Russian Journal of General Chemistry, Vol. 75, No. 3, 2005, pp. 461–467. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 3, 2005, pp. 497–503.

Influence of the Structure of the Organic Moiety of Copper(II) Porphyrins on Their Reactivity toward Acids

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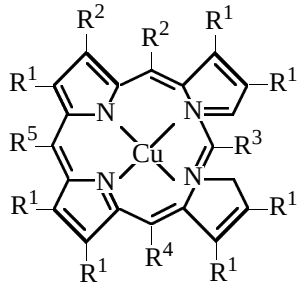
Received June 6, 2003

Abstract—The acid-induced dissociation of copper(II) porphyrin complexes with a high degree of *meso*- and β-substitution in the ligand was studied. The copper(II) complexes with octaethylporphyrins containing 0, 1, 2, 3, and 4 *meso*-phenyl substituents were ranked with respect to the stability. Octa-β-alkyl and unsymmetrical *meso*-phenyl substitution affects not only the quantitative characteristics of dissociation of the complexes but also the kinetic relationships of the process.

A versatile procedure for preparing metal porphyrins [1] is the reaction of free porphyrin bases with salts of double-charged metal cations. This procedure allows preparation of complexes with the majority of natural and synthetic porphyrins under similar conditions. On the contrary, the conditions for the reverse reaction, dissociation of the complexes, vary within very wide limits: in some cases, the acidity of water or alcohol is sufficient to effect the dissociation, and in other cases sulfuric acid monohydrate is required. With variation of the metal cation, the thermodynamic and kinetic stabilities of metal porphyrins vary in parallel [2]. The series of kinetic stability were obtained for complexes of a synthetic porphyrin, tetraphenylporphine [2], and of natural pheophytin [2]. The kinetic stability of complexes of *p* and *d* metals with pheophytin in $AcOH–H_2SO_4$ varies within the range spanning seven orders of magnitude depending on the electronic structure and oxidation state of the metal.

The stability of porphine complexes depends to a still greater extent on substituents in the *meso*- and β-positions. For example, octa-β-ethylporphine forms a stable complex with Pb(II) [4], whereas attempted synthesis of the related *meso*-tetraphenylporphine complex results in formation of a mixture of two complexes: that of Pb(II) with the reduced form of tetraphenylporphine (*meso*-tetraphenylchlorin) and that of Pb(IV) with tetraphenylporphine [5]. The effect of porphine substitution on the stability of the complexes was not studied systematically.

In this study we examined the reactivity toward acids of Cu(II) complexes with highly substituted (in the *meso*- and β-positions) porphine ligands (**I**–**IV**). The kinetics of dissociation of complexes **V**–**VIII** was studied previously [6–8]. Thus, we obtained the stability data for a full series of Cu(II) complexes with octaethylporphines differing in the degree of *meso*-substitution with phenyl groups.



I–**VIII**

I, $R^1 = CH_3$, $R^2 = C_6H_5$, $R^3 = R^4 = R^5 = H$; **II**, $R^1 = C_2H_5$, $R^2 = R^3 = C_6H_5$, $R^4 = R^5 = H$; **III**, $R^1 = C_2H_5$, $R^2 = R^3 = R^4 = C_6H_5$, $R^5 = H$; **IV**, $R^1 = CH_3$, $R^2 = R^3 = R^4 = R^5 = C_6H_5$; **V**, $R^1 = C_2H_5$, $R^2 = C_6H_5$, $R^3 = R^4 = R^5 = H$; **VI**, $R^1 = C_2H_5$, $R^2 = R^4 = C_6H_5$, $R^3 = R^5 = H$; **VII**, $R^1 = C_2H_5$, $R^2 = R^3 = R^4 = R^5 = C_6H_5$; **VIII**, $R^1 = C_2H_5$, $R^2 = R^3 = R^4 = R^5 = H$.

Complexes **I** and **II** do not decompose in glacial acetic acid at 298 K and on heating; complex **III** dissociates very slowly, with the conversion half-time of 30 days. On adding small amounts of 100% H_2SO_4 to acetic acid, porphyrins **I**–**III** (CuP) dissociate at measurable rates in accordance with Eq. (1):

$$CuP + 4H^+ \longrightarrow H_4P_2^+ + Cu^{2+}. \qquad (1)$$

The occurrence of reaction (1) causes changes in the electronic absorption spectra of the complexes in the course of dissociation. An example for complex **II** is shown in Fig. 1. The presence of well-defined iso-

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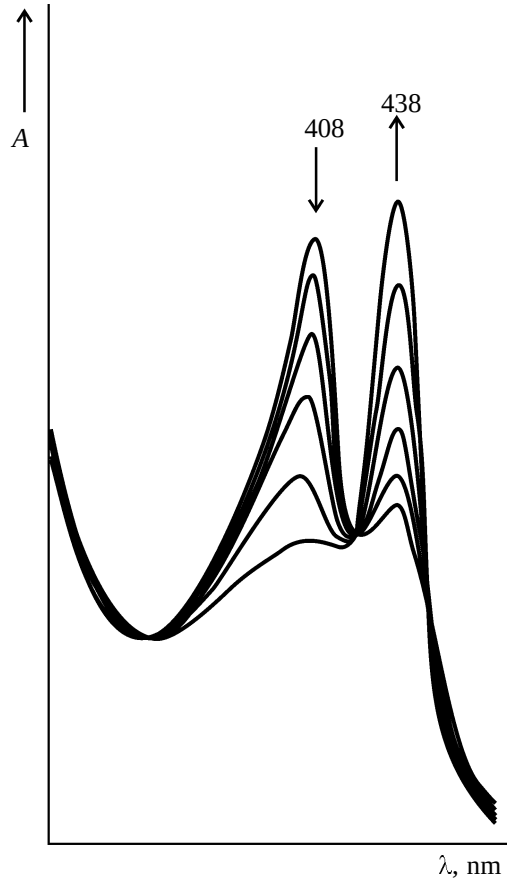


Fig. 1. Variation of the electronic absorption spectrum of complex **II** in the course of dissociation in AcOH–0.004 M H_2SO_4 (293 K).

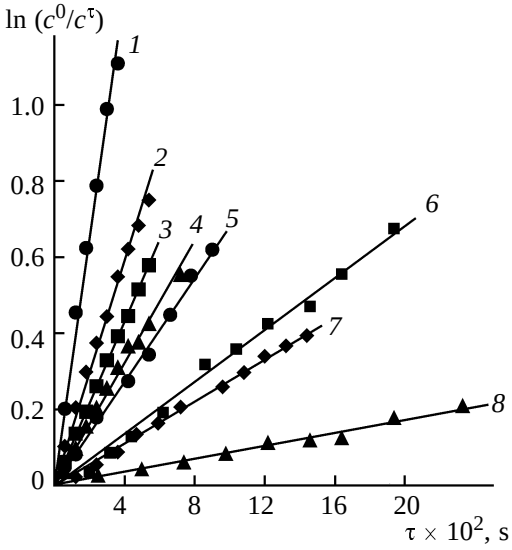


Fig. 2. Kinetic curves [$\ln(c^0/c^\tau)$ vs. time τ] of dissociation of complexes (*1*, *2*) **III**, (*3*–*5*, *7*) **II**, and (*6*, *8*) **I**. c_1^0, M: (*1*) 0.00033, (*2*) 0.00016, (*3*, *5*) 0.003, (*4*) 0.004, (*6*) 0.100, (*7*) 0.002, (*8*) 0.025. *T*, K: (*1*, *2*, *5*, *7*) 298, (*3*) 308, (*4*) 288, (*6*) 303, and (*8*) 313. (c_1^0) Initial H_2SO_4 concentration; approximation quality $R^2 > 0.98$.

bestic points (λ_{max} 386, 425, and 471 nm) is indicative of the coexistence of two colored species in the complex–acid system throughout the process. The electronic absorption spectra in the UV–visible range allow the initial and final compounds to be identified as the starting metal porphyrin and the porphyrin double-protonated at the nitrogen atoms, respectively. The linear plots $\ln(c^0/c^\tau) = f(\tau)$ (Fig. 2; c^0 and c^τ are the concentrations of the complexes in the initial time and in time τ, respectively) show that reaction (1) is first-order with respect to the metal porphyrin. The corresponding apparent rate constants k_{app} are given in Table 1. For each of complexes **I**–**III**, as for the previously studied complexes **IV**–**VIII**, the dissociation rate grows with an increase in the H_2SO_4 concentration. However, the dependence of the reaction rate on the initial concentration of H_2SO_4 in AcOH for copper porphyrins **I**–**VIII** is different, suggesting different reaction mechanisms.

For complexes **II** and **III**, k_{app} is a nonlinear function of the H_2SO_4 concentration (Fig. 3), fairly adequately described by a power function (2). In Eq. (2), the parameters $const_1$ and $const_2$ have the sense of the true rate constant k and the reaction order n with respect to the acid:

$$k_{app} = const_1(c_1^0)^{const_2} = k(c_1^0)^n, \quad (2)$$

where c_1^0 is the initial H_2SO_4 concentration.

When plotted in the log–log coordinates, Eq. (2) gives a linear correlation (R^2 0.996–0.998) with a slope close to 2. The true rate constants calculated for $n = 2$ and the corresponding activation parameters are given in Table 2, together with the true second-order (with respect to c_1^0) rate constants for complexes **V** and **VI**, calculated from the k_{app} values given in [6, 7].

The experimentally found kinetic equation (3) for complexes **II** and **III** is as follows:

$$-dc_2/d\tau = kc_2(c_1^0)^2, \quad (3)$$

where c_2 is the concentration of copper porphyrin.

In the case of **I**, the slope of the correlation between $\log k_{app}$ and $\log c_1^0$ corresponds to the reaction order with respect to c_1^0 of 1.5 (Fig. 5a). The fractional reaction order with respect to the acid concentration indicates that the kinetic equation for the dissociation of **I** is more complex. A linear correlation observed in the coordinates k_{app}/c_1^0–c_1^0 (Fig. 5b) allows us to write the following equations for the rate constant and rate of dissociation of complex **I**:

Table 1. Apparent rate constants of dissociation of Cu(II) complexes **I**–**IV** with *meso*-phenyloctaalkylporphyrins in $AcOH–H_2SO_4$

Comp. no.	$c^0_{H_2SO_4}$, M	T, K	$k_{app} \times 10^3$, s^{-1}
I	0.025	323	0.11 ± 0.01
		313	0.070 ± 0.006
		303	0.046 ± 0.004
		298	0.037 ± 0.001
	0.050	323	0.26 ± 0.02
		313	0.19 ± 0.01
		303	0.13 ± 0.01
		298	0.108 ± 0.002
	0.075	323	0.65 ± 0.05
		313	0.42 ± 0.02
		303	0.25 ± 0.02
		298	0.193 ± 0.015
	0.100	323	0.97 ± 0.09
		313	0.60 ± 0.04
		303	0.35 ± 0.02
		298	0.25 ± 0.02
II	0.002	308	0.51 ± 0.04
		298	0.32 ± 0.04
		288	0.20 ± 0.03
	0.003	308	1.07 ± 0.04
		298	0.68 ± 0.03
		288	0.42 ± 0.04
	0.004	308	1.99 ± 0.06
		298	1.26 ± 0.07
		288	0.84 ± 0.04
	0.005	308	2.7 ± 0.2
		298	1.8 ± 0.1
		288	1.20 ± 0.05
III	0.00015	308	2.1 ± 0.2
		298	1.5 ± 0.1
		293	1.1 ± 0.1
	0.00025	298	5.1 ± 0.4
		293	3.4 ± 0.2
		288	2.1 ± 0.1
	0.00033	298	8.4 ± 0.4
		293	5.9 ± 0.4
		288	3.8 ± 0.3
	0.00041	288	6.6 ± 0.6
IV	0	298	Unstable

$$k_{app} = k_1c_1 + k_2(c^0_1)^2, \quad (4)$$

$$-dc_2/d\tau = [k_1c^0_1 + k_2(c^0_1)^2]c_2. \quad (5)$$

It follows from the linear dependences $k_{app}/c^0_1–c^0_1$ (Fig. 5b) that k_2 exceeds k_1 by more than an order of magnitude (Table 3).

Taking into account the spectrophotometric data, we can suggest the following scheme of successive transformations (6)–(9) describing overall reaction (1):

$$CuP + H_2SO_4 \xrightarrow[\text{slowly}]{k_1} [CuH_2P]^{2+} + HSO_4^{2-}, \quad (6)$$

$$[CuH_2P]^{2+} + 2H_2SO_4 \xrightarrow[\text{fast}]{k_2} H_4P^{2+} + 2HSO_4^- + Cu^{2+}, \quad (7)$$

$$H_2SO_4 + AcOH \underset{}{\overset{K_1}{\rightleftharpoons}} AcOH_2^+ + HSO_4^-, \quad (8)$$

$$HSO_4^- + AcOH \underset{\text{improbable}}{\overset{K_2}{\rightleftharpoons}} AcOH_2^+ + SO_4^{2-}. \quad (9)$$

The kinetic equation for the slow step has the form

$$-dc_2/d\tau = kc_2c_1, \quad (10)$$

where c_1 is the equilibrium concentration of H_2SO_4.

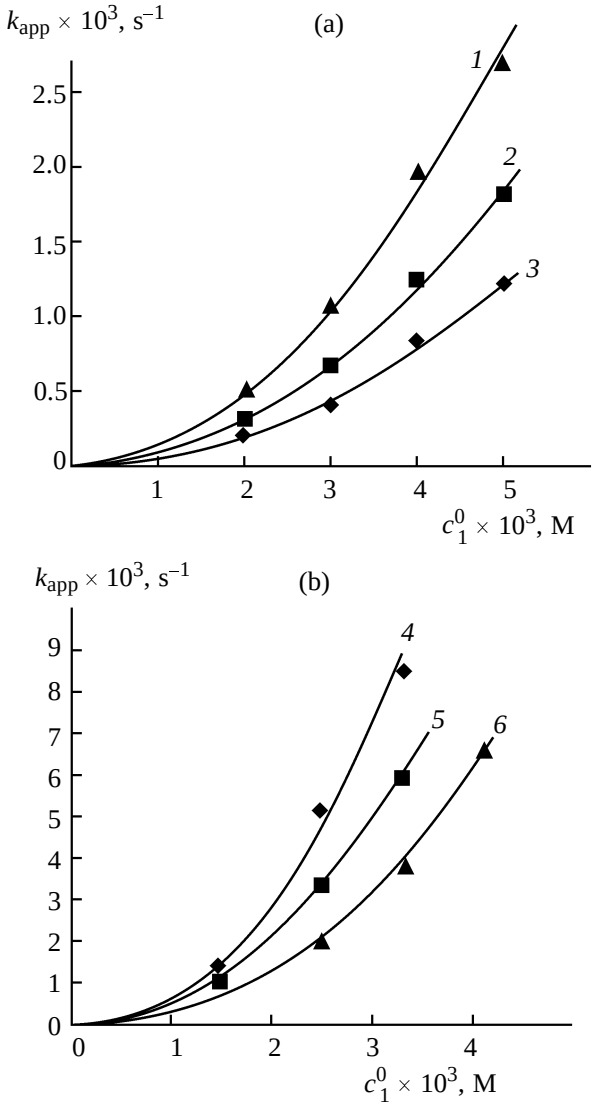


Fig. 3. Plots of k_{app} vs. c^0_1 for complexes (a) **II** and (b) **III**. T, K: (*1*) 308, (*2*, *4*) 298, (*5*) 293, and (*3*, *6*) 288 ($R^2 > 0.995$).

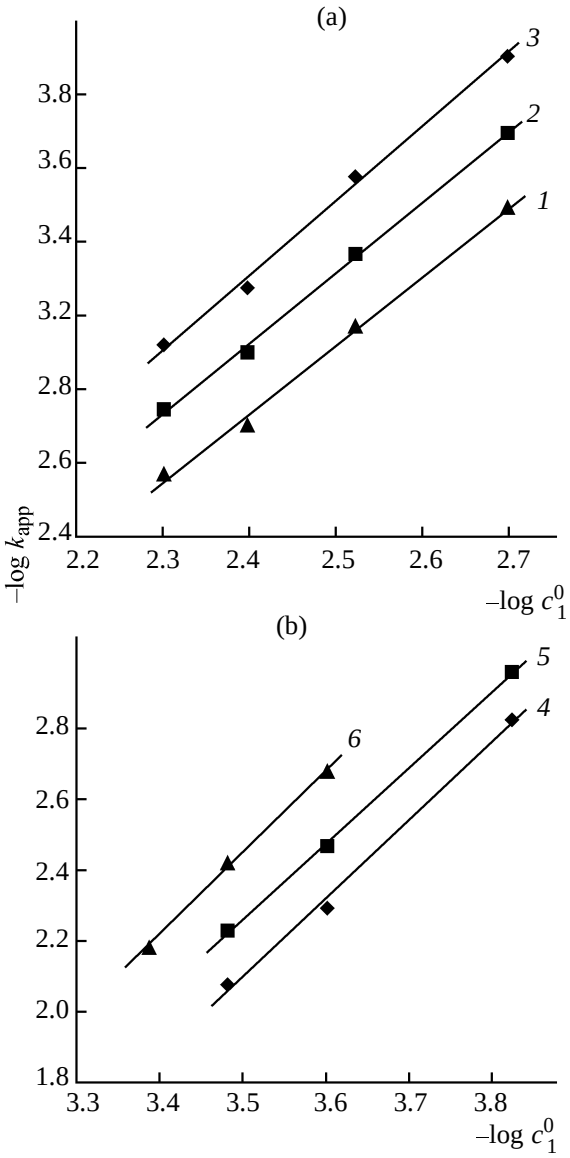


Fig. 4. Plots of $\log k_{app}$ vs. $\log c_1^0$ for complexes (a) **II** and (b) **III**. *T*, K: (*1*) 308, (*2*, *4*) 298, (*5*) 293, and (*3*, *6*) 288 ($R^2 > 0.995$).

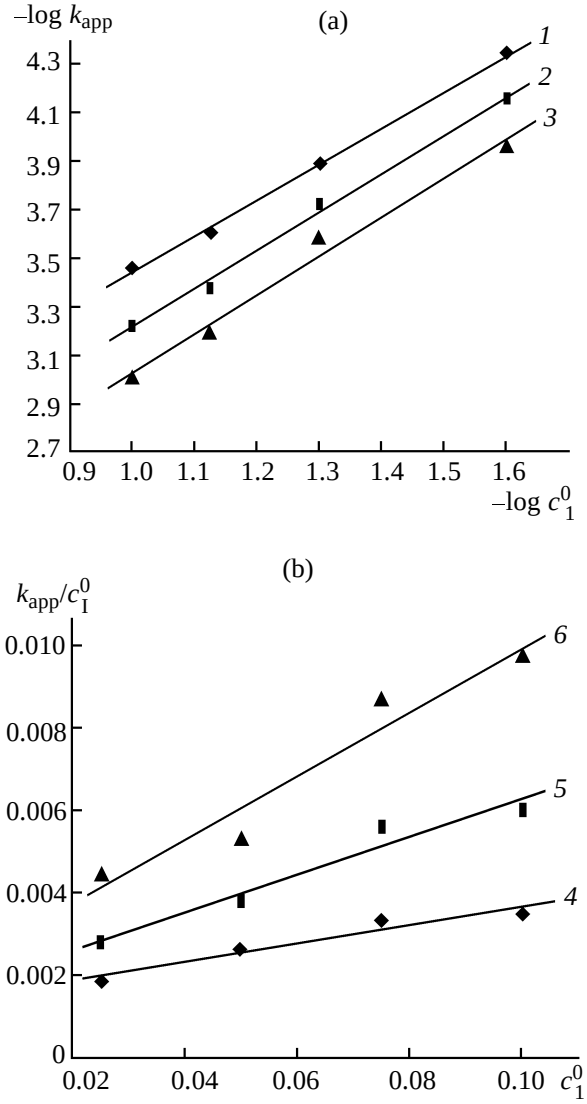


Fig. 5. Plots of (a) $\log k_{app}$ vs. $\log c_1^0$ and (b) k_{app}/c_1^0 vs. c_1^0 for complex **I**. *T*, K: (*1*, *6*) 303, (*2*, *5*) 313, and (*3*, *4*) 323 [R^2 (*1*, *2*) 0.99, (*3*) 0.98, (*4*) 0.93, (*5*) 0.95, and (*6*) 0.94].

From the equation for the constant of equilibrium (8), we obtain

$$c_1 = (1/K_1)(c_3)^2, \quad (11)$$

where c_3 is the equilibrium concentration of $AcOH_2^+$.

Taking into account (11), Eq. (10) can be transformed into

$$-dc_2/d\tau = k_1(1/K_1)c_2(c_3)^2. \quad (12)$$

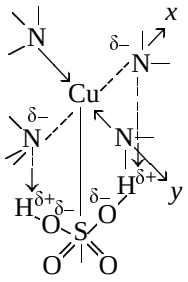
At low concentrations of H_2SO_4 in AcOH (10^{-4}–10^{-3} M), equilibrium (8) is virtually completely shifted to the right, i.e., c_1^0 is approximately equal to the equilibrium concentration of $AcOH_2^+$. Thus, Eq. (12) is identical to the experimental kinetic equation (3) for complexes **II** and **III**, and the constant k in Eq. (3) is equal to k_1/K_1. From the known value of K_1 (pK_1 4.3 [9]), we can calculate the rate constants for the limiting step (6): k_1^{298} 3.83×10^{-3} and 3.71 for complexes **II** and **III**, respectively.

The spectra in Fig. 1, the lack of the spectrum of the intermediate complex $[CuH_2P]^{2+}$ with the bidentate coordination of the macrocycle in the system of the electronic absorption spectra of the reaction mix-

Table 2. Kinetic parameters of the dissociation of complexes **II**–**VI** in the mixed solvent AcOH–H_2SO_4

Comp. no.	c_1^0, M	T, K	k, l mol^{-1} s^{-1}	E_a, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
II	0.002–0.005	308	120 ± 3		
		298	77 ± 3	33 ± 1	–105 ± 3
		288	49 ± 2		
III	0.00015–0.00041	298	(74 ± 3) × 10^3		
		293	(52 ± 3) × 10^3	52 ± 2	14 ± 6
		288	(36 ± 3) × 10^3		
V	0.05–0.15	313	0.15 ± 0.02		
		303	0.08 ± 0.02	51 ± 4	–105 ± 13
		298	0.055 ± 0.02		
		293	0.04 ± 0.01		
VI	0.01–0.05	333	2.0 ± 0.2		
		323	1.1 ± 0.1		
		313	0.64 ± 0.05	33 ± 1	–150 ± 3
		303	0.38 ± 0.03		
		298	0.28 ± 0.01		

ture CuP–acid, and the low stability of such SAT complexes known from the literature [2] confirm that step (6) with transition state **IX** is the limiting step:



IX

The above-considered scheme of reactions (6)–(9) is apparently valid for complex **I** also. However, in going to a medium with a higher concentration of H_2SO_4, in which complex **I** dissociates (Table 1), it becomes necessary to take into account the concentation of molecular H_2SO_4 species in equilibrium (8). In this case, the starting complex **I** will decompose along two pathways:

$$\mathrm{CuP} \xrightarrow[k_1']{\mathrm{AcOH_2^+}} [\mathrm{CuH_2P}]^{2+} + \mathrm{AcO^-}, \qquad \mathrm{CuP} \xrightarrow[k_2']{\mathrm{H_2SO_4}} [\mathrm{CuH_2P}]^{2+} + \mathrm{SO_4^{2-}}. \quad (13)$$

The reaction rate will be determined in accordance with (14):

$$-dc_2/d\tau = (k_1'c_3 + k_2'c_1)c_2. \quad (14)$$

After transformations similar to those described above, taking into account Eq. (5), we obtain $k_1 = k_1'$, $k_2 = k_2'/K_1$, and $c_1^0 \cong c_3$. The latter fact indicates that, in the expression $c_1^0 = c_3 + c_1$, the equilibrium concentration of H_2SO_4 can still be neglected.

The above examples of the dissociation of metal porphyrins show that changes in the detailed mechanism of the process are associated with changes in the acid–base properties of the mixed solvent AcOH–H_2SO_4. In a wide range of solvent compositions, more significant changes in the kinetics of dissociation of metal porphyrins should be expected.

The reactivity (k^{298}) of copper complexes with *meso*-phenyl-substituted octaethylporphine increases with an increase in the number of phenyl groups. Indeed, as found previously [6, 7], complex **VIII** dissociates only on reaching the H_2SO_4 concentration in AcOH of 0.10 M. Complex **VIII** dissociates at a measurable rate even in 100% AcOH without H_2SO_4 additions (k_{app}^{298} 4.7 × 10^{-4} s^{-1}). Thus, the complexes can be ranked in the following order of decreasing kinetic stability (increasing k^{298}): **VIII** > **V** > **VI** > **II** > **III** > **VII**.

Table 3. Constants in Eq. (5) and activation parameters of the dissociation of complex **I**

T, K	k_1, l mol^{-1} s^{-1}	k_2, l^2 mol^{-2} s^{-1}
323	0.0022	0.078
313	0.0017	0.046
303	0.0014	0.023
E_a, kJ mol^{-1}	18 ± 3	49 ± 5
$\Delta S^{\neq}$, J mol^{-1} K^{-1}	–249 ± 8	–122 ± 17

Table 4. Electronic absorption spectra in $CHCl_3$ and R_f values for complexes **I**–**IV**

Comp. no.	λ_{max}, nm (log ε)	R_f
I	395 (4.97), 530 (4.33), 567 (4.44)	0.444
II	414 (5.48), 544 (4.15), 579 (4.08)	0.665
III	424 (4.94), 556 (4.12), 591 (3.93)	0.725
IV	430 (4.65), 568 (3.90)	0.595

[a] Alufol, eluent hexane–benzene, 1 : 1.

This order shows that a decrease in the kinetic stability is due to the electron-withdrawing properties of phenyl substituents. The phenyl substitution decreases the electron density on the bonds and atoms of the macroring and the strength of the N→Cu donor–acceptor bonds. This conclusion is confirmed by the relationship between the activation parameters of the complexes. For the reactions with isoentropic activation (complexes **II** and **V**), the activation energy increases with an increase in the stability of the complex. For **VI**, in accordance with the stability order, we could expect an intermediate value of E_a between the values for **II** (33 kJ mol^{-1}) and **V** (51 kJ mol^{-1}). However, actually E_a for **VI** is very low because of sharply decreased $\Delta S^{\neq}$ (increased role of solvation of the transition state). Complex **III** surpasses in stability only **VII**. However, its dissociation is characterized by high E_a. This complex dissociates in a medium with minor additions of H_2SO_4 (~10^{-4} M), in which the concentration of charged species is low. Apparently, this accounts for the decreased role of solvation of the transition state (positive $\Delta S^{\neq}$) and increased E_a.

It could be expected that the electronic effect of the *meso*-phenyl substitution in the above series will result in increased contribution of the Cu→N π-dative bonding to the stability of the complexes. However, actually this is not the case. Apparently, the geometric factor in substitution should also be taken into account along with the electronic effects of phenyl groups. According to single crystal X-ray diffraction studies [10, 11] and optimization of the molecular geometries by the ZINDO 1 method [6] taking into account the π-dative interaction of the metal cation with the porphyrin ligand, the coordination center of octaethylporphine remains planar on introduction of one phenyl substituent. Upon further *meso*-substitution, the deformation of the macroring grows, and the structure of the complex of tetraphenyl-substituted octaethylporphine becomes crimped. With an increase in the deformation of the aromatic macroring, the conditions for π-dative bonding Cu→N get worse, which results in destabilization of the complexes.

The steric effect of phenyl substituents also follows from the comparison of the kinetic stabilities of complex **II** and its symmetrically substituted isomer **VI**. The rates of dissociation of **II** and **VI** are equal at different concentrations of H_2SO_4 in AcOH: in the case of **VI**, the H_2SO_4 concentration ensuring the same dissociation rate is higher by a factor of 15.

Octamethylporphine, its *meso*-phenyl derivatives, and their copper complexes are very poorly soluble in organic solvents; some of them are virtually insoluble. Therefore, experiments in solution were possible only with monophenyl- and tetraphenyl-substituted octamethylporphine (complexes **I** and **IV**). The stability of these compounds in solutions appeared to be similar to the stability of the related octaethylporphine derivatives. Tetraphenyl-substituted complexes **IV** and **VII** decompose at room temperature in 100% AcOH containing no H_2SO_4 additions. Monophenyl-substituted complexes **I** and **V** dissociate at equal rates in 0.05–0.1 M solutions of H_2SO_4 in AcOH.

In dissociation of the compounds of the octaethylporphine series (**II**, **III**, **V**, **VI**) in the mixed solvent, the limiting step is first-order with respect to H_2SO_4 [Eq. (10)]. Contrastingly, in dissociation of the compounds of the octamethylporphine series (with **I** as example), the kinetic equation for the limiting step [Eq. (14)] includes, along with c_1, also the $[AcOH_2^+]^1$. The increased order with respect to the acid reagent in the latter case is apparently due to the increase in the basicity of the macroring and coordinated nitrogen atoms in going from ethyl to methyl substituents.

EXPERIMENTAL

Metal porphyrins **I**–**IV** were prepared by the reaction of $CuAc_2 \cdot H_2O$ (analytically pure grade) with the corresponding porphyrins in refluxing DMF for 20–30 min and were isolated by extraction with chloroform and repeated washing of the chloroform solution with water. The compounds were purified by column chromatography on Al_2O_3 (Brockmann grade II) with $CHCl_3$ as eluent. The purity of the complexes was judged from the absence of changes in the electronic absorption spectra after successive purification steps (Table 4). The required porphyrins were synthesized by A.S. Semeikin as described in [12, 13].

Solutions of H_2SO_4 in AcOH were prepared by adding an accurately weighed portion of sulfuric acid monohydrate into the required amount of AcOH. Acetic acid (chemically pure grade) was dehydrated by stepwise freezing–thawing. Sulfuric acid monohydrate was prepared from 30% oleum (chemically pure grade) and concentrated H_2SO_4 (chemically pure grade) with conductometric monitoring.

The rates of reactions of **I**–**III** with acids were determined spectrophotometrically. The electronic absorption spectra of the solutions were recorded on Hitachi U-2000 and SF-26 spectrophotometers with a temperature-controlled cell. The accuracy of the temperature control was ±0.1 K. The variations of the optical density of solutions of **I**–**III** in a proton-donor solvent in the course of thermostating were monitored at a working wavelength in the vicinity of the absorption maximum of the released porphyrin ligand.

The apparent (k_{app}) and true (k) rate constants and the reaction order with respect to proton-donor species (n) were determined with the Microsoft Excel program by optimization of the dependences $\ln(c^0/c^\tau)-\tau$ and $k_{app}-c_1^0$, respectively. The activation energies were found with the Arrhenius equation. The activation entropies were calculated with the basic equation of the transition state theory, transformed to the following form [14]:

$$\Delta S^{\neq} = 19.11\log k^T + E_a/T - 19.1\log T - 205. \quad (15)$$

ACKNOWLEDGMENTS

The study was made within the framework of the Integrated Program of the Russian Academy of Sciences "Purposeful Synthesis of Substances with the Preset Properties and Development of Functional Materials Based on Them" and was supported by the RF President Grant (no. MK-531.2003.4).

REFERENCES

1. Adler, A.D., Longo, F.R., Kampas, F., and Kim, J., *J. Inorg. Nucl. Chem.*, 1970, vol. 32, no. 7, p. 2443.
2. Berezin, B.D., *Koordinatsionnye soedineniya porfirinov i ftalotsianina* (Coordination Compounds of Porphyrins and Phthalocyanine), Moscow: Nauka, 1978.
3. Lomova, T.N., Volkova, N.I., and Berezin, B.D., *Zh. Neorg. Khim.*, 1987, vol. 32, no. 4, p. 969.
4. Ferguson, J.A., Meyer, T.J., and Whitten, D.G., *Inorg. Chem.*, 1972, vol. 11, no. 11, p. 2767.
5. Molodkina, O.V., Lomova, T.N., and Mozhzhukhina, E.G., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1998, no. 10, p. 2052.
6. Suslova, E.E., *Cand. Sci. (Chem.) Dissertation*, Ivanovo, 2001.
7. Klyueva, M.E., Suslova, E.E., and Lomova, T.N., *Zh. Obshch. Khim.*, 2003, vol. 73, no. 8, p. 1377.
8. Suslova, E.E., Lomova, T.N., and Klyueva, M.E., Abstracts of Papers, *XXI nauchnaya sessiya Rossiiskogo seminara po khimii porfirinov i ikh analogov* (XXI Scientific Session of the Russian Workshop on the Chemistry of Porphyrins and Their Analogs), Ivanovo, 2000, p. 30.
9. Fialkov, Yu.A., *Rastvoritel' kak sredstvo upravleniya khimicheskim protsessom* (Solvent as a Means for Controlling a Chemical Process), Moscow: Znanie, 1988.
10. Sparks, L.D., Medforth, C.J., Park, M.-S., Chamberlain, J.R., Ondrias, M.R., Senge, M.O., Smith, K.M., and Shelnutt, J.A., *J. Am. Chem. Soc.*, 1993, vol. 115, no. 2, p. 581.
11. Renner, M.W., Barkigia, K.M., Zhung, Y., Medforth, C.J., Smith, K.M., and Fajer, J., *J. Am. Chem. Soc.*, 1994, vol. 116, no. 19, p. 8582.
12. Dudkina, N.S., Shatunov, P.A., Kuvshinova, E.M., Pukhovskaya, S.G., Semeikin, A.S., and Golubchikov, O.A., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 12, p. 2042.
13. Klyueva, M.E., Lomova, T.N., Berezin, B.D., and Semeikin, A.S., *Zh. Neorg. Khim.*, 2003, vol. 48, no. 8, p. 1365.
14. Lomova, T.N., *Doctoral (Chem.) Dissertation*, Ivanovo, 1990.