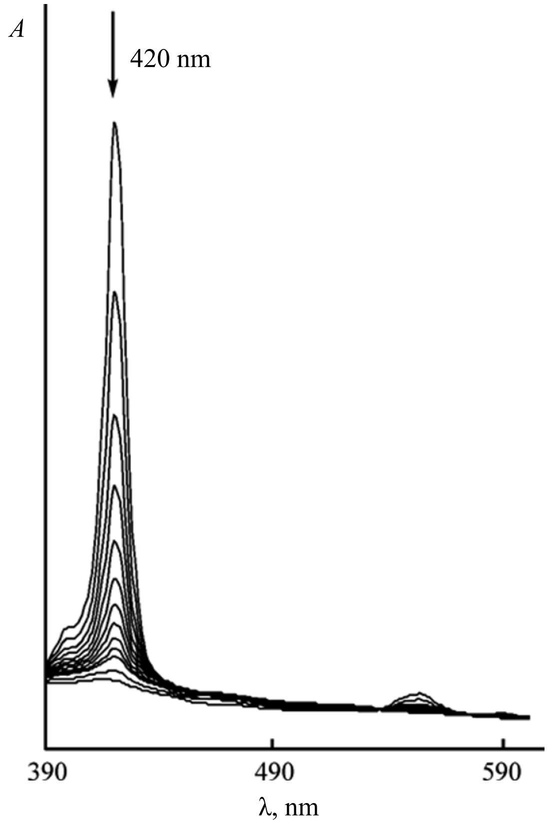


Fig. 1. Changes in EAS of MgR during oxidation ($c_{\mathrm{perox}} = 0.23\times10^{-6}$ M, $c_{\mathrm{MgR}} = 1.77\times10^{-5}$ M).

The addition of a base to the working solution is accompanied by a change in the structure and composition of the reagents [11], which in turn affects the process rate. The process is also accompanied by the destruction of the chromophore. The maximum in

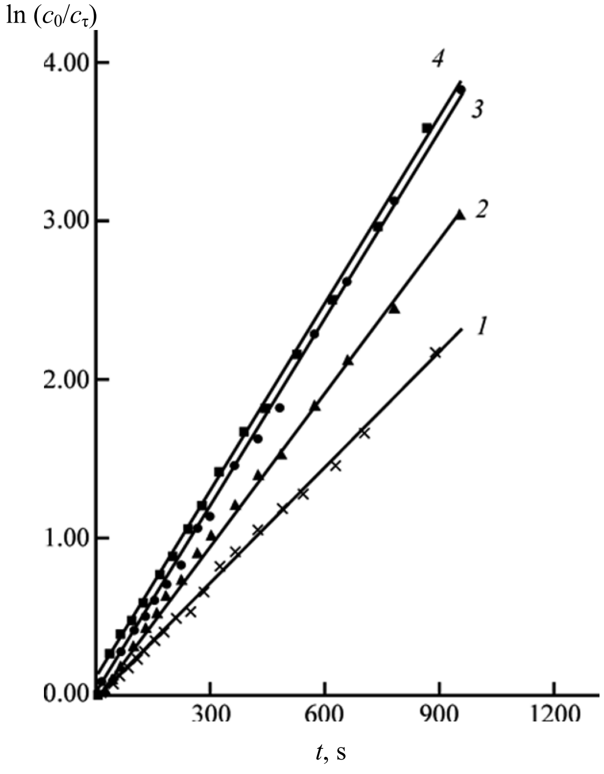


Fig. 2. The dependence of ln (c_0/c_τ) on τ ($c_{\mathrm{perox}} = 0.23\times10^{-6}$ M) at 295 K: (*1*) $c_{\mathrm{MgR}} = 0.93\times10^{-5}$ M, (*2*) 1.44×10^{-5} M, (*3*)1.77×10^{-5} M, and (*4*) 2.11×10^{-5} M.

Table 1. Kinetic parameters of oxidation of MgR with *o*-xylene peroxides at 295 K

$c_{MgP}\times10^5$, M	$k_{ef}\times10^3$, s^{-1}
c_{perox} 0.23×10^{-6} M	
0.93	2.28
1.44	3.15
1.77	3.74
2.11	4.17
k_v 12.88 s^{-1} mol^{-1} l^1	

Table 2. Kinetic parameters of oxidation of MgR with *o*-xylene peroxides in the presence of imidazole (c_{perox}= 0.23×10^{-6} M, c_{MgP} = 1.77×10^{-5} M)

c_{Im}, M	$k_{ef}\times10^3$, s^{-1}	Δλ, nm
0	3.74	0
7.0×10^{-7}	4.72	0
1.98×10^{-6}	5.97	1
1.50×10^{-5}	2.36	2
1.50×10^{-4}	1.80	3
1.50×10^{-3}	0.82	3
4.50×10^{-3}	0.70	3

EAS is shifted by 1–3 nm (depending on the concentration of imidazole). The presence of imidazole in the concentration from 10^{-7} to 10^{-6} M leads to an increase in k_{ef}. With increasing concentration of Im to 10^{-5}–10^{-3} M the k_{ef} value begins to decrease (Table 2). This is due to the fact that coordination of magnesium porphyrinate with organic base occurs at a low concentration of the latter, thus the uncoordinated molecule of the base remaining in the solution may bind to molecules of hydrogen peroxide and deactivate them. [12]

The comparison of kinetic characteristics of the reactions of magnesium porphyrinate and analogous zinc porphyrinate with organic peroxides shows that the oxidation rate of the zinc derivative is lower by 3 orders of magnitude [13]. This is due to the influence of the nature of the metal atom in the structure of the macrocycle on its steric strain and, as a consequence, its reactivity.

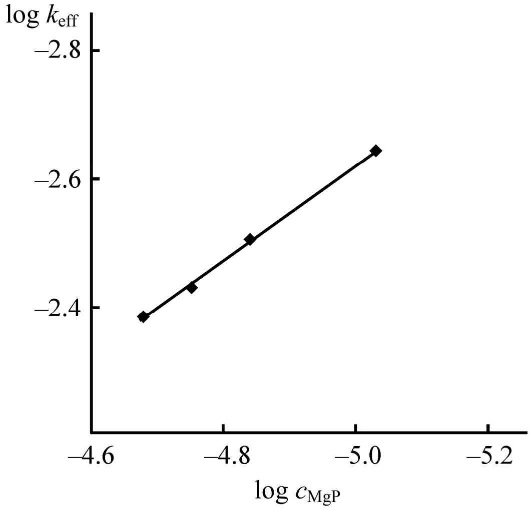


Fig. 3. The effective reaction rate constant vs the concentration of magnesium porphyrinate.

The geometric structure of magnesium porphyrinates and of the reaction intermediates was calculated by the quantum-chemical method PM3. The molecule MgR is nonplanar, is characterized by D_{4v} symmetry and a small degree of the saddle deformation (Figs. 4a, 5). The formation of the C$_\alpha$–OR and C$_m$–OR bonds during the reaction is accompanied by a significant increase in the degree of deformation of the magnesium porphyrinate macrocycle (Figs. 4a, 5), which may eventually lead to the destruction of the chromophore. The presence of the base molecules in the complex causes a change in its symmetry to C_{4v} and increases the steric strain. Saddle-shaped deformation of the macrocycle is pronounced (Fig. 4b). The interaction of this complex with peroxide leads to an even greater increase in the degree of deformation of the porphyrin ligand (Figs. 4b, 5). This promotes a more rapid breach of the macroheterocyclic conjugated π-system that has been observed in the course of the experimental studies.

Based on the above, it can be concluded that the nature of the metal atom, the presence of a base and the variation of its concentration, as well as accounting for the conformational factors are effective ways to control the reaction under investigation.

EXPERIMENTAL

The electron absorption spectra (EAS) were recorded on a Cary 50 instrument at T = 295 K. The irradiation of the reaction mixture was performed using a mercury lamp of medium pressure of type TUNGSRAM 20W F33.

Mg-5,15,di(*ortho*-methylhydroxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrin was synthesized by the known method [14]. EAS of the porphyrin ligand in xylene [λ$_{max}$, nm (log ε)] are as follows: 590 (3.49), 554 (3.67), 420 (4.68).

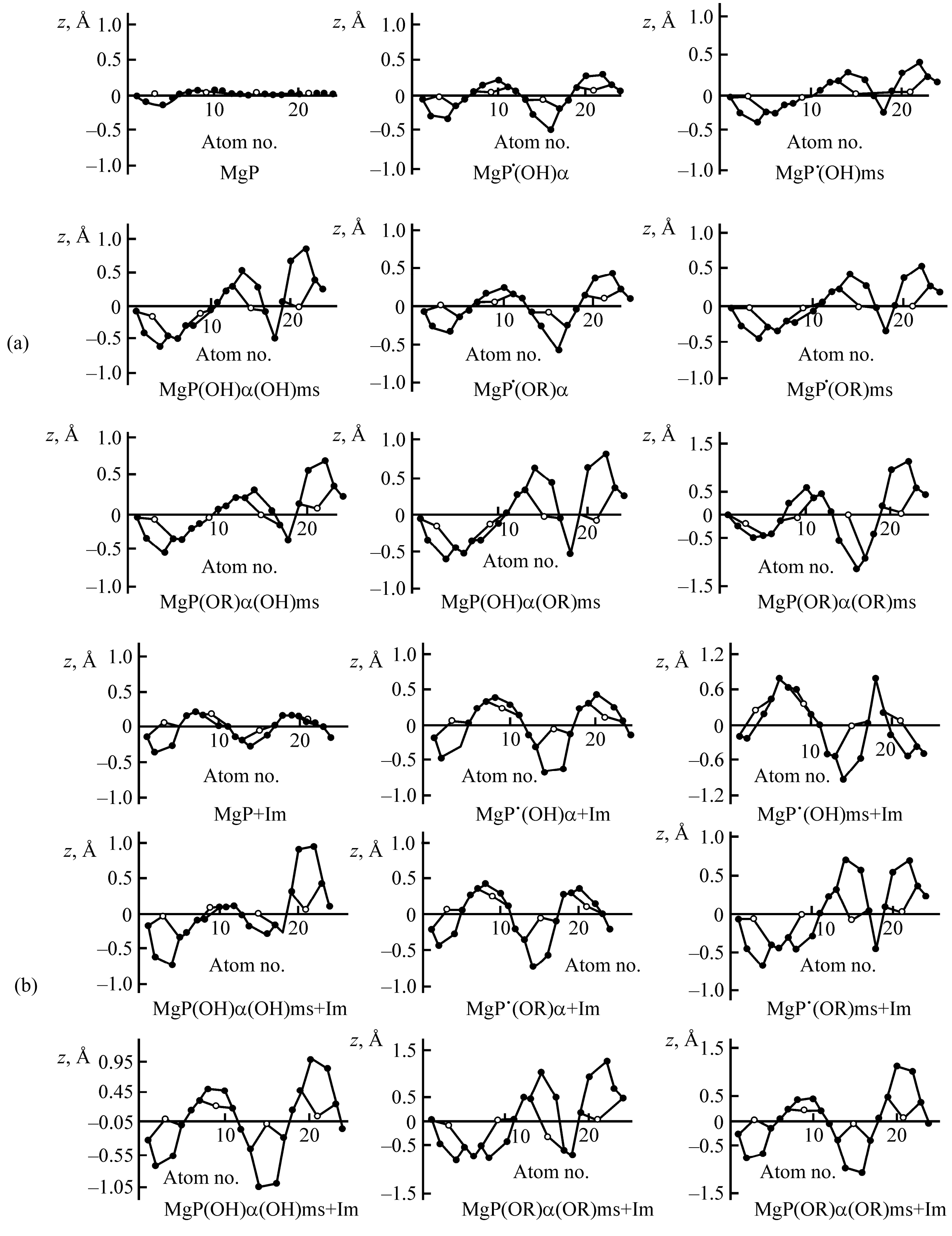
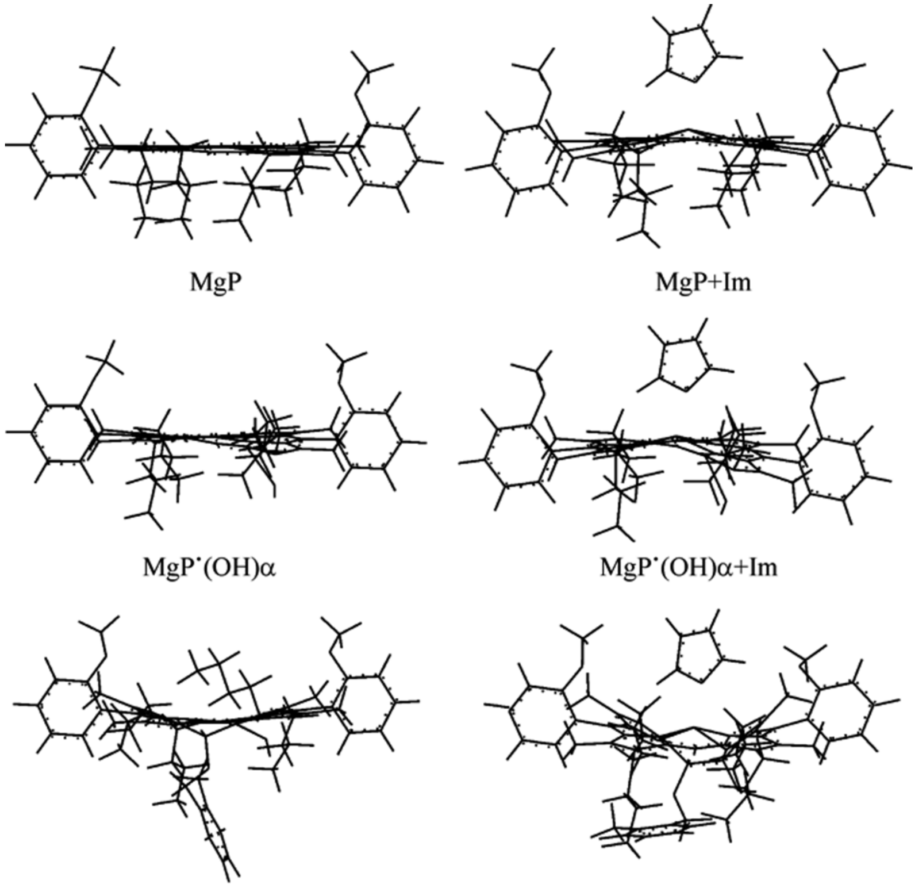


Fig. 4. Deviation from the mean plane of the tetrapyrrole macrocycle of its core atoms along the Z axis for MgP and the reaction intermediates without imidazole (a) and in the presence of imidazole (b), according to quantum-chemical calculations by the PM3; (light circles) are nitrogen atoms, (dark circles) are carbon atoms.



MgP MgP+Im

MgP•(OH)α MgP•(OH)α+Im

MgP(OH)α(OR)ms MgP(OH)α(OR)ms+Im

Fig. 5. The optimized structures of MgP and some intermediates of the oxidation reaction calculated by quantum-chemical method PM3.

The initial concentration of peroxides in *o*-xylene was determined by the photometric method using indicator leyco methylene blue [15]. The method of obtaining the kinetic parameters of the investigated reaction is described in detail in [16]. Effective rate constants (k_{ef}) were determined from the change in the optical density of the solution at the working wavelength (λ = 421–432 nm) at regular intervals according to the formally first-order Eq. (4) at an excess of magnesium porphyrinate.

$$k_{ef} = 1/\tau \ln (c_0/c_\tau). \quad (4)$$

Here c_0, c_τ are the concentrations of peroxide at time 0 and τ.

The optimization of the values of k_v and k_{ef} and the determination of standard deviations was performed by the least-squares method using the programs Microsoft Excel and ggh.exe (QB-45) by the method of Guggenheim. The relative error was ≈ 5–10%.

Quantum-chemical calculations were performed at the level of CNDO approximation [17] by PM3 method [2–4, 18] with complete optimization of geometry. The condition of the count was specified to the gradient 0.0002 kJ mol^{-1} Å^{-1}.

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