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Kinetics of Complexation of *meso*-Diphenyl-Substituted Alkylporphyrins with Zinc Acetate in Acetonitrile

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Abstract—Kinetics of interaction of diphenyl-substituted porphyrins and their derivatives with substituents in the phenyl fragments with zinc acetate in acetonitrile solution is studied. The effect of the solvent on the rate of coordination is shown. Kinetic parameters of complexation are calculated.

The kinetics of porphyrin complexation with metal salts in nonaqueous solutions has been studied in [1–3]. The use of the metal complexes in various branches of science and technique (for example, as catalysts and semiconductors) is of interest [1].

Porphyrin molecules (H_2P) show their biological and catalytic activities only in combined state in metal complexes. Formation of metalloporphyrins is accompanied by the removal of two protons from two NH groups, almost complete destruction of the coordination sphere of the initial metal salt, and by the formation of a fundamentally new coordination sphere with extremely strong metal–porphyrin interaction [1].

Properties of metalloporphyrins depend on the nature of the substituents bonded to the porphyrin ring and of the metal, which coordinates the donor atoms of the macromolecule. The mechanism of transfer of the electronic effects of the substituents to the reaction center of the molecule is still unclear; further investigation of coordination properties of porphyrins is necessary.

The purpose of this work was to study $Zn(Ac)_2$ complexation with phenyl-substituted porphyrins in the medium of a weakly coordinated solvent (in the 288–318 K range).

EXPERIMENTAL

Synthesis of substituted alkylporphyrins was performed according to the following procedures.

5,15-Bis(2'-nitrophenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-buthylporphine (a mixture of atropoisomers) (**I**) was prepared by condensation of 3,3'-dibuthyl-4,4'-dimethyldipyrrolylmethane with *o*-nitrobenzaldehyde according to the procedure reported in [4]. The yield was 60%; R_f(silufol)—0.22, 0.29 (1 : 1 benzene–hexane); electronic absorption spectrum [λ_{max}, nm (logε)]: 632 (3.62); 579 (3.91); 546 (3.90); 512 (4.23); 411 (5.24) (chloroform).

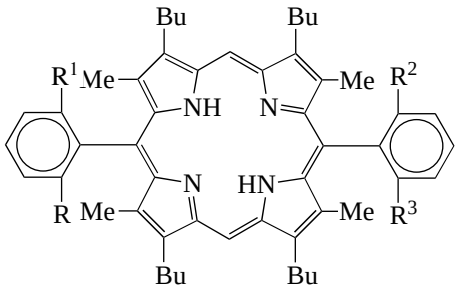
5,15-Bis(2'-aminophenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-buthylporphine (a mixture of atropoisomers) (**II** and **III**). A portion of complex **I** (0.5 g, 0.6 mmol) was stirred with a solution of $SnCl_2 \cdot 2H_2O$ (2.5 g, 11 mmol) in 20 ml of concentrated hydrochloric acid and 20 ml of methanol for 10 h; the resulting dark green solution was poured into a solution of KOH (20 g) in 50 ml H_2O. After cooling, the solution was filtered off, the resulting solid was washed with water, dried and chromatographed on Al_2O_3 (Brockman III type of activity, eluent $CHCl_3$). The dark red zone was concentrated, and aminoporphyrin was precipitated with petroleum ether. The yield was 410 mg (86%); R_f (silufol)—0.3, 0.48 (chloroform); electronic absorption spectrum [λ_{max}, nm (logε)]: 625 (3.50); 574 (3.92); 541 (3.85); 509 (4.26); 410 (5.33) (chloroform).

The mixture of atropoisomers was separated by double chromatography on Al_2O_3 (Brockman III type of activity, eluent benzene).

5α,15β-Bis(2'-aminophenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-buthylporphine (II). R_f (silufol)—0.83 (benzene); electronic absorption spectrum [λ_{max}, nm (logε)]: 626 (2.58); 575 (3.94); 542 (3.77); 508 (4.16); 410 (5.23) (chloroform).

5α,15α-Bis(2'-aminophenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra-*n*-buthylporphine (III). R_f (silufol)—0.4 (benzene); electronic absorption spectrum [λ_{max}, nm (logε)]: 625 (3.50); 574 (3.92); 541 (3.85); 509 (4.26); 410 (5.33) (chloroform).

5,15-diphenyltetramethyltetrabutylporphine (IV) was prepared as reported elsewhere [4].



I: R = R^2 = NO_2,

R^1 = R^3 = H or R = R^3 = NO_2,

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Selected kinetic parameters of formation of metalloporphyrins in acetonitrile

Porphyrin	k_v, s^{-1} mol^{-1} l*				E_a, kJ/mol	$\Delta S^{\neq}$, J/(mol K)
	288	298	308	318		
I	–	4.72	10.34	20.66	57 ± 6	–49 ± 5
II	3.37	5.44	7.61	9.92	26 ± 3	–156 ± 16
III	3.19	4.85	6.73	9.59	28 ± 3	–146 ± 15
IV	8.03	12.89	20.2		34 ± 3	–118 ± 12
V	2.30	3.41	5.79		34 ± 3	–129 ± 13

* Accuracy of k_v determination is not less than 10%.

$R^1 = R^2 = H$ (mixture of atropoisomers);

II: $R = R^2 = NH_2$, $R^1 = R^3 = H$;

III: $R = R^3 = NH_2$, $R^1 = R^2 = H$;

IV: $R = R^1 = R^2 = R^3 = H$.

Acetonitrile (AN) was purified and dried as reported elsewhere [5]. Reagent grade zinc acetate $Zn(Ac_2)$ was recrystallized from glacial acetic acid as described in [6].

Kinetic measurements were carried out on a Hitachi-U-2000 spectrophotometer with a temperature-controlled cell section by standard technique [7]. The virtual reaction rate constants (k_v) were calculated from the equation of the pseudofirst order.

RESULTS AND DISCUSSION

It was found in the systematic study of complexation [1] that the reaction:

$$MX_m \cdot (n-m)Solv + H_2P \cdot pSolv \longrightarrow MP \cdot qSolv + 2HX \cdot 2Solv + (n-m+p-q-2r)Solv \quad (1)$$

proceeds via a consistent mechanism with associative–dissociative activation of the NH bond, and its kinetic parameters drastically depend on the structure of the porphyrin molecule and on the metal and solvent nature.

Depending on the donor–acceptor properties of substituents in the porphyrin macrocycle, the rate of complexation may change by hundreds of times; however, it is difficult to foresee the changes in reactivity of the porphyrin ligand versus the substituent nature.

Kinetics of reaction (1) depends on the solvating ability of the solvent. Composition and stability of a solvate shell of both porphyrin and transition state in the reaction change with the change of the substituent nature.

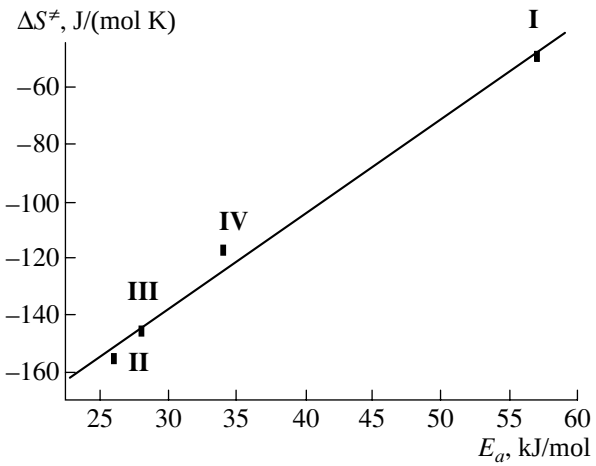
The experimental data (table) allow to find the effect of substitution in the *meso*-position and in the phenyl rings of the substituent on the kinetic parameters of reaction (1).

Introduction of two phenyl fragments in the *meso*-position of the porphyrin molecule results in acceleration of reaction (1) as compared to unsubstituted alkylporphyrin 3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphine $H_2P(CH_3)_4(C_4H_9)_4$ (**V**) without phenyl rings in the *meso*-position of the ring [2]. This may occur due to the electron-accepting properties of the phenyl fragments, connected with the conjugated π-system of the porphyrin; they appear as weakening of the N–H bond in the pyrrol rings, which decreases the electronic density on the annular nitrogen atoms. Weakening of the N–H bond, as a rule, increases the rate of porphyrin coordination with metal salts. A decrease in the electronic density on the annular nitrogen atoms may also decelerate complexation. If the reaction rate increases upon introduction of the electron-accepting substituent, the main factor of the process is the weakening of the N–H bonds of the annular nitrogen atoms. In the poorly coordinated solvent AN, the electron-accepting substituents decelerate the reaction of coordination [3]. Introduction of amino groups in the phenyl fragments of the porphyrin molecule also decreases the rate of complexation. Probably, protonation of amino groups proceeds in the solution.

The protonated amino group is the electron acceptor; this also decreases electronic density on the ternary nitrogen atoms. Experimental data show that different arrangement of the substituents (α, β) and (α, α) has no significant effect on the state of the π-electronic structure of the macrocycle.

Low values of entropy change ($\Delta S^{\neq}$) suggest strengthening of solvation of the transition state of the system as compared to its initial state. The resulting values of E_a and $\Delta S^{\neq}$ allow us to propose that solvation ability of the solvent has significant effect on the complexation rate. The experimental data show that complex **I** in the transition state is less solvated [$\Delta S^{\neq}$ = –49 J/(mol K)] as compared to complexes **II** and **III**, where solvation of the transition state is –156 or –146 J/(mol K), respectively.

For all systems under study, energy of formation of the transition state in complexation is compensated by solvation of the system with the solvent molecules. Linear character of this dependence (figure) for all porphy-



Kinetic compensation effect of complexation of porphyrins with $Zn(Ac)_2$ in acetonitrile.

rins investigated point to similar mechanisms of complexation.

Therefore, in the poorly coordinated (acetonitrile) solvent, the limiting stage of complexation is the detachment of the protons at the pyrrol nitrogen atoms. In addition, the solvating properties of acetonitrile have significant effect on coordination.

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