ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 7, pp. 1537–1543. © Pleiades Publishing, Ltd., 2009.
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Effect of Imidazole on the Structure and Properties of Zn-5,15-di(*o*-methoxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrin in Reaction with Organic Peroxides

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Received February 2, 2009

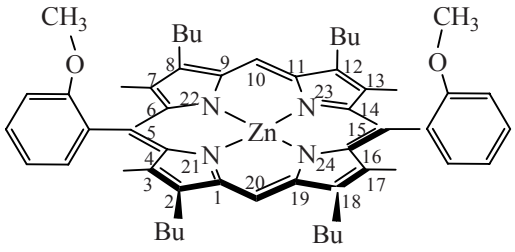
Abstract—The reaction of Zn-5,15-di(*o*-methoxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrin with organic peroxides in the presence of imidazole was studied in order to investigate the effect of modification and deformation of the macrocycle on the redox properties of metalloporphyrins. The kinetic characteristics of the reaction were obtained. It was found that the introduction of imidazole into the reaction mixture resulted in an increase in the rate of oxidation of zincporphyrin. Quantum-chemical calculations of the reagents and intermediates of the oxidation reaction were performed at the PM3 level of theory. The deformational distortions of the free macrocycle and during the course of the reaction were estimated. The effect of the structure modification and the degree of deformation of the macrocyclic ligand on the parameters of the process [effective (k_{eff}) and true (k_v) rate constants] was found.

DOI: 10.1134/S1070363209070238

In continuation of our systematic studies of the effect of modification and deformation of the macrocycle of metalloporphyrins on their redox properties in the present work the reaction of Zn-5,15-di(*o*-methoxyphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetrabutylporphyrin (ZnP) with peroxides of *o*-xylene in the presence of imidazole at 295 K was studied spectrophotometrically [1]. A tentative mechanism is suggested and the parameters of the reaction determined. Quantum chemical method PM3 [2–5] was used to obtain the geometrical characteristics and to assess the state of ZnP and (Im)ZnP in the course of their reaction with peroxides.

After exposure to light, *o*-xylene contains organic peroxides in the amount sufficient to participate in redox transformations [6–8]. Oxidation of ZnP occurs on the periphery of the macrocycle [9–11], is followed by the disruption of the chromophore and is characterized by the true rate constant k_v equal to 0.046 l mol^{-1} s^{-1} [12].

The oxidation of ZnP (c_{ZnP} = 2.16×10^{-5}–4.06×10^{-5} M) with organic peroxides of *o*-xylene ($c_{peroxide}$ = 1.9×10^{-6} M) in the presence of imidazole (c_{Im} = 4.1×10^{-5}–4.1×10^{-3} M) was performed under the conditions of active illumination at 295 K. Introduction of imidazole results in the formation of the axial complex (Im)ZnP [13] and substantially increases the rate of the reaction. The reaction is followed by disruption of the macrocyclic ligand, as is the case also for ZnP (without imidazole) (Fig. 1).



The reaction under investigation may follow two different mechanisms: (1) hydroxylation (Scheme 1) and (2) radical polymerization [9, 12, 14–16].

Varying the imidazole concentration leads to variation in the structure and composition of the reagents. Let us consider the process when c_{Im} =

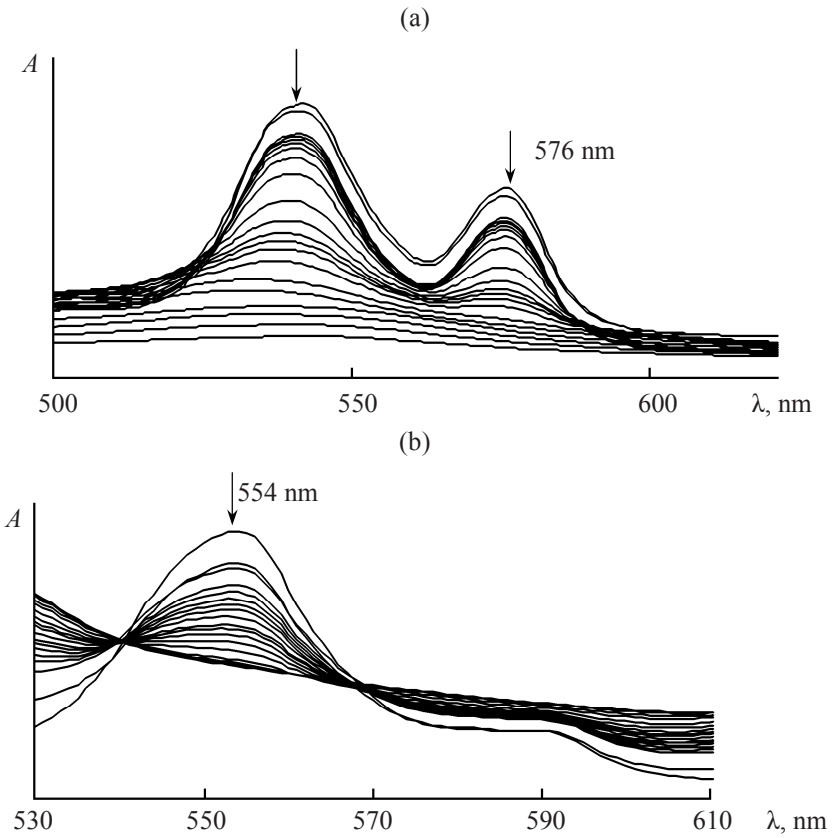
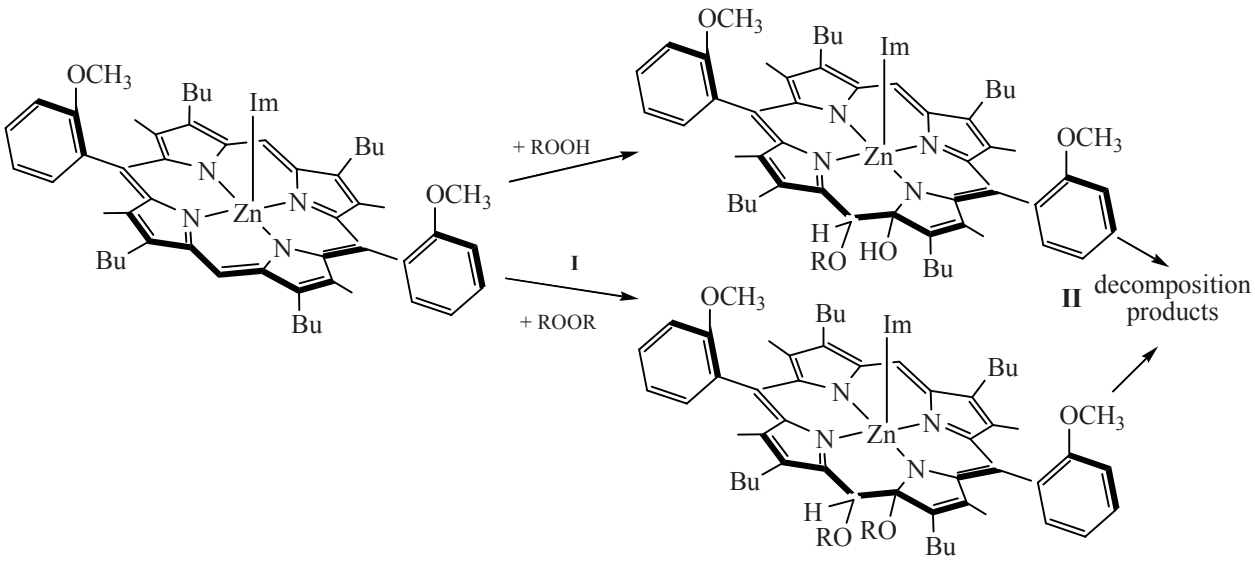


Fig. 1. Changes in EAS of ZnP during oxidation in *o*-xylene $c_{peroxide} = 1.9\times10^{-6}$ M) at 295 K in the presence of imidazole: (a) $c_{Im} = 4.1\times10^{-5}$ M $c_{ZnP} = 3.10\times10^{-5}$ M; *t*, s: 1–0; 16–14880; (b) $c_{Im} = 4.1\times10^{-3}$ M $c_{ZnP} = 4.06\times10^{-5}$ M. 1–0; 7–4140.

4.1×10^{-5} M. The electron absorption spectrum (EAS) of ZnP remains practically unchanged [the shift of the absorption bands ($\Delta\lambda$) is 1 nm] (Fig. 2a), which is indicative of negligible concentration of complex (Im) ZnP in the working solution as compared to the dominating concentration of ZnP. In this case, the rate of the oxidation reaction is a sum of the rates of parallel reactions with participation of (Im)ZnP and

Scheme 1.



ZnP, the contribution of the latter being substantially larger. Therefore, it can be assumed that the reaction proceeds mainly with ZnP. For the imidazole concentration of $c_{Im} = 4.1\times10^{-4}$ M a change of intensity and a shift of the principal bands in the EAS of zincporphyrin ($\Delta\lambda$ = 6 nm) is observed (Fig. 2b). This suggests the presence of comparable concentrations of ZnP and (Im)ZnP in the working solution. In this case, the formation of two types of intermediates occurs: for the first mechanism (Scheme 1) these are $ZnP(RO)_2$, $ZnP(HO)_2$ and $(Im)ZnP(RO)_2$, $(Im)ZnP(HO)_2$; for the second mechanism these are the radical forms of ZnP and (Im)ZnP. Further increase in the imidazole concentration ($c_{Im} = 4.1\times10^{-3}$ M) leads to complete conversion of ZnP into (Im)ZnP ($\Delta\lambda$ = 14 nm) (Fig. 2c). In this case the reaction of oxidation proceeds with participation of only the molecular complex (Im)ZnP.

The rate-limiting step is the formation of the intermediates followed by fast step of the macrocycle disruption.

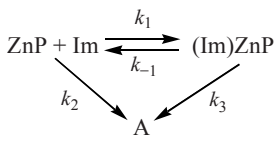
The reaction of oxidation was performed under the pseudo-first order conditions on the peroxide (n = 1) as followed from the linear dependence $\ln (c_o/c_\tau) = f(t)$ (Fig. 3).

$$dc_{peroxide}/d\tau = kc^n_{peroxide}. \quad (1)$$

The effective rate constants k_{eff} increase directly proportionally to the complex concentration (Fig. 4). The dependences found are described by the regression equations: $\log k_{eff} = 0.6438\log c_{ZnP} - 1.184$, $\log k_{eff} = 0.756\log c_{ZnP} = 0.504$ and $\log k_{eff} = 0.654\log c_{ZnP} = 0.286$ for $c_{Im} = 4.1\times10^{-5}$ M, $c_{Im} = 4.1\times10^{-4}$ M, and $c_{Im} = 4.1\times10^{-3}$ M, respectively. The order of the reaction on the complex (m) and the value of the true rate constant were obtained by the least-squares treatment of dependence (2) (Fig. 4). For all three cases $m \approx 1$.

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

When ZnP and (Im)ZnP ($c_{Im} = 4.1\times10^{-5}$ M–4.1×10^{-4} M) take part in the process, as in the scheme bellow.



Here A denotes the products of decomposition, the equation for the reaction rates has the form:

$$dc_A/dt = k_2[ZnP][proxide] + k_3[(Im)ZnP][proxide], \quad (3)$$

$$[(Im)ZnP] = K_e[ZnP][Im], \quad (4)$$

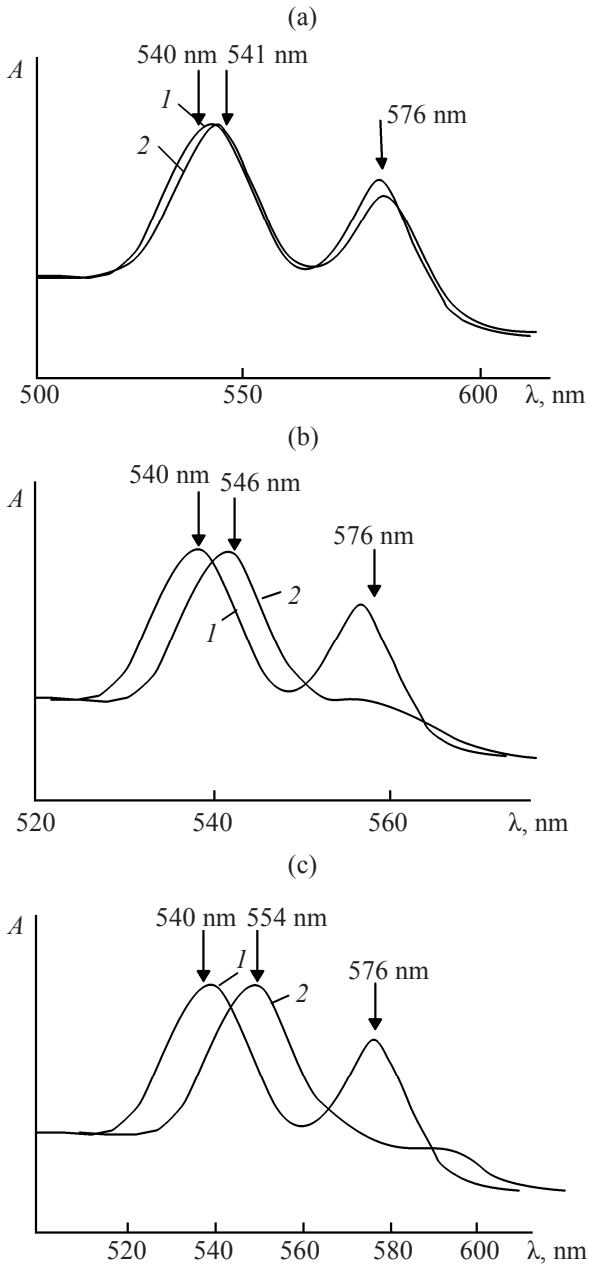


Fig. 2. Changes in EAS of ZnP with variation of concentration of imidazole: (a) $c_{Im} = 4.1\times10^{-5}$ M $c_{ZnP} = 3.10\times10^{-5}$ M; (b) $c_{Im} = 4.1\times10^{-4}$ M $c_{ZnP} = 3.80\times10^{-5}$ M; (c) $c_{Im} = 4.1\times10^{-3}$ M, $c_{ZnP} = 4.06\times10^{-5}$ M.

where $K_e = k_1/k_{-1}$ denotes the equilibrium constant. Substituting (4) in (3) we obtain:

$$dc_A/dt = k_2[ZnP][peroxide] + k_3K_p[ZnP][Im][peroxide]$$
$$= [ZnP][peroxide](k_2 + k_3K_e[Im]). \quad (5)$$

Denoting $k_3K_e[Im] = k'_3$, Eq. (5) can be rewritten as:

$$dc_A/dt = (k_2 + k'_3)[ZnP]peroxide]. \quad (6)$$

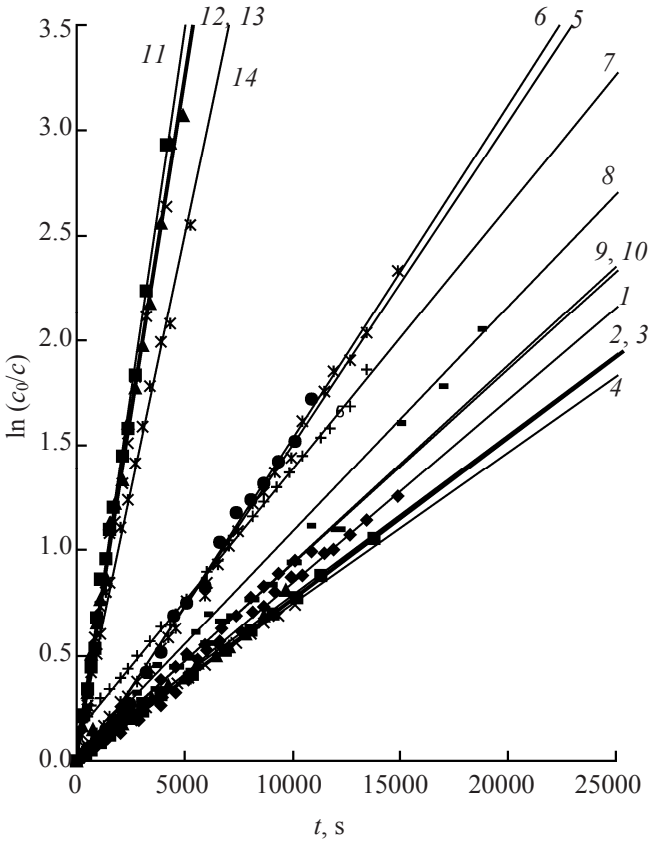


Fig. 3. Dependence of ln (c_0/c_τ) on τ for oxidation of ZnP with peroxides in *o*-xylene ($c_{peroxide}$ = 1.9×10^{-6} M) at 295 K in the presence of imidazole: c_{Im} = 4.1×10^{-5} M: (*1*) c_{ZnP} = 3.10×10^{-5} M, (*2*) 3.02×10^{-5} M, (*3*) 2.64×10^{-5} M, (*4*) 2.33×10^{-5} M; c_{Im} = 4.1×10^{-4} M: (*5*) c_{ZnP} = 3.80×10^{-5} M, (*6*) 3.62×10^{-5} M, (*7*) 3.21×10^{-5} M, (*8*) 2.69×10^{-5} M, (*9*) 2.20×10^{-5} M, (*10*) 2.16×10^{-5} M; c_{Im} = 4.1×10^{-3} M: (*11*) c_{ZnP} = 4.06×10^{-5} M, (*12*) 3.84×10^{-5} M, (*13*) 3.43×10^{-5} M, and (*14*) 2.74×10^{-5} M.

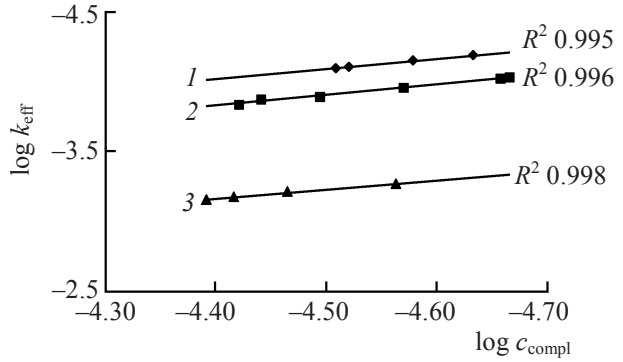


Fig. 4. Dependence of effective rate constant of oxidation on concentration of the zinc complex in the presence of imidazole: (*1*) c_{Im} = 4.1×10^{-3} M, (*2*) c_{Im} = 4.1×10^{-4} M, and (*3*) c_{Im} = 4.1×10^{-5} M.

Since under the conditions of the experiment it was impossible to determine k_2 and k_3 separately, the experimentally found value was the summary constant $k_v = k_2 + k_3'$, (for c_{Im} = 4.1×10^{-5} M, k_v = 0.065 l mol^{-1} s^{-1}, for c_{Im} = 4.1×10^{-4} M, k_v = 0.313 l mol^{-1} s^{-1}).

For the reaction with participation of (Im)ZnP (c_{Im} = 4.1×10^{-3} M, k_v = 0.518 l mol^{-1} s^{-1}), the reaction rate equation has the form:

$$(Im)ZnP \xrightarrow{k} A,$$

$$-dc_{(Im)ZnP}/dt = k_v[(Im)ZnP][peroxide]. \quad (7)$$

The obtained kinetic characteristics refer to the rate-limiting step of the reaction of the peroxide and the complex.

The analysis of the k_v values and the data from [12] allows a conclusion that the introduction of imidazole substantially affects the electronic and conformational properties of the macrocycle and leads to the increase in the rate of oxidation of the complex. From comparing the k_v values for the reactions with the participation of complexes ZnP (**I**), Zn-5,15-di(*o*-methoxyphenyl)-2,3,7,8,12,13,17,18-octamethylporphyrin (**II**) [15] and the zincporphyrin covered with the 2,5-dimethoxyphenylene "lid" (**III**) [16] in the presence of imidazole the rates of oxidation increase in the following order: **II** < **I** < **III**. The obtained trend is due to the effect of substituents and the degree of deformation of the complex.

The increase in the rate of oxidation of complex **I** relative to the oxidation of compound **II** is due to the introduction of four butyl groups and to increased steric hindrances in the macrocycle, that results in the redistribution of the electron density favoring more facile rupture of the conjugated bond C_m=C_α in the macrocycle in the course of the reaction. For complex **III**, the main contribution into the increase in the rate of oxidation comes from the conformational factor.

The presence and the degree of deformation of the macrocycle in the reagents and intermediates of the investigated reaction were estimated by quantum-chemical calculations performed at the PM3 level of theory [2–5].

The optimized molecule ZnP is nonplanar with the dominating saddle-type deformation of the macrocycle. Upon the reaction of ZnP with the peroxide the degree of deformation of the porphyrin ligand increases, the structure becomes unstable due to the arising substantial strains, leading eventually to violation of conjugation of the macrocycle and its

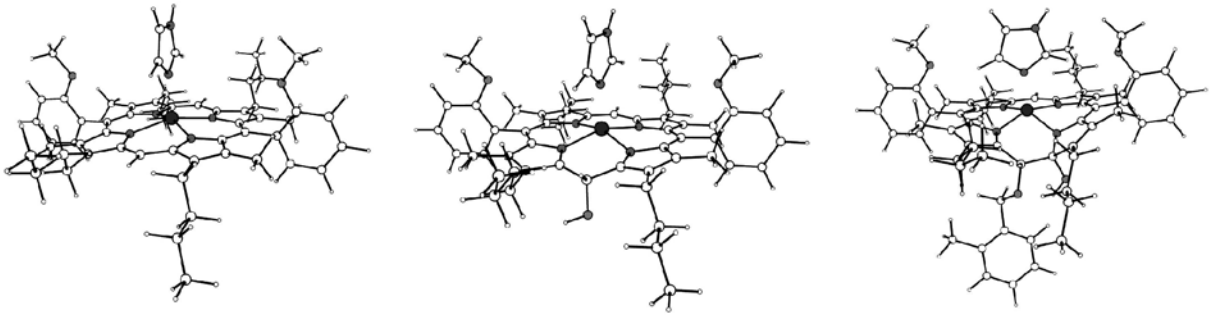


Fig. 5. Structure of (Im)ZnP and some intermediates of the reaction of oxidation as calculated by PM3 method.

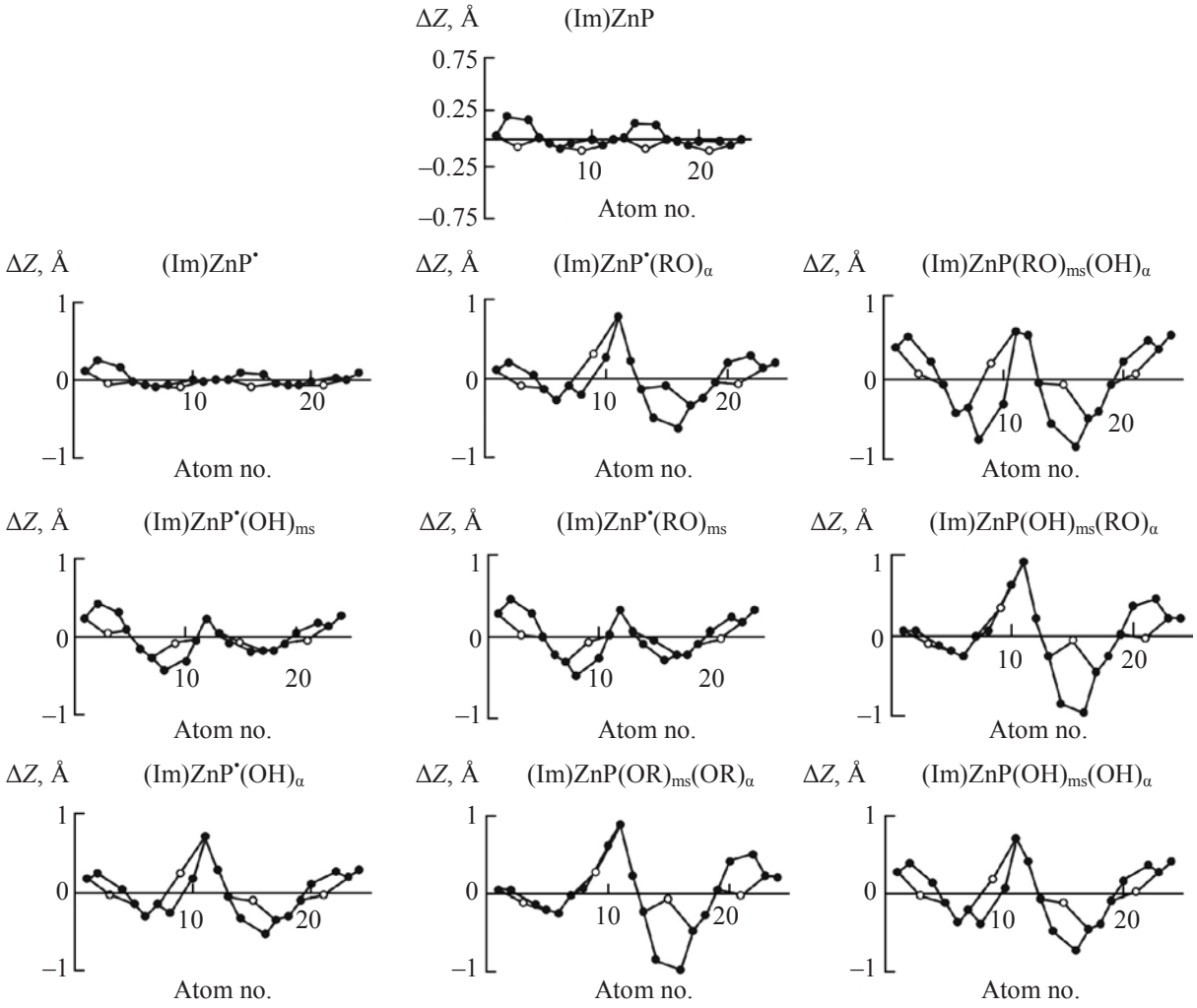


Fig. 6. Deviation of the skeletal atoms of the porphyrin macrocycle from the mean plane of the molecule (Δ*Z*) in (Im)ZnP and in the intermediates of the reaction of oxidation from the PM3 calculations; (○) nitrogen atoms and (●) carbon atoms.

disruption [12]. The molecule of (Im)ZnP is sterically more strained (Fig. 5) than ZnP [12] and is characterized by the presence of dominating "cupola-shape" deformation with small contribution of the ruffled and saddle-type deformation (Fig. 6). The methoxy groups deviate from the plane of the phenyl fragments by 14°. The perimeter of the coordination plane N_4 having the form of parallelogram is 11.7046 Å.

Geometric characteristics of the sterically strained zincporphyrin and the intermediate of the oxidation reaction (numeration of atoms in the macrocycle is in line with the IUPAC nomenclature)

Complex	$Zn–N_{22}$ $Zn–N_{24}$ Å	$Zn–N_{21}$ $Zn–N_{23}$ Å	$N_{21}–N_{23}$ $N_{22}–N_{24}$ Å	Ct–Zn Å	$Zn–N_L$	P_{N4} Å	$N_{21}ZnN_{24}$ $C_{19}N_{24}Zn$ deg	$C_1C_{20}C_{19}$ $C_9C_{10}C_{11}$ deg	$C_{20}C_{19}C_{18}$ $C_2C_1C_{20}$ deg	$C_{20}C_{19}N_{24}$ $C_{18}C_{19}N_{24}$ deg	$O_1–O_2$[a]
ZnP	2.0677	2.0623	4.0881	0.0289		11.6096	93.42	125.98	123.03	127.96	10.1339
	2.0208	2.0615	4.1234				122.61	126.93	123.31	109.00	
(Im)ZnP	2.1084	2.1173	4.1230	0.3729	2.0963	11.7046	92.28	127.68	122.88	127.92	10.3530
	2.0813	2.1144	4.1574				121.44	126.33	125.17	109.12	
$(Im)ZnP(RO)_m(OH)_\alpha$	2.0529	2.0875	4.1709	0.3986	2.0767	11.6481	86.12	120.45	114.42	118.20	9.4109
	2.2423	2.048	4.0579				130.89	126.29	121.35	101.63	
$(Im)ZnP(RO)_\alpha(OH)_m$	2.0603	2.1014	4.1307	0.5871	2.0790	11.6507	85.52	119.16	109.02	113.03	9.8353
	2.2283	2.0499	4.0832				128.19	126.27	122.11	102.14	
(Im)ZnP(RO)(RO)	2.0686	2.1273	4.1264	0.5533	2.0913	11.6334	87.04	119.10	109.51	114.01	9.7624
	2.1531	2.0512	4.0740				127.69	126.29	122.81	102.06	
(Im)ZnP(HO)(OH)	2.0673	2.1199	4.1359	0.4917	2.0871	11.6416	88.50	120.97		119.06	9.5135
	2.1344	2.0709	4.0849					126.65	120.96	102.37	
$(Im)ZnP^{\bullet}(RO)_m$	2.1029	2.1259	4.1480	0.4141	2.0708	11.7264	89.59	126.43	120.88	129.17	10.0139
	2.1246	2.1162	4.1459				124.61	126.74	121.45	109.95	
$(Im)ZnP^{\bullet}(OH)_m$	2.1140	2.1149	4.1691	0.3954	2.0759	11.7513	90.40	117.68	120.95	128.82	10.1741
	2.1294	2.1122	4.1432				124.12	126.88	120.57	110.22	
$(Im)ZnP^{\bullet}(RO)_\alpha$	2.0678	2.0769	4.1525	0.5683	2.0821	11.6613	87.37	127.44	110.54	114.53	9.7879
	2.2376	2.0640	4.0740				126.33	126.71	123.36	102.41	
$(Im)ZnP^{\bullet}(OH)_\alpha$	2.0641	2.0729	4.1595	0.5315	2.0809	11.6642	88.39	128.35	112.44	115.83	9.6424
	2.2294	2.0690	4.0762				126.05		123.06	102.46	
$(Im)ZnP^{\bullet}$	2.1346	2.1124	4.1409	0.3956	2.0817	11.7853	94.47	138.98	128.62	121.72	10.3088
	2.1377	2.1056	4.2018				120.17	127.51	128.20	109.65	

[a] Distance between the oxygen atoms of the OCH_3 groups.

The formation of intermediates in the reaction of oxidation of (Im)ZnP(I) is followed by an increase in the torsion and planar deformation of the macrocycle (Figs. 5, 6, the table). The deviation of the zinc from the N_4 plane (Ct–Zn) increases, the values of the bond angles are changed (the largest variations are foxed in close vicinity to the site of location of the OH or RO groups) as well as the size of the coordination cavity (see the table). Note sharp increase in the saddle-type deformation and degree of ruffling of the macrocycle (Fig. 6).

Therefore, it can be concluded that the presence of imidazole in the working solution is followed by the formation of the axial complex (Im)ZnP(I), whose electronic and conformational effects increase the rate of oxidation. The variation in the base concentration leads to variation in the composition of the reacting species and affects the course of the process.

EXPERIMENTAL

Zn-5,15-di(*o*-methoxyphenyl)-2,8,12,18-tetramethyl-3,7,1,17-tetrabutylporphyrin was prepared by standard procedure [17, 18]. Electron absorption spectra (EAS) were registered on a Cary 50 instrument in *o*-xylene at 295 K, λ_{max}, nm (ε): 410 (5.22), 540 (4.20), 576(4.04).

The initial concentration of peroxides in *o*-xylene was determined photometrically using leucomethylene blue as an indicator [19]. The method of studying the kinetics of the reaction of complexation is fully described in [20]. Effective rate constants (k_{eff}) for the reaction of oxidation were determined on the working wavelength λ = 541 nm (for $c_{Im} = 4.1\times10^{-5}$ M), 546 nm (for $c_{Im} = 4.1\times10^{-4}$ M) and 554 nm (for $c_{Im} = 4.1\times10^{-3}$ M) by the change of optical density of the solution in certain time intervals from the formal first order Eq. (1) under the conditions of excess of metalloporphyrin.

$$k_{eff} = (1/\tau)\ln (c_o/c_\tau), \quad (8)$$

where c_0, c_τ denote the concentrations of peroxides at times 0 and τ.

Optimization of k_{eff} value and determination of mean square deviations were determined by the least-squares method using the Microsoft Excel and ggh.exe (QB-45) programs by the Guggenheim method that gave the coinciding results. The relative error of determination of k_{eff} was 3–5%.

Quantum-chemical calculations were performed by semiempirical method PM3 [4, 5, 22] using the CNDO approximation [21] with full geometry optimization.

ACKNOWLEDGMENTS

This work was supported by the Program of Russian Academy of Science "Theoretical and experimental investigation of the nature of chemical bond and mechanisms of most important chemical reactions and processes," and Grant of Russian Foundation for Basic Research (grant no. 09-03-00736).

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