## Kinetics of the Dissociation of Transition Metal Complexes with α,α-Dipyrrolylmethene in Acetic Acid–Benzene as a Binary Proton-Donating Solvent

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**Abstract**—The kinetics of the dissociation of Co(II), Ni(II), and Zn(II) complexes with 4,4'-dibutyl-3,3',5,5'-tetramethyldipyrrol-2,2'-ylmethene was studied in acetic acid–benzene as a binary proton-donating solvent. The metal nature was found to affect the kinetic parameters of the process. Assumptions were made about the limiting step of the process and the effectiveness of *d* metal ions in the template synthesis of porphyrins from dipyrrolylmethenes.

Dipyrrolylmethenes have found wide application in preparative organic chemistry for the synthesis of artificial and natural porphyrins [1, 2]. The template synthesis of macrocyclic porphyrin complexes by reactions of metal ions with simpler ligands such as the linear diand tetrapyrroles proved to be highly effective. In such reactions, a metal ion serves as a matrix for orientation and fixing of initial polypyrrole ligands to facilitate the subsequent formation of macrocyclic tetrapyrrole molecules of porphyrin. Because d metal acetates are commonly used in the template synthesis of porphyrins, acetic acid accumulates in reaction products. The efficiency of the template synthesis of porphyrins is determined, to a large extent, by both the reactivity of dipyrrolylmethene toward different metal ions and the kinetic stability of the resulting metal complexes in mixed proton-donating solvents. Obviously, methods of template synthesis can be modified through a search for dipyrrolylmethene chelate complexes with an optimum kinetic stability. However, the dissociation kinetics of dipyrrolylmethene complexes in proton-donating media has not been described quantitatively to date.

In this study, the kinetic data on the dissociation of complexes  $ML_2$  (M = Zn(II), Ni(II), and Co(II); HL = 4,4'-dibutyl-3,3',5,5'-tetramethyldipyrrol-2,2'-ylmethene) in a binary AcOH-benzene solvent are discussed.



## **EXPERIMENTAL**

Complexes  $ML_2$  were prepared by complexation reaction between HL and metal acetates as described in [2]. The purity of the complexes obtained was confirmed by TLC on Silufol UV-254 plates, as well as by a good agreement of their electronic absorption spectra with the literature data [3].

Reagent-grade benzene was additionally purified as described in [4]; 100% AcOH was prepared by fractional thawing of glacial acetic acid. A fraction (about 300 ml) was withdrawn from 1000 ml of the frozen acid and melted the last. The water content of individual solvents did not exceed 0.02% (the Fischer method).

The dissociation kinetics of complexes  $ML_2$  was studied by the spectrophotometric method in a temperature range from 298 to 318 K. The electronic absorption spectra of pigments in solutions were recorded on a Specord M40 spectrophotometer in a thermostatically controlled ( $\pm 0.1$  K) cell.

According to the requirements in spectrophotometric analysis, the concentration of complexes was (1 to 2)  $\times 10^{-5}$  mol l<sup>-1</sup>, and the acid was taken in a great excess relative to a complex (from 0.0004 to 0.972 mol l<sup>-1</sup>). The concentration of a complex was checked by measuring the optical density of its solution at an operating wavelength close to the long-wavelength absorption peak of the complex. For excess acid relative to a complex, the effective rate constants of dissociation ( $k_{\rm eff}$ ) were calculated by the formally first-order equation

$$k_{\rm eff} = \frac{1}{\tau} \ln \frac{A_0 - A_\infty}{A_\tau - A_\infty},$$

where  $A_0$ ,  $A_{\tau}$ , and  $A_{\infty}$  are the optical densities of a solution of the complex at the initial point, at time  $\tau$ , and after completion of the reaction, respectively ( $A_{\infty}$  at the operating wavelength approaches zero). Optimization of  $k_{\text{eff}}$  and determination of standard deviations  $\rho$  were

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**Fig. 1.** Changes in the electronic absorption spectra of complexes  $ML_2$  (M = (a) Zn, (b) Ni, and (c) Co) during their dissociation in AcOH–benzene at 298.15 K and  $c_{AcOH}^0$  = (a) 0.6633, (b) 0.0012, and (c) 0.672 mol  $l^{-1}$ ;  $\tau = (1)$  0 and (2)  $\infty$  min (the other curves refer to intermediate times).

carried out by the least-squares method with the Microsoft Excel program. The activation energies of dissociation of complexes were calculated by the Arrhenius equation, and the entropy of activation in a wide temperature range was calculated through the use of the basic equation of the transition state theory, rewritten as

$$\Delta S^{\neq} = 19.1 \cdot \log k^{T} + \frac{E \pm \Delta E}{T} - 19.1 \log T - 205,$$

where  $k^T$  is the constant at temperature *T*, *E* is the energy of activation, and  $\Delta E$  is its mean absolute deviation. The numerical value of  $\Delta S^{\neq}$  was determined as its arithmetic mean over all the temperatures studied.

## **RESULTS AND DISCUSSION**

The dissociation of complexes  $ML_2$  ( $M = Co^{2+}$ ,  $Ni^{2+}$ , and  $Zn^{2+}$ ) in AcOH–benzene resulted in the decreasing intensity of their electronic absorption bands with simultaneous growth of the band of the protonated ligand (Fig. 1) [5]. This suggests that the following processes occur:

$$ML_2 + 2AcOH \longrightarrow M(AcO)_2 + 2HL,$$
$$HL + AcOH \longrightarrow AcOH \cdot HL.$$

The isosbestic points remain intact in the spectra because colored compounds exist in solution as two forms, namely, the complex and the protonated dipyrrolylmethene.

Our experimental data show that the dissociation rates of  $CoL_2$ ,  $ZnL_2$ , and  $NiL_2$  are proportional to the

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concentration of the complex  $c \pmod{l^{-1}}$ ; this dependence can be written as the first-order kinetic equation

$$\frac{dc}{d\tau} = k_{\rm eff} c_{\rm ML_2}$$

which is confirmed by linearization of the plots in  $\ln(c^0/c_{\tau})$  vs.  $\tau$  coordinates ( $\rho = 0.98-0.99$ ) (Fig. 2) and the constancy of the rate constants throughout the reaction. The effective rate constants determined from the linear plots of  $\ln(c^0/c_{\tau})$  vs.  $\tau$  (Fig. 2), as well as the energies and entropies of activation, are given in Table 1.

The overall reaction order was estimated with consideration of the data in [6-8]. In those studies, it was demonstrated that acetic acid in benzene solutions exists in monomolecular and dimeric forms and that a decrease in the concentration of AcOH shifts the equilibrium between these forms toward the monomer; the activity coefficient of the acid is close to unity. Data on the dependence of the activity coefficient on the concentration of acetic acid in  $C_6H_6$  in a temperature range from 298.15 to 318.15 K were taken from [8] and used in our additional calculations. The results obtained show that the activity coefficient of acetic acid in benzene in the concentration range studied is constant and equal to unity. Taking into account the low autoprotolysis constants of AcOH  $(10^{-10} \text{ to } 10^{-18})$  [6] and the low dielectric constant of benzene [9], one can assume that the monomolecular form of acetic acid is the main proton carrier in a proton-donating AcOH-benzene solvent in the concentration range under discussion. For this reason, the reaction order in acetic acid was determined by analyzing the dependence of the dissociation rate on the initial concentration of acetic acid in benzene (Fig. 3). This dependence for complexes  $CoL_2$ ,  $ZnL_2$ , and  $NiL_2$ 

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**Fig. 2.** Plots of  $\ln(c^0/c_{\tau})$  vs.  $\tau$  for the dissociation of ZnL<sub>2</sub> in

AcOH–benzene for  $c_{AcOH}^0$  (*T*, K) = (*1*) 0.3316 (298.15), (*2*) 0.4975 (303.15), (*3*) 0.6633 (313.15), and (*4*) 0.8955 (318.15) mol l<sup>-1</sup>.

is nonlinear and is well described by the power equation

$$k_{\rm eff} = {\rm const}_1 (c_{\rm AcOH}^0)^{{\rm const}_2}$$

In physical sense,  $const_1$  and  $const_2$  are the true rate constant  $k_v^T$  and the reaction order in acid, respectively. The latter constant was found to be two for all the pro-



**Fig. 3.** Plots of  $k_{\text{eff}}$  vs.  $c_{\text{AcOH}}^0$  in benzene for the dissociation of ZnL<sub>2</sub> at (*1*) 298.15, (*2*) 303.15, (*3*) 313.15, and (*4*) 318.15 K.

cesses studied ( $\rho = 0.999-0.987$ ). The true rate constants, the reaction order in acid, and the activation energies  $E_v$  and entropies  $\Delta S^{\neq}$  of dissociation of the complexes studied in a mixed AcOH-benzene solvent are given in Table 2.

Because the dissociation of complexes  $ML_2$  is a first-order reaction in the complex and a second-order reaction in acetic acid, its rate constant in the range of

$c_{\rm AcOH}^0$ , mol l <sup>-1</sup>		$k_{\rm eff} \times 1$	$E_{\rm l}$ [L mol <sup>-1</sup> ]	$\Delta S \neq I (m a   K)^{-1}$					
	298.15 K	303.15 K	313.15 K	318.15 K	<i>L</i> , KJ IIIOI	$-\Delta S', J (1101 \text{ K})^{-1}$			
CoL <sub>2</sub>									
0.336	0.69	1.06	2.33	3.75	65.9	111			
0.504	1.57	2.41	5.54	7.98	64.3	109			
0.672	2.54	4.56	9.40	14.93	64.2	106			
0.972	4.75	7.50	16.48	25.53	64.0	101			
ZnL <sub>2</sub>									
0.3316	0.86	1.02	2.07	3.25	53.0	152			
0.4975	1.70	2.06	3.92	5.48	49.2	159			
0.6633	2.53	5.28	7.98	10.13	50.4	152			
0.8955	5.37	7.09	14.01	20.84	53.4	136			
NiL <sub>2</sub>									
0.0004	2.06	2.68	5.22	6.99	49.0	159			
0.0006	6.11	8.16	14.6	19.94	46.4	158			
0.0008	11.9	15.23	28.56	40.22	48.3	146			
0.0012	24.00	30.86	58.68	75.33	46.9	145			

Table 1. Kinetic data on the dissociation of complexes CoL<sub>2</sub>, ZnL<sub>2</sub>, and NiL<sub>2</sub> in a mixed AcOH-benzene solvent\*

\* The error in  $k_{\text{eff}}$  determination is 3 to 5%; the corresponding errors for E and  $\Delta S^{\neq}$  are no larger than 10 and 15%, respectively.

**Table 2.** True rate constants and the activation parameters of the dissociation of complexes  $CoL_2$ ,  $ZnL_2$ , and  $NiL_2$  in a mixed AcOH–benzene solvent

<i>Т</i> , К	$k_v^T(\text{const}_1),$ $l^2 \operatorname{mol}^{-2} \operatorname{s}^{-1}$	const <sub>2</sub>	ρ	$E_{v},$ kJ mol <sup>-1</sup>	$\Delta S^{\neq},$ J (mol K) <sup>-1</sup>				
CoL <sub>2</sub>									
298.15	$5.7 \times 10^{-4}$	1.92	0.999	$69 \pm 8$	$-80\pm6$				
303.15	$9.5 \times 10^{-4}$	2.00	0.997						
313.15	$20.5 \times 10^{-4}$	1.98	0.999						
318.15	$31.3 \times 10^{-4}$	1.97	0.998						
$ZnL_2$									
298.15	$6.0 \times 10^{-4}$	1.80	0.986	$51\pm 6$	$-123 \pm 25$				
303.15	$9.9 \times 10^{-4}$	2.06	0.988						
313.15	$17.1 \times 10^{-4}$	1.96	0.993						
318.15	$23.2 \times 10^{-4}$	1.87	0.987						
NiL <sub>2</sub>									
298.15	2279	2.04	0.999	$35 \pm 4$	$-72 \pm 14$				
303.15	2660	2.02	0.999						
313.15	4541	2.01	0.999						
318.15	5272	1.99	0.998						

AcOH concentrations under consideration can be written as

$$\frac{dc_{\mathrm{ML}_2}}{d\tau} = k_v c_{\mathrm{ML}_2} (c_{\mathrm{AcOH}})^2.$$

According to the dissociation rate constants (Tables 1, 2), the kinetic stability of complexes  $ML_2$  in a binary AcOH–benzene solvent changes in the order  $NiL_2 < ZnL_2 \approx CoL_2$ . The kinetic stability of  $NiL_2$  is approximately seven orders of magnitude lower than those of  $ZnL_2$  and  $CoL_2$ . The energy of activation depends only slightly on the concentration of acetic acid in benzene and noticeably increases in the above sequence. All the

processes studied are characterized by negative  $\Delta S^{\neq}$  values, which suggests a highly solvated system in the transition state.

Based on the comparatively low energies of activation and the negative  $\Delta S^{\neq}$  values, one can assume that protonation of nitrogen atoms in coordinated dipyrrolylmethene is the rate-limiting step followed by rapid decomposition of metal complexes with dipyrrolylmethene:

$$ML_2 + 2AcOH \xrightarrow{slowly} M(AcOH \cdot L)_2$$
  
$$\xrightarrow{rapidly} M(AcO)_2 + 2HL.$$

It can be seen in Fig. 1 that the molecular form of the ligand does not accumulate in the reaction mixture; i.e., the protonation of dipyrrolylmethene also proceeds very rapidly to give  $AcOH \cdot HL$ .

Hence, one can conclude that the optimum conditions for the formation of the porphyrin macrocycle from dipyrrole fragments can be created by using  $Co^{2+}$ or  $Zn^{2+}$  ions as a matrix added to a solution in the acetate form.

## REFERENCES

- 1. Falk, H., *The Chemistry of Linear Oligopyrroles and Pigments*, New York: Springer, 1989.
- Askarov, K.A., Berezin, B.D., Evstigneeva, R.P., et al., Porfiriny: Struktura, Svoistva, Sintez (Porphyrins: Structure, Properties, and Synthesis), Moscow: Nauka, 1985.
- 3. Guseva, G.B., Antina, E.V., Semeikin, A.S., *et al.*, *Zh. Obshch. Khim.*, 2002, vol. 72, no. 1, p. 135.
- Gordon, A.J. and Ford, R.A., *The Chemist's Companion:* A Handbook of Practical Data, Techniques and References, New York: Wiley, 1972.
- 5. Guseva, G.B., Antina, E.V., Berezin, M.B., *et al.*, *Zh. Obshch. Khim.*, 2002, vol. 72, no. 1, p. 135.
- Kreshkov, A.P., Analiticheskaya khimiya nevodnykh rastvorov (Analytical Chemistry of Nonaqueous Solutions), Moscow: Khimiya, 1982.
- 7. Gorbunov, T.V., Shilov, V.V., and Batalin, G.I., *Zh. Strukt. Khim.*, 1973, vol. 14, no. 3, p. 424.
- Lark, B.S., Banipal, T.S., and Singh, S., J. Chem. Eng. Data, 1984, vol. 29, p. 277.
- 9. Akhadov, Ya.Yu., *Dielektricheskie parametry chistykh zhidkostei* (Dielectric Parameters of Pure Liquids), Moscow: MAI, 1999.