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Complex Formation of Tetra(3,5-di-*tert*-butylphenyl)porphine with Copper(II) and Zinc(II) Acetates in Organic Solvents

M. B. Berezin[a], B. D. Berezin[a,b], and S. A. Syrbu[b]
[a] *Institute of Solution Chemistry, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045 Russia*
[b] *Ivanovo State University of Chemical Technology, Ivanovo, Russia*
E-mail: mbb@isc-ras.ru

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Abstract—The effect of accumulation of the *tert*-butyl groups in the phenyl rings of tetraphenylporphine on the complex formation rate of tetra(3,5-di-*tert*-butylphenyl)porphine (**I**) with copper(II), zinc(II), and cadmium(II) acetates in acetic acid and in a mixed ethanol–benzene solvent was studied by the chemical kinetics method with spectrophotometric monitoring. The activation characteristics of the complex formation were calculated. The complex with zinc was found to form three times more slowly that the copper complex. Benzene additives to the organic solvent decreased the reaction rate because of steric hindrance created by the benzene molecules that formed stable solvates with compound **I**.

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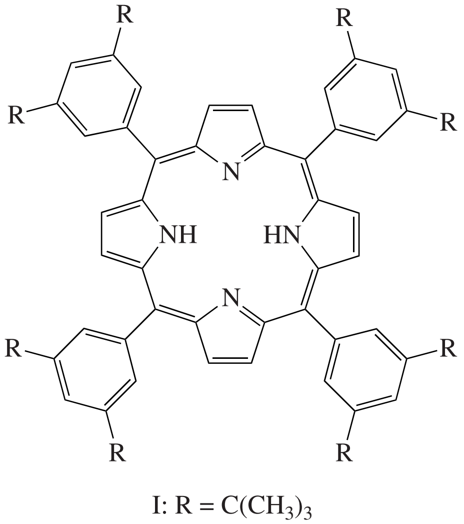
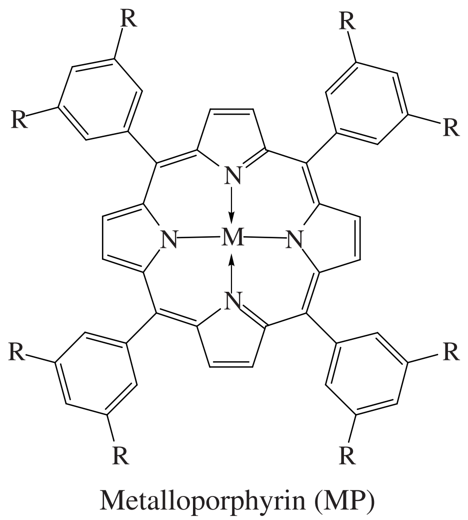
INTRODUCTION

Research in the area of the chemistry of porphyrins is still urgent and becomes more required due to the extension of their practical application. The synthesis of porphyrins with unusual physicochemical properties is widely used. The tetraphenylporphine derivatives remain to be most accessible among synthetic porphyrins. The metal complexes of these derivatives are applied as active components of new materials used in catalysis, biomonitoring and chemical monitoring, extraction, qualitative and quantitative analyses, nonlinear optics, and in diverse fields of molecular design and medicine [1–3]. Therefore, the study of the reactivity of new porphyrins remains urgent.

Tetra(3,5-di-*tert*-butylphenyl)porphine (**H_2P, I**), unlike tetraphenylporphine (**H_2TPhP, II**), has a branched system of hydrophobic (C_4H_9) substituents in the 3,5-positions of the phenyl rings. That is why, compound **I** is well soluble in nonpolar organic solvents (benzene, tetrachloromethane, cyclohexane, etc.) and is almost insoluble in polar solvents (alcohols, ketones, dimethylformamide, and others). Therefore, the complex formation of compound **I** was studied in glacial acetic acid (H_2P is soluble in CH_3COOH due to the formation of hydrogen bonds $-COOH\cdots N\leq$ and the protonated form of the ligand H_4P^{2+}, whose UV spectrum exhibits an absorption band at 655 nm, Fig. 1) and in an ethanol–benzene (1 : 1) mixed solvent.



I: R = $C(CH_3)_3$
II: R = H



Metalloporphyrin (MP)

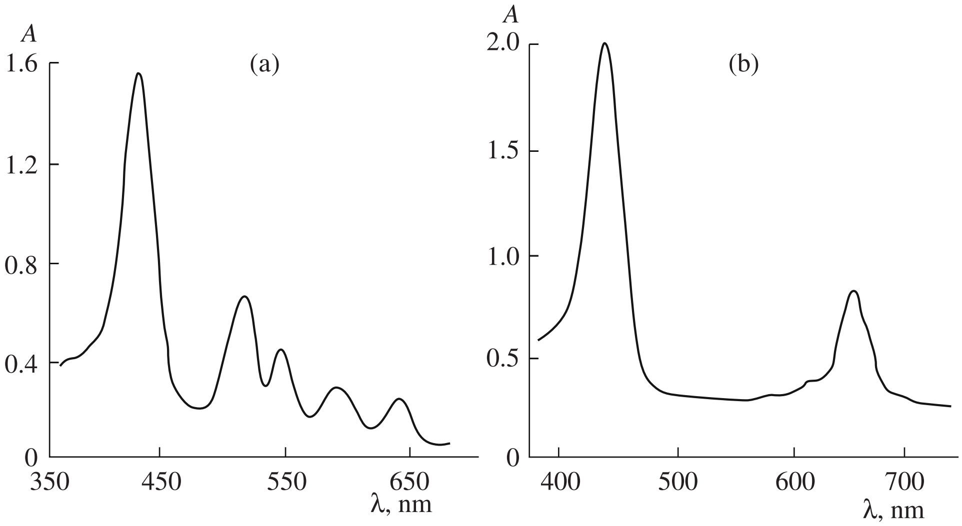


Fig. 1. UV spectrum of H_2P in (a) benzene and (b) acetic acid.

EXPERIMENTAL

Porphyrin **I** was synthesized by a described procedure [4]. After the major portion of the organic solvent was distilled off, the porphyrin was precipitated with alcohol, filtered off, washed on the filter with dimethylformamide, hot water, and acetone, and dried. The dry residue was dissolved in a minimum amount of benzene and twice chromatographed on alumina (Brockmann activity III) using benzene as the eluent. The eluate was evaporated, and the porphyrin was precipitated with methanol, filtered off, and dried at 100°C under reduced pressure. ^{1}H NMR ($CDCl_3$), δ (ppm): 9.03 s (8H, β-H), 8.22 s (8H, *o*-H), 7.90 s (4H, *n*-H), 1.64 s (72H, *t*-Bu), –2.55 s (2H, NH) (tetramethylsilane as the internal standard, Bruker AC 200 spectrometer). The salts and solvents for kinetic measurements were prepared by known procedures [5, 6].

The spectrophotometric method was used to study the formation of the metalloporphyrins. The absorbance was measured with SF-26 and Cary-300 spectrophotometers. The method of spectrophotometric monitoring the change in the concentrations of the colored porphyrin-ligand and metalloporphyrin formed is based on the linear dependence between the absorbance of the solution and the concentration of the substance

$$A = \varepsilon l c. \tag{1}$$

The following equation can be applied to the system of two colored substances (porphyrin–metalloporphyrin):

$$c^0/c_\tau = \frac{A_0 - A_\infty}{A_\tau - A_\infty}, \tag{2}$$

where A_0, A_τ, and A_∞ is the initial, current, and final absorbance, respectively; c is the porphyrin-ligand concentration.

The measurements were carried out at the wavelength near the absorption band maximum of the ligand or near the absorption band maximum of the metalloporphyrin (Fig. 2). The porphyrin-ligand concentration did not exceed (1–5) × 10^{-5} mol/l in all experiments. The salt concentration was ten and more times higher than the ligand concentration. Under these conditions, the systems studied obey the first reaction order with respect to the porphyrin and salt (Figs. 3, 4). In this case, the kinetic equation takes the form

$$-\frac{dc_{H_2P}}{dt} = k_{app} c_{H_2P} \tag{3}$$

or in the integral form with allowance for Eq. (2)

$$k_{app} = \frac{1}{\tau}\ln(c^0/c_\tau) = \frac{1}{\tau}\ln\frac{A_0 - A_\infty}{A_\tau - A_\infty}. \tag{4}$$

The units of the concentration are of no importance. Since the A value in Eq. (1) is proportional to c (mol/l), the porphyrin-ligand concentration was also expressed in mol/l.

The activation energy (***E$_a$***) was calculated from the Arrhenius plots of the reaction rate constants of metalloporphyrin formation vs. temperature. The activation entropy ($\Delta S^{\#}$) was calculated by the main equation of the transition state theory.

RESULTS AND DISCUSSION

Tetraphenylporphine and its numerous derivatives are among the most important porphyrins used in science and various areas of engineering and technology [1–3]. The fourfold phenylation of the *meso*-positions substantially changes the properties of the porphine itself due to the drawing back of the electron density from the –CH= methine bridges to the benzene ring.

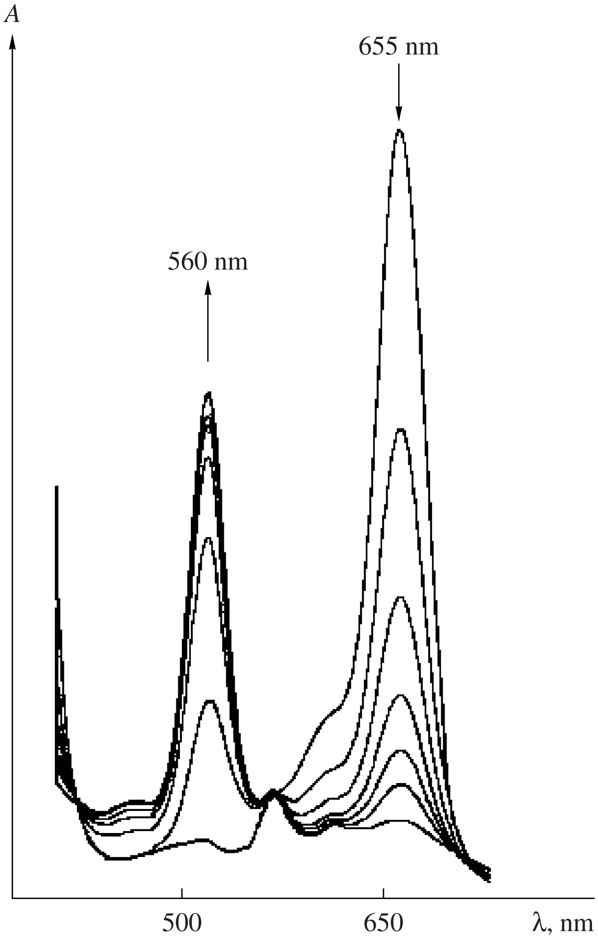


Fig. 2. Change in the UV spectrum during the formation of CuP in CH_3COOH.

The phenyl rings in compound **II** are σ-electronic acceptors (–*I* effect) toward the π system of the porphyrin macrocycle. As a result, the sixteen-membered chromophore of tetraphenylporphine is stabilized and the N–H bonds of the coordination site are polarized. As a consequence, the complex formation of H_2TPhP with the metal salts is accelerated

$$H_2TPhP + [MX_2(S)_{n-2}] \longrightarrow MTPhP + 2HX + S. \quad (5)$$

If M = Cu(II), S is ethanol, and X is the acetate ion, reaction (5) is fourfold accelerated compared to that of the porphine [7, 8]. Unlike the porphines substituted at the β-pyrrole positions, whose double protonation is accompanied by the hypsochromic shift of the long-wavelength band (λ_1) in the UV spectrum, tetraphenylporphine and its phenyl-substituted derivatives in the H_4TPhP^{2+} state manifest the bathochromic shift, which can be a result of the C_{meso}–C_{phenyl} bond extension in the $H_2TPh\,P^{(*)}_{(S)}$ singlet excited state. As a result, the benzene residues are conjugated with the macrocycle, which is retained in H_4TPhP^{2+}, but the C_6H_5 groups manifest the +*I* effect, and the extension of the π system of the chromophore is accompanied by the bathochromic shift of λ_1.

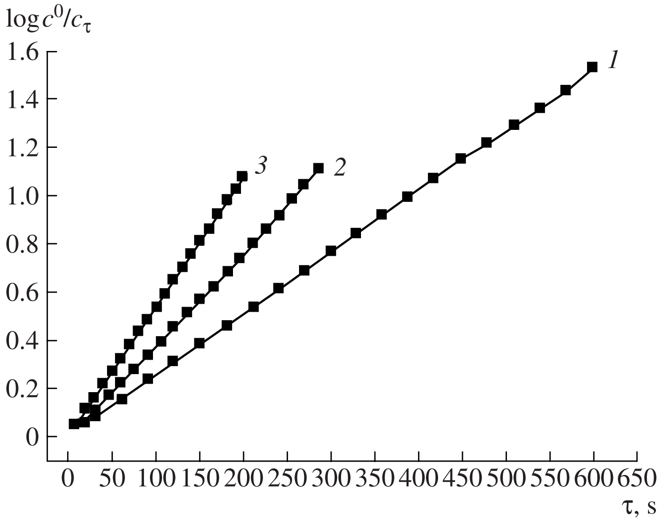


Fig. 3. Time plots of $\log c^0/c_\tau$ for the reaction of H_2P with $Cu(Ac)_2$ in acetic acid at 293.15 K and $c_{salt} \times 10^{-3}$: (*1*) 0.586, (*2*) 1.263, and (*3*) 2.55 mol/l.

Since the rates of complex formation with metals and their kinetic stability under the action of proton-donating solvents are practically significant, their detailed study is important. The kinetics and mechanisms of formation of the metalloporphyrins were analyzed [7, 8]. Their dissociation was considered [9]. It is shown in cited works that four factors exert a strong effect on the coordination properties of porphyrins with *d* metals: the strength of the M–N chemical bond, the macrocyclic effect [10–12], the electronic effects of substituents, and the solvation of transition states.

The influence of alkyl substitution in the phenyl residues on the properties of tetraphenylporphine remains almost unstudied [13]. There are few studies on tetra(*tert*-butylphenyl)porphyrins [14, 15]. Unlike the simple phenyl substitution of the *meso*-positions of the porphine for the C_6H_5 group (weak –*I* effect), the replacement by the $C_6H_3[3,5\text{-}C(CH_3)_3]_2$ group creates a strong positive inductive effect (+*I* effect). The latter enhances the basicity of the tertiary –N= atoms and the electron density on the N–H bonds. One should expect a decrease in the coordinative ability with respect to metal ions in porphine **I** and an increase in its basic properties according to the reaction

$$H_2P + 2CH_3COOH \rightleftharpoons H_4P^{2+} + 2CH_3COO^-. \quad (6)$$

Therefore, only H_2P reacts when reaction (5) occurs in an acetic acid medium. It is shown [15, 16] that H_4P^{2+} is incapable of coordinating metal ions. In addition to the electronic effects, steric effects of the substituents also prevent the occurrence of reaction (5) involving

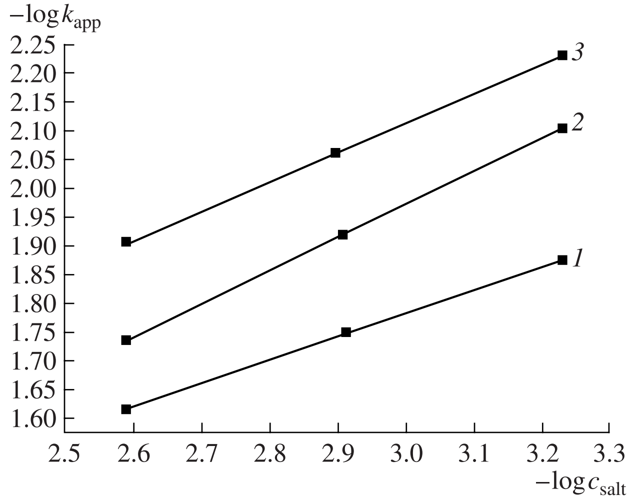


Fig. 4. Plots of $-\log k_{app}$ vs. $-\log c_{salt}$ for CuP formation at (*1*) 298, (*2*) 293, and (*3*) 288 K.

H_2P [17, 18] due to the shielding of the H_2N_4 reaction center [11].

It follows from the kinetic data (Table 1) that in an interval of the copper acetate concentrations of (2.55–0.586) × 10^{-3} mol/l the true rate constants ($\boldsymbol{k_v}$) correspond to bimolecular reaction (5) with H_2P and the second-order kinetic equation

$$-\frac{dc_{H_2P}}{dt} = k_v c_{H_2P} c_{MAc_2}. \quad (7)$$

In this case, the high concentration dependence of k_v is observed in the temperature interval from 288 to 298 K. Such a dependence is usually characteristic of the Zn, Co, and Ni salts in reaction (5) and, to a less extent, of the Cu salts and is caused by a change in the coordination sphere of the salt of the reactant (in the case, acetate MAc_2) with an increase in the concentration [7, 13]. It should be kept in mind that $CuAc_2$ in glacial acetic acid is dimerized [13].

In a solution of $CuAc_2$ with a concentration of 0.6 mmol/l, the rate constants for reaction (1) with H_2TPhP are 0.013 s^{-1} at 293 K [13], whereas for the reaction involving H_2P the rate constant is 0.0079 s^{-1}. The decrease in the rate for the reaction with H_2P is caused by the suppression of the acceleration of reaction (5) due to the +*I* effect of the *tert*-butyl groups, possibly, by a sharp decrease in the ratio of the concentrations of the reactive (H_2P) and nonreactive (H_4P^{2+}) forms due to protonation (6) rather than by the shielding of the H_2N_4 reaction center with the bulk "tops" of the $C(CH_3)_3$ groups. This conclusion is confirmed by the UV spectral data for H_2P in CH_3COOH (Fig. 1). The spectrum shows that the H_4P^{2+} concentration prevails over the H_2P concentration.

The low activation energies and entropies also show that CuP is formed via reaction (5) with H_2P and not with H_4P^{2+}. The decrease in the activation energy (Table 1) with an increase in the copper acetate concentration is due to the destabilization of $CuAc_2(CH_3COOH)_{n-2}$ and the loss of a part of the solvate shell (possibly, external). This is observed as a considerable decrease in the activation entropy.

The apparent rate constants ($\boldsymbol{k_{app}}$) for reaction (5) with $CuAc_2$ in glacial acetic acid with a 10% benzene additive were measured ($k_{app} = k_v c_{CuAc_2}$). They remain almost unchanged; i.e., the state of the reactants in reaction (5) is unchanged.

Unlike $CuAc_2(CH_3COOH)_{n-2}$, the coordination sphere of $ZnAc_2(CH_3COOH)_4$ in an interval of the chosen concentrations of (2.2–0.54) × 10^{-3} mol/l undergoes no changes. The first order with respect to the porphyrin and the first order with respect to the salt in reaction (8) of ZnP formation are rigidly fulfilled (Table 2)

Table 1. Kinetic parameters for the formation of CuP in CH_3COOH

T; E_a; $\Delta S^{\#}$	$c_{Cu(Ac)_2}$, mol/l					
	2.55 × 10^{-3}		1.26 × 10^{-3}		0.586 × 10^{-3}	
	k_{app}, s^{-1}	k_v, l s^{-1} mol^{-1}	k_{app}, s^{-1}	k_v, l s^{-1} mol^{-1}	k_{app}, s^{-1}	k_v, l s^{-1} mol^{-1}
288 K	0.0124 ± 0.00112	4.85	0.0088 ± 0.00071	6.94	0.0059 ± 0.00032	10.07
293 K	0.0184 ± 0.00152	7.20	0.0120 ± 0.00093	9.50	0.0079 ± 0.00088	13.53
298 K	0.0268*	10.53*	0.0199 ± 0.00120	15.77	0.0145 ± 0.00095	24.69
E_a, kJ/mol	55 ± 1		58 ± 1		64 ± 2	
$\Delta S^{\#}$, J mol^{-1} K^{-1}	–48 ± 10		–32 ± 7		–10 ± 5	

* Obtained by extrapolation.

Table 2. Kinetic parameters for the formation of ZnP in CH_3COOH

T; E_a; $\Delta S^{\#}$	$c_{Zn(Ac)_2}$, mol/l					
	2.098×10^{-3}		1.056×10^{-3}		0.540×10^{-3}	
	k_{app}, s^{-1}	k_v, l s^{-1} mol^{-1}	k_{app}, s^{-1}	k_v, l s^{-1} mol^{-1}	k_{app}, s^{-1}	k_v, l s^{-1} mol^{-1}
288 K	0.0062 ± 0.00075	2.94	0.0031 ± 0.00035	2.91	0.0016 ± 0.00012	2.94
293 K	0.0099 ± 0.00082	4.69	0.0049 ± 0.00052	4.66	0.0025 ± 0.00014	4.68
298 K	0.0141 ± 0.00120	6.74	0.0077 ± 0.00042	7.32	0.0041 ± 0.00039	7.64
E_a, kJ/mol	59 ± 5		66 ± 1		68 ± 1	
$\Delta S^{\#}$, J mol^{-1} K^{-1}	-39 ± 9		-15 ± 5		-7 ± 3	

Table 3. Kinetic parameters (k_{app}, s^{-1}; k_v, l s^{-1} l mol^{-1}) of the reactions of CuP, ZnP, and CdP formation in an ethanol–benzene (1 : 1) mixed solvent*

Salt ($c_{salt} \times 10^3$ mol/l)	298.15 K		308.15 K		318.15 K		328.15 K		338.15 K		E_A, kJ/mol	$\Delta S^{\#}$, J mol^{-1} K^{-1}
	$k_{app} \times 10^4$	k_v	$k_{app} \times 10^4$	k_v	$k_{app} \times 10^4$	k_v	$k_{app} \times 10^4$	k_v	$k_{app} \times 10^4$	k_v		
$Cu(CH_3COO)_2$ (2.87)	7.47	0.259	14.25	0.495	25.15	0.896					49 ± 1	-100 ± 15
$Zn(CH_3COO)_2$ (2.59)		0.027**			2.45	0.095	4.32	0.166	7.51	0.289	50 ± 1	-110 ± 25
$Cd(CH_3COO)_2$ (0.506)		0.0256**			0.73	0.144	1.62	0.326	3.49	0.689	70 ± 1	-49 ± 11
$Cd(CH_3COO)_2$ (2.57)		0.0288**	1.90	0.0739	5.18	0.202	12.58	0.489			79 ± 3	-16 ± 15

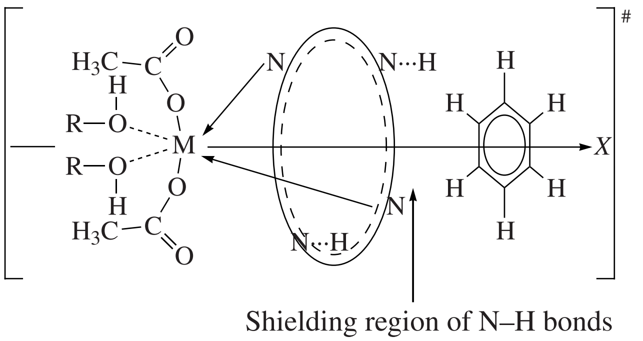
Notes: * Determination accuracy is ±5%.
** Obtained by extrapolation.

$$\begin{gathered} H_2P + [ZnAc_2(CH_3COOH)_4] \\ \rightleftarrows [H_2P\cdots ZnAc_2(CH_3COOH)_2]^{\#} \\ \text{Transition state} \\ \longrightarrow ZnP + CH_3COOH. \end{gathered} \tag{8}$$

The ZnP complex is formed threefold more slowly than CuP. This is typical of H_2TPhP and H_2P and also of all porphyrins studied to the present time. The introduction of eight *tert*-butyl groups in the 3,5-positions of the phenyl fragments of tetraphenylporphine decreases the complex formation rate by four times compared to that of H_2TPhP. This is much higher than the decrease observed for CuP. Therefore, the conditions of $ZnAc_2$ solvate coordination with H_2P are much less favorable than those in the case of $CuAc_2$. It is most likely that in reaction (8) zinc acetate experiences a substantial counteraction of the *tert*-butyl groups when the transition state is formed.

Reaction (5) with copper, zinc, and cadmium acetates in an ethanol–benzene mixture was carried out in the temperature interval from 308 to 338 K, because at 298 K this reaction proceeds too slowly (Table 3). The rate of CuP formation in this solvent is 40 times lower than that in acetic acid. The activation energy increases from 49 to 55 kJ/mol, and the activation entropy decreases by 52 J mol^{-1} K^{-1}, which is due to the stronger solvation of the transition state in an ethanol–benzene mixture. The rates of ZnP and CdP formation in this medium turned out to be tenfold lower than that of CuP formation and by 250 times lower than the rate in CH_3COOH (Tables 1, 2). It can be assumed that in a C_6H_6–C_2H_5OH (1 : 1) medium porphyrins, especially H_2T (3,5-di-*tert*-butylphenyl)porphine), decrease their reactivity because of the shielding of the H_2N_4 reaction center by the solvate shell of the benzene molecules strongly bound to the π system of the $C_{12}N_4$ macrocycle due to their π–π interaction. The composition and high stability of the $CuP \cdot C_6H_6$ and $ZnP \cdot C_6H_6$ crystal solvates were studied in several works including [15]. It can be assumed that the introduction of eight *tert*-butyl groups into H_2TPhP enhances this π–π interaction with benzene. For instance, the rates of tetraphenylporphine coordination by zinc acetate ($c = 2.22 \times 10^{-3}$ mol/l) in an ethanol–benzene (1 : 1) medium are documented [13]. It turned out that $k_v^{298} = 0.335$ s^{-1} l mol^{-1}, $E_a = 61$ kJ/mol, and $\Delta S^{\#} = -59$ J mol^{-1} K^{-1}; i.e., the coordination rate is an order of magnitude higher than that for H_2P. Thus, reaction (8) is inhibited in an ethanol–benzene mixed solvent due to the shielding of the coordination site by the *tert*-butyl groups and the solvate shell with the strongly bound benzene molecule.

It seems most probable that the benzene–porphyrin solvate destabilizes the transition state, creating hindrance for the cleavage of two N–H bonds and removal of protons to the solvent medium



The most expensive activation steps should be surmounted to surpass the transition state by the reacting system (porphyrin–salt): the removal of the N–H protons as H^{+}···S (S is C_2H_5OH) to the solution and the removal of two C_2H_5OH molecules from the solvate shell of metal acetates. The leaving ligands (two C_2H_5OH and CH_3COO^{-}) leave the formed metalloporphyrin behind the top of the potential barrier and meet no steric hindrance.

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