Structure of Phenyl Derivatives of Octaethylporphyrin and Dissociation Kinetics of Their Mn³⁺, Co²⁺, and Cu²⁺ Complexes in Acetic Acid

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Abstract—Octaethyl-, 5-phenyloctaethyl-, 5,15-diphenyloctaethyl-, 5,10,15,20-tetraphenyloctaethyl, and dodecaphenylporphyrins were prepared, and their geometries were optimized by the method of molecular mechanics. The deformation of the porphyrin macroring grows as the number of phenyl groups is increased. The dissociation kinetics of the manganese, cobalt, and copper complexes of the porphyrins in solutions of sulfuric acid in acetic acid were studied. The kinetic parameters of the dissociation of metal porphyrins were analyzed in relation to the porphyrin structure and nature of the metal.

Kinetic studies of formation and dissociation of copper complexes with octaethylporphyrin I and its 5-phenyl (II), 5,15-diphenyl (III), and 5,10,15,20-tet-raphenyl (IV) derivatives, and also with dodecaphenylporphyrin V, showed that the reaction kinetics very strongly depends on the extent of deformation of the porphyrin macroring.



 $\begin{array}{l} R^1 = Et, \ R^2 = R^3 = R^4 = R^5 = H \ (\mathbf{I}); \ R^1 = Et, \ R^2 = Ph, \\ R^3 = R^4 = R^5 = H \ (\mathbf{II}); \ R^1 = Et, \ R^2 = R^4 = Ph, \ R^3 = R^5 = \\ H \ (\mathbf{III}); \ R^1 = Et, \ R^2 = R^3 = R^4 = R^5 = Ph \ (\mathbf{IV}); \ R^1 = R^2 = \\ R^3 = R^4 = R^5 = Ph \ (\mathbf{V}). \end{array}$

The molecular-mechanics calculations (MM^+ force field, see figure) suggest that macrocycle **I** is virtually planar. In **II**, the β -carbon atoms of the first, third, and fourth pyrrole rings in the porphyrin core deviate by 0.1, 0.3, and 0.25 Å, respectively. In **III**, the β -carbon atoms of the first and third pyrrole rings deviate upwards, and those of the second and fourth pyrrole rings, downwards from the least-squares plane by up to 0.55 Å. In **IV**, this deviation reaches 1.4 Å. Thus, the calculations show that the deformation of the aromatic tetrapyrrole macroring grows as the number of bulky peripheral substituents is increased.

The dissociation kinetics of the copper (CuP), cobalt (CoP), and manganese [(AcO)MnP] complexes of I-V were studied in solutions of H_2SO_4 in acetic



Deviation of the carbon and nitrogen atoms of the porphyrin macroring from the mean plane drawn through four nitrogen atoms: (a) **I**, (b) **II**, (c) **III**, and (d) **IV**. The atom numbering is shown for **IV** as example.

Porphyrin	E, kJ mol ⁻¹	λ, ^a nm	$k_{\mathrm{app}} imes 10^3$, s ⁻¹					
			288 K	298 K	308 K	318 K	328 K	
Ι	35.7 ± 1.3	559	_		0.12 ± 0.02	0.18 ± 0.01	0.281 ± 0.018	
II	27.7 ± 0.1	562	_	$0.12\pm\!0.02$	0.178 ± 0.016	$0.25\pm\!0.04$	-	
III	22.1 ± 0.7	563	—	$0.61\pm\!0.03$	0.81 ± 0.03	$1.07\pm\!0.03$	-	
IV	$18.2\pm\!0.7$	562	—	3.6 ± 0.2	4.5 ± 0.2	5.7 ± 0.3	_	
V	—	574	b					
CoP								
Ι	56 ± 2	556	_	0.99 ± 0.02	2.00 ± 0.03	4.15 ± 0.15	-	
II	38 ± 2	533	_	1.65 ± 0.16	2.76 ± 0.05	$4.57\pm\!0.12$	-	
III	34.5 ± 0.4	540	1.60 ± 0.1	2.60 ± 0.2	4.11 ± 0.17	_	_	
IV	29.4 ± 0.3	569	3.87 ± 0.13	5.80 ± 0.2	8.61±0.19	_		
V	_	b						
(AcO)MnP ^c								
Ι	139.1 ± 1	549	-	-	0.302 ± 0.024	1.71 ± 0.11	8.30 ± 0.3	
II	125 ± 1	559	_	-	0.45 ± 0.02	2.07 ± 0.16	8.9 ± 0.21	
III	116 ± 1	564	_	-	0.591 ± 0.027	2.4 ± 0.17	9.4 ± 0.14	
IV	80 ± 0.7	578	2.22 ± 0.03	6.85 ± 0.13	19.20 ± 0.11	_	-	
V	_	_			_D	I	I	

Kinetic parameters of dissociation of copper, cobalt, and manganese complexes of porphyrins I-V in acetic acid containing 2 wt % H_2SO_4

^a Analytical wavelength. ^b The reaction is instantaneous in CH_3CO_2H . ^c H_2SO_4 content 10 wt %.

acid. The H_2SO_4 content was 2% for CuP and CoP and 10% for (AcO)MnP. All the metal complexes MP dissociate in these proton-donor media to form the double-protonated species H_4P^{2+} :

$$MP + 4H^+ \longrightarrow M^{2+} + H_4 P^{2+}.$$
(1)

The electronic absorption spectra of the reacting systems exhibit clear isobestic points: 566, 578, 567, and 597 nm for CuP; 508, 513, 516, and 518 nm for CoP; 555, 572, 454, and 667 nm for (AcO)MnP (data for I–IV, respectively). The kinetic experiments were performed at a ~100-fold excess of H_2SO_4 relative to MP, which allowed calculations of the apparent rate constants (k_{app}) by Eq. (2):

$$k_{\rm app} = (1/\tau) \ln \left[(A_0 - A_\infty) / (A_\tau - A_\infty) \right],$$
 (2)

where A_0 , A_{τ} , and A_{∞} are the optical densities of solutions at the initial moment, at time τ , and after reaction completion, respectively. The activation energy *E* was calculated by Eq. (3):

$$E = 8.3T_1T_2/(T_2 - T_1)\ln(k_2/k_1).$$
(3)

The kinetic parameters of dissociation of CuP, CoP, and (AcO)MnP are listed in the table.

lations for I-V with the kinetic parameters of dissociation of the corresponding Mn³⁺, Co²⁺, and Cu²⁺ complexes in the binary solvent CH₃CO₂H–H₂SO₄ shows that, as the extent of deformation of the porphyrin macroring grows, the dissociation rate constant increases and the activation energy decreases. The complexes of the most deformed dodecaphenylporphyrin V [3] instantaneously dissociate even in straight CH₃CO₂H.

Comparison of the results of MM⁺ structural calcu-

It is known that deformation of the porphyrin macroring decreases its aromaticity and increases the π -electron density on the central nitrogen atoms [4–6], with a sharp increase in the basicity of the porphyrins [7]. When metal complexes of **I**–**V** are formed, the deformation becomes somewhat weaker, but the pattern as a whole remains the same [8]. Hence, as the distortion of the planar structure of the metal porphyrin increases, the M–N bonds become more accessible for the attack of solvated proton, and the complex as a whole becomes less stable.

As for the influence of the central cation, the dissociation rate of the metal complexes increases in the order Mn(I-V) < Cu(I-V) < Co(I-V). As expected, the complexes of triple-charged manganese appeared to be the most stable in proton-donor media, which is

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 73 No. 4 2003

due to the high strength of the Mn–N covalent bonds. The higher stability of the copper complexes, as compared to cobalt complexes, is due to the tendency of the Cu²⁺ d^9 cation to form square planar complexes [9] fitting the geometry of the porphyrin ligands. The Co²⁺ d^7 cation tends to form octahedral complexes [9]. Apparently, when the Co–N bonds are attacked by a solvated proton, the released solvent molecules (CH₃CO₂H) solvate the metal cation, facilitating dissociation.

EXPERIMENTAL

Chemically pure grade acetic acid was dehydrated by refluxing with the calculated amount of acetic anhydride for 20 h and distilled with a Vigreux column. The water content in the solvent, determined by Fischer titration, was 0.03%. Sulfuric acid monohydrate was prepared by saturation of 95% H_2SO_4 with oleum; the water content was monitored potentiometrically.

Octaethylporphyrin I, 5-phenyloctaethylporphyrin II, 5,10-diphenyloctaethylporphyrin III, 5,10,15,20tetraphenyloctaethylporphyrin IV, and dodecaphenylporphyrin V were prepared according to [1].

Copper(II), cobalt(II), and manganese(III) complexes of porphyrins I-V were prepared by refluxing porphyrins with excess $Cu(OAc)_2$, $Co(OAc)_2$, and $Mn(OAc)_3$ in DMF. The metal porphyrins were purified by chromatography on Al_2O_3 (Brockmann grade III, eluent chloroform). The purity of the complexes was checked by electronic absorption spectroscopy and TLC.

The kinetics of solvoprotolytic dissociation of the metal porphyrins in acetic acid containing H_2SO_4 was studied spectrophotometrically (SF-46 and Specord M-400 devices, quartz cells with ground-glass stoppers). In all the systems, clear isobestic points were observed. The experiments were performed at 288–

328 K. The temperature fluctuations in the temperature-controlled chamber did not exceed ± 0.1 K.

The structural calculations were performed by the method of molecular mechanics (MM⁺). The deviations of the carbon atoms of the porphyrin macroring from the least-squares plane drawn through four N atoms are given in the figure.

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