# Dissociation Kinetics of Cobalt and Zinc β-Octabromo-*meso*-Tetraphenyland β-Octaethyl-*meso*-Tetraphenylporphyrin Complexes

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**Abstract**—Kinetics of solvoprotolytic dissociation of zinc and cobalt porphyrin complexes with a porphyrin macrocycle distorted to different extents ( $\beta$ -octaethyl-*meso*-tetraphenylporphyrin and  $\beta$ -octabromo-*meso*-tetraphenylporphyrin) have been studied in binary proton-donating solvents. The main factor decreasing the stability of the porphyrin complexes is the distortion of the planar structure of the macrocycle. The reactivity of the cobalt porphyrins is governed by both structural and electronic effects.

DOI: 10.1134/S0023158407020024

## INTRODUCTION

Porphine, the progenitor of the porphyrin family, has the rigid planar structure of a tetrapyrrole macrocycle [1]. However, numerous porphyrins have recently been synthesized in which the pyrrole macrocycle is distorted (in particular, by many bulky substituents at the periphery of the molecule) [2]. The studies of coordination properties of these compounds revealed a strong correlation between the degree of distortion of the porphyrin macrocycle and the formation rate and stability of metal porphyrins in proton-donating media [3, 4]. It is of interest to study the stability of spatially distorted porphyrin complexes in proton-donating media because the cobalt and iron complexes are active in hydrocarbon oxidation yielding a carboxylic acid as the major product or as a by-product [5].

In the present work, the dissociation kinetics of cobalt and zinc complexes with spatially distorted porphyrins, namely,  $\beta$ -octaethyl-*meso*-tetraphenylporphyrin (I) and  $\beta$ -octabromo-*meso*-tetraphenylporphyrin (II), was studied in binary proton-donating solvents.



## **EXPERIMENTAL**

The solvents were purified using standard procedures [6–8]. Acetic acid (reagent grade) was dehydrated by fractional freezing and was then distilled. Trifluoroacetic acid (pure grade) was mixed with concentrated sulfuric acid in a ratio of 10 : 1. Dehydrated CF<sub>3</sub>COOH was distilled from the mixture, and the fraction with the boiling point 72–73°C was again distilled. Benzene (reagent grade) was dehydrated with calcium chloride and distilled. The residual water content, determined by Fischer titration, did not exceed 0.03% for acetic acid and 0.01% for benzene.

The electronic absorption spectra and the solvoprotolytic dissociation rates of the metal porphyrins were measured on a Specord M-400 spectrophotometer in temperature-controlled ground-glass-stoppered cells at T = 288-338 K. The temperature changes did not exceed ±0.1 K. The experimental procedure and kinetic calculations are described elsewhere [9].

The initial concentration of a metal porphyrin in kinetic experiments was  $(1-2) \times 10^{-5}$  mol/l. The concentration of trifluoroacetic acid in acetic acid solutions was varied between 0.02 and 0.2 mol/l for the cobalt complex of porphyrin I and between 2 and 7 mol/l for the cobalt complex of porphyrin II. The concentration of acetic acid in its binary mixtures with benzene was varied between 10 and 100 vol %.

The porphyrins were synthesized by standard procedures [3, 10]. The zinc and cobalt complexes were synthesized by reacting a porphyrin with excess metal acetate in boiling dimethylformamide. The porphyrins were purified by chromatography on alumina (activity grades II and III). The eluent was a chloroform-benzene mixture, whose composition was chosen with con-



**Fig. 1.** Time dependences of  $\ln(c_0/c_i)$  for the dissociation of the zinc  $\beta$ -octabromo-*meso*-tetraphenylporphyrin complex ( $c_{\text{ZnP}} = 1.2 \times 10^{-5} \text{ mol/l}$ ) at (1) 288, (2) 298, and (3) 308 K in the acetic acid–benzene binary solvent (1 : 4 vol/vol).

sideration for the individual features of the porphyrins. The purity of the porphyrins was checked by electronic absorption spectroscopy against earlier reported data [3, 10, 11].

#### **RESULTS AND DISCUSSION**

As a rule, the dissociation of porphyrin complexes in individual proton-donating solvents cannot be studied by kinetic methods. The use of mixed solvents (an acetic acid-benzene mixture for the Zn complexes and an acetic acid-trifluoroacetic mixture for the cobalt porphyrins) and the variation of their composition make it possible to establish the acidity necessary for dissociation to occur at the rate optimum for kinetic measurements. The porphyrin complexes with *d*-metals dissociate in proton-donating media to form a solvated metal cation (or a solvated salt) and a metal porphyrin (MP) in free or protonated form [1, 12–14]

$$MP + 4H_{solv}^{+} \longrightarrow M_{solv}^{2+} + H_4P^{2+}.$$

The dissociation of the complexes was studied in at least 1000-fold excess of the acid over the metal porphyrin. This made it possible to determine the partial order of the dissociation reaction with respect to MP, which was equal to unity in all cases. The first-order apparent rate constants are invariable within the exper-

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**Fig. 2.** log  $k_{app}$  versus log  $c_{CF_3COOH}$  for the cobalt  $\beta$ -octaethyl-*meso*-tetraphenylporphyrin complex at 308 K in the acetic acid-trifluoroacetic acid system. The slope of the straight line is  $1.02 \pm 0.05$ ; the correlation coefficient is 0.995.

imental error and show no systematic trend. This is clear from the plots of  $\ln(c_0/c_i)$  versus t (where  $c_i$  and  $c_0$ are the current and initial concentrations of the metal porphyrin, respectively, and t is time) for the zinc complex of porphyrin II in the C<sub>6</sub>H<sub>6</sub>–CH<sub>3</sub>COOH medium, which are shown as a typical example in Fig. 1.

The plot of  $\ln k_{app}$  versus  $\ln c_{CF_3COOH}$  is presented in Fig. 2. These data suggest that the dissociation of the cobalt complex of porphyrin I is first-order with respect to trifluoroacetic acid:

$$dc_{\rm ZnP}/dt = kc_{\rm ZnP}c_{\rm CF_2COOH}$$

The dissociation of the cobalt complex of porphyrin **II** in binary mixtures of acetic and trifluoroacetic acids proceeds at a measurable rate at much higher  $CF_3COOH$  concentrations of 2 to 7 mol/l, when the system is essentially nonideal. The empirical equation relating the apparent rate constant to the  $CF_3COOH$ concentration has the form

$$\log k_{\rm app} = (8.7 \pm 0.8) + (4.9 \pm 0.5) \log c_{\rm CF_3COOH}.$$

Numerous studies of the kinetics of dissociation of coordination compounds of phthalocyanine and porphyrins in proton-donating media [1] demonstrated that the transition state of the reacting system is reached upon the dissociation of two M–N bonds of the metal porphyrin.

Because the acetic acid-benzene system is nonideal toward the dissociation of the zinc complexes of porphyrins **I** and **II** at all temperatures examined, the dependences of  $\ln k_{app}$  on  $\ln c_{ACOH}$  are nonlinear. Using the activity coefficients of acetic acid in its binary mixtures with benzene, which were calculated from data available from the literature [15], we constructed  $\ln k_{app}$ - $\ln a_{ACOH}$  plots. Such a plot for the reaction of the zinc complex of porphyrin **II** at 298 K is shown in



Fig. 3.  $\ln k_{app}$  versus  $\ln a_{ACOH}$  at 298 K for the zinc  $\beta$ octabromo-meso-tetraphenylporphyrin complex in the benzene-acetic acid system.

Fig. 3. The slope of the straight line is unity at acetic acid concentrations of 0.1 to 0.7. The break in the plot is likely due to a change in the solvating power of the medium, since acetic acid in this system is not only a proton-donating species but also a solvating agent. Thus, the dissociation of the zinc complexes of porphyrins I and II is first-order with respect to the acetic acid activity. Therefore, the labile zinc complexes of porphyrins I and II dissociate under the action of CH<sub>3</sub>COOH molecules and the transition state of this reaction is reached already upon the dissociation of one M–N bond of the metal porphyrin.

The dissociation of this bond results in substantial spatial strains in the coordination center MN<sub>4</sub>H<sup>+</sup> caused by steric and electrostatic effects. Evidently, the monoprotonated complex MHP<sup>+</sup><sub>solv</sub> has a distorted macrocyclic structure. This facilitates the dissociation of a second M–N bond even if the metal porphyrin is initially planar. In the case of low-stability porphyrin complexes, which are spatially distorted even in the initial state, the distortion of the MHP<sup>+</sup><sub>solv</sub> fragment increases to such an extent that the other M-N bonds dissociate, obviously beyond the peak of the activation barrier.

In the acetic acid-benzene composition range examined, the zinc tetraphenylporphyrin complex without  $\beta$ -substituents dissociates very slowly. The extrapolation of the data plotted in Fig. 3 to 100% acetic acid leads to  $k_{app} = 9 \times 10^{-3} \text{ s}^{-1}$  for the dissociation of the zinc complex of porphyrin **II**. This value is 50 times larger than that of the same constant for the zinc tetraphenylporphyrin complex [1]. Thus, the introduction of either eight electron-donating ethyl groups or eight electron-withdrawing bromine atoms into the  $\beta$ -positions of tetraphenylporphyrin destabilizes the zinc complexes of  $\hat{\mathbf{I}}$  and  $\hat{\mathbf{II}}$ . Therefore, the effect of these substituents is structural rather than electronic. It should be kept in mind that, in the series of undistorted Zn porphyrins, electron-withdrawing substituents stabilize the complex and electron-donating substituents destabilize the complex [1].

Tetraphenylporphyrin and its complexes with cations matching the size of the coordination cavity  $N_4$ have a nearly planar tetrapyrrole macrocycle [16, 17]. Porphyrin I and its complexes have a saddlelike conformation in which one pair of opposite pyrrole rings is below the mean plane of the macrocycle and the other pair is above this plane [17, 18]. The deviation of the  $\beta$ -carbon atoms from the mean plane of 24 atoms of the macrocycle is 110-130 nm. The calculations of the geometric parameters of porphyrins I and II performed using molecular mechanics methods (force field MM+) [4, 19, 20] also showed that these porphyrins have a saddlelike distorted macrocycle and the macrocycle of porphyrin II is more distorted due to the large covalent radius of the bromine atom. Therefore, it is not surprising that the Zn complexes of porphyrin **II**, which contains electron-withdrawing substituents (Br atoms), dissociate more rapidly than the complexes of porphyrin I, which contains eight electron-donating ethyl groups (Table 1).

The substitution of Br atoms for the eight ethyl groups in the complexes of the  $d^6$  cation Co<sup>2+</sup> (passing from I to II), as distinct from the complexes of the  $d^{10}$ cation Zn<sup>2+</sup>, results in a sharp decrease in the solvoprotolytic dissociation rate: the rate constant decreases by a factor of several thousands and the activation energy increases by 66 kJ/mol (Table 2). Evidently, in this case, reactivity is governed by both structural and electronic effects and the conjugation effect dominates over the I effect of the bromine atoms.

Table 1. Kinetic parameters of dissociation of the zinc(II) complexes of porphyrins I and II in the benzene–acetic acid binary solvent

Porphyrin	a <sub>AcOH</sub>	$k_{\rm app}^{288} \times 10^3$ , s <sup>-1</sup>	$k_{\rm app}^{298} \times 10^3$ , s <sup>-1</sup>	$k_{\rm app}^{308} \times 10^3,  {\rm s}^{-1}$	<i>E</i> , kJ/mol
<b>I</b> *	0.855	$1.59\pm0.04$	$2.31\pm0.04$	$3.24\pm0.07$	$26.1\pm0.2$
II**	0.855	$1.88\pm0.03$	$3.30\pm0.10$	$5.64\pm0.12$	$40.4\pm0.3$

\* $c_{I} = 1 \times 10^{-5}$  mol/l; the measurements were carried out at  $\lambda = 570$  and 692 nm. \*\* $c_{II} = 1 \times 10^{-5}$  mol/l; the measurements were carried out at  $\lambda = 613$  and 755 nm.

<b>Table 2.</b> Kinetic parameters of dissociation of the cobalt(II) complexes of porphyrins I and II in acetic acid with trifluoro-acetic acid additives at 298 K							
Porphyrin	c <sub>CF3COOH</sub> , mol/l	$\lambda_a$ , nm	$k_{\rm app} \times 10^4,  {\rm s}^{-1}$	<i>E</i> , kJ/mol			

Porphyrin	$c_{\rm CF_3COOH}$ , mol/l	$\lambda_a$ , nm	$k_{\rm app} \times 10^4$ , s <sup>-1</sup>	<i>E</i> , kJ/mol
<b>I</b> *	0.069	550	$65.8 \pm 0.1$	$15.7 \pm 0.7$
II**	5.2	446, 487	$0.59\pm0.04$	$81.8\pm0.5$

 $*c_{\mathbf{I}} = 1.1 \times 10^{-5} \text{ mol/l.}$ 

 $**c_{II} = 1 \times 10^{-5} \text{ mol/l.}$ 

Bromine atoms, which exert a +*C* effect, increase the electron density on the  $d_{z^2}$  orbital of the central cobalt cation, enhancing the reverse,  $\pi$ -dative Co–N interaction, resulting in a decrease in the effective negative charge on the nitrogen atoms of the ligands. This charge is attacked by a solvated proton, which causes a sharp decrease in the solvoprotolytic dissociation rate and an increase in the activation energy.

It should be mentioned in conclusion that, from the standpoint of stability in proton-donating media, the cobalt complexes of spatially distorted porphyrins can be used as catalysts of hydrocarbon oxidation.

## ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 03-03-96458r2003tschr-a.

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