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Thermodynamics and Kinetics of Reaction of (Oxo)(hydroxo)molybdenumtetraphenylporphyrin with Pyridine

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Abstract—The reaction of *meso*-tetraphenylporphyrin with Mo(VI) oxide in boiling phenol resulted in a stable complex O=Mo(OH)TPP. Thermodynamics and kinetics of the reaction between (oxo)(hydroxo)molybdenumtetraphenyporphyrin with pyridine in toluene were studied by spectrophotometric method. This reaction was found to occur in three equilibrium elementary stages: replacement of OH^- by Py ($K_1 = 9.1 \times 10^3$ l/mol, $k_1 = 5.25$ s^{-1} mol^{-1} l), the formation of dication (dipyridine)(hydroxo)molybdenumtetraphenylporphyrin as a result of cleavage of a double bond Mo=O ($K_2 = 39.3$ l/mol, $k_2 = 1.83 \times 10^{-2}$ s^{-1} mol^{-1} l), and the formation of cationic complex$[Mo(Py)_3TPP]^{3+} \cdot 3OH^-$ ($K_3 = 1.0$ l/mol, $k_3 = 1.19 \times 10^{-3}$ s^{-1} mol^{-1} l).

Complexes of Mo in oxidation states +4 and +5 with porphyrins belong to mixed-ligand coordination compounds. The reactions of the ligand substitution in such compounds, mainly with metalloporphyrins (**MP**) of double- and triple-charged metal cations, have been widely studied by domestic and foreign scientists [1–5]. However, complexes with high-charge metal cations, in particular, Mo complexes, have been investigated to a lesser extent [6–10]. Nevertheless, these reactions still evoke interest, because the filed of application of the mixed ligand porphyrin complexes increases [11].

Previously [12], the reaction of Mo(V) tetraphenylporphyrin complex with sulfur-containing ligand (hydrogen sulfide) was studied. Spectrophotometric data showed that this reaction occurs in one stage with equilibrium constant 83 l/mol, which allows one to use it in activation of gas-separating membranes and H_2S detectors. This work is devoted to spectrophotometric study of the rates and equilibria of the reaction between (oxo)(hydroxo)molybdenum(V)tetraphenyporphyrin **O=Mo(OH)TPP** (**I**) with pyridine (**Py**) in toluene.

EXPERIMENTAL

Complex **I** was synthesized using procedure [13]: *meso*-tetraphenylporphyrin (**H_2TPP**) (0.1 g, 0.16 mmol) was boiled with MoO_3 (0.076 g, 0.53 mmol) in 0.8 g of phenol at 454 K for 4 h. The procedure was finished when the electronic absorption spectrum of a sample of the reaction mixture dissolved in chloroform did not contain absorption band typical of H_2TPP (λ_{max}, nm: 648.0, 592.0, 551.0, 516.0, 485.0, 420.0). In order to isolate the obtained complex, phenol was distilled off in vacuum, the residue was dissolved in a minimum volume of $CHCl_3$ and twice chromatographed on Al_2O_3 with the use of chloroform. The yield of the complex was 60%. The electronic absorption spectrum in chloroform (λ_{max}, nm ($\log\varepsilon$)): 620.0 (2.94), 584.0 (2.92), 456.0 (3.78).

Thermodynamics of the reaction between **I** and Py in toluene was studied by spectrophotometric titration. Solutions of MP in toluene were prepared directly before use. The optical density of a series of solutions with $c_{O=Mo(OH)TPP}$ = const at different Py concentrations was measured at a wavelength of 456 nm and at 501 nm for high Py concentrations. The electronic absorption spectra were recorded on SF-26 and Specord M40 instruments. The solutions were thermostatted in a spectrophotometer cell to an accuracy of ±0.1 K. The equilibrium constants (***K***) for three-component equilibrium mixture were found from the equation

$$K = \frac{\dfrac{A_p - A_0}{A_\infty - A_0}}{1 - \dfrac{A_p - A_0}{A_\infty - A_0}} \cdot \frac{1}{c_L - c^0_{MP}\dfrac{A_p - A_0}{A_\infty - A_0}}, \qquad (1)$$

where c^0_{MP} and c_L are the initial concentrations of MP and Py, respectively, in toluene; A_0, A_p, and A_∞ are the optical densities at the working wavelength for solutions of MP, equilibrium mixture at a definite concentration of Py, and of the obtained axial complex. The numerical K values were determined from Eq. (1) by the least-squares method using Microsoft Excel program. The relative error in determination of K did not exceed ±14%.

Kinetics of O=Mo(OH)TPP reactions with Py in toluene was studied spectrophotometrically at 298 K

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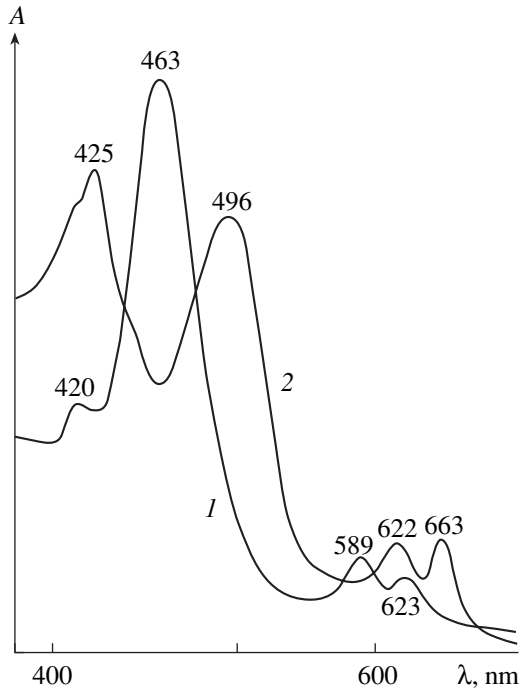

Fig. 1. The electronic absorption spectra of O=Mo(OH)TPP in (*1*) toluene and (*2*) same in the presence of 1.16 mol/l Py.

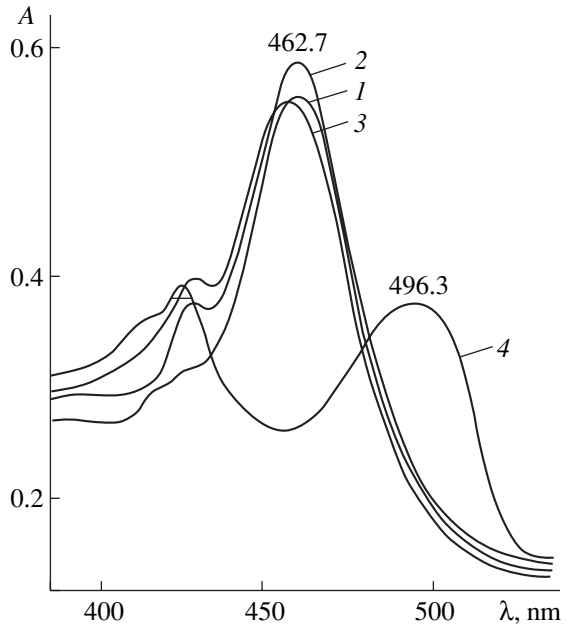

Fig. 2. The electronic absorption spectra of O=Mo(OH)TPP in toluene with different amounts of Py: $c_{O=Mo(OH)TPP}$ = 1.11×10^{-5} mol/l; c_{Py} = (*1*) 0, (*2*) 8.27×10^{-4}, (*3*) 1.29×10^{-1}, (*4*) 1.16 mol/l.

using the data on the optical density change at the working wavelengths 456 and 501 nm. The rate constants were calculated from formally first-order equation at Py excess with respect to MP:

$$k_{eff} = \frac{1}{\tau} \ln \frac{A_0 - A_\infty}{A_\tau - A_\infty}, \quad (2)$$

where A_0, A_τ, and A_∞ are the optical densities of MP solutions at the working wavelength at time 0, τ and after the reaction termination. The optimization of the effective rate constant (k_{eff}) and the determination of standard deviation were performed using the least-square method with Microsoft Excel program. The relative error in determining k_{eff} was ±2–10%.

Toluene was purified using standard procedure [14], water content in a dried solvent was 8.9×10^{-3} mol/l.

IR spectra of the samples were recorded on a Specord IR-75 spectrometer in a range of 400–4000 cm^{-1} (with KBr pellets).

RESULTS AND DISCUSSION

The composition of a mixed-ligand coordination sphere in Mo(V) complexes was previously determined in [15]. The electronic absorption spectra of complex **I**, obtained in this work, fully agrees with that reported in [15]. In this complex, acido ligands O^{2-} and OH^- are in the *trans*-position with respect to the plane of a macrocyclic ligand [16]. Owing to this arrangement, the metal atom is shifted from the N_4 plane toward oxo ligand (O^{2-}) to a lesser extent as compared to metalloporphyrins, whose acido ligands lie on one side of a macrocycle plane (for instance, $(Cl)_2ZrTPP$). As a result of the metal drawing in a macrocycle plane, which is followed by strengthening of the dative Mo–N π-bonds in **I**, the complex does not undergo dissociation at the M–N bonds even in superacids [15], where the axially coordinated ligands can be replaced by another acido ligands occurring in high excess in a solution. The reactions of the ligand replacement by Py in **I** were studied in toluene, since the latter has high solvent ability and reacts neither with the complex nor with Py.

The electronic absorption spectrum of complex **I** in toluene shows significant changes on addition of an excess (with respect to the complex) of Py (Fig. 1). In an interval of Py concentrations 8.27×10^{-6}–1.16 mol/l, the changes in the electronic absorption spectra of complex **I** are different (Fig. 2), but are reversible in all cases. As the Py content increases from 8.27×10^{-6} to 8.27×10^{-4} mol/l, the optical density of a solution substantially increases, though the O=Mo(OH)TPP concentration remains unchanged (Fig. 2, *2*). At Py concentrations from 8.27×10^{-4} to 1.29×10^{-1} mol/l, the intensity of a band at 462.7 nm decreases, and this band is lightly shifted to 457.6 nm (Fig. 2, *3*). With further increase in Py concentration (1.29×10^{-1}–1.16 mol/l), a new band appears with λ_{max} = 496.3 nm (Fig. 2, *4*); at higher concentrations of Py (1.16 mol/l and higher), this spectrum does not undergo further changes. Thus, spectrophotometric titration of complex **I** with pyri-

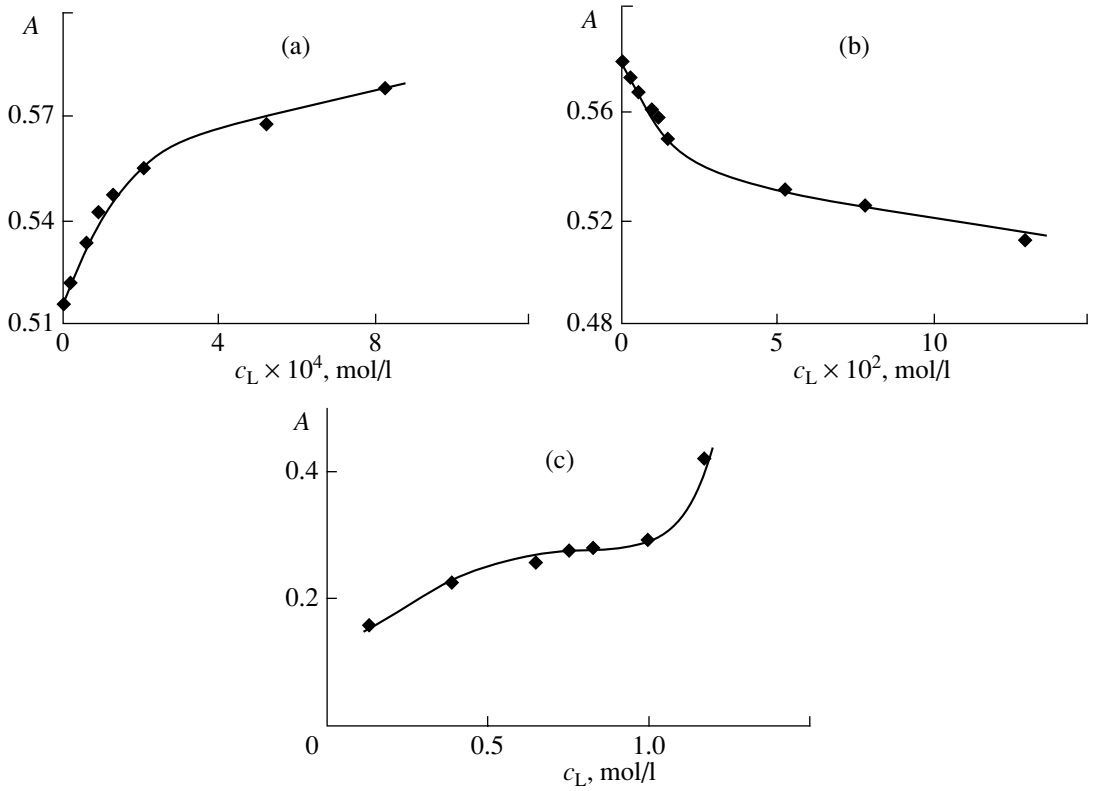

Fig. 3. Curves of O=Mo(OH)TPP titration with pyridine in toluene: c_{Py} = (a) 8.27×10^{-6}–8.27×10^{-4}, (b) 8.27×10^{-4}–1.29×10^{-1}, and (c) 1.29×10^{-1}–1.16 mol/l.

dine revealed three stages of the reaction of complex **I** with Py.

It was found that the equilibrium at the first stage is attained within 50 min. The number of extra ligands, i.e., Py molecules ($n_1 = 1.08$) added at the first reaction stage was found from the experimental plot $\log\frac{A_p - A_0}{A_\infty - A_p} - \log c_L$ (fig. 4, *1*). The stoichiometric ratio of **I** : Py equal to 1 : 1 and the spectral pattern (Fig. 2, *1*, *2*) make it possible to write down the first reaction state as the process of replacement of OH^- by Py:

$$O{=}Mo(OH)TPP + Py \overset{K_1}{\rightleftharpoons} [O{=}Mo(Py)TPP]^+ \cdot OH^-. \quad (3)$$

The equilibrium constant K_1 calculated from Eq. (1) for three-component equilibrium system (3) is equal to $(9.1 \pm 1.2) \times 10^3$ mol/l; this value is rather high for reactions of metallopoprhyrins with bases [1]. The replacement of OH^- by Py is, obviously, more preferable than the additional coordination of Py, since in the course of experiment, the electronic absorption spectrum of MP does not change basically, but only the optical density is increased at the working wavelength of 456 nm near the O=Mo(OH)TPP maximum.

Realization of reaction (3) is confirmed by the kinetic experiment. Since the equilibrium at the first stage of reaction of **I** with Py is established with time, one can use a linear section in the kinetic curve in coordinates of Eq. (2) to measure the rate of a forward reaction k_1 and the detailed equilibrium principle to calculate the rate of a reverse reaction k_{-1}. The effective rate constants k_1^{eff} determined at different initial concentrations of Py are listed in Table 1.

The true rate constants k_1 and the reaction order m_1 in c_{Py} obtained from a linear dependence (Fig. 5, *1*)

$$\log k_1^{eff} = \log k_1 + m_1 \log c_{Py}, \quad (4)$$

are, respectively, 5.25 s^{-1} mol^{-1} l and 0.96. The reverse rate constant is 5.75×10^{-4} s^{-1} (Table 2).

Thus, the experimental kinetic equation of the first stage of the reaction is

$$-dc_{MP}/d\tau = k_1 c_{MP} c_{Py} \quad (5)$$

which is adequately interpreted within the framework of one-stage substitution reaction following the associative mechanism through intermediate state with extended coordination sphere:

$$O{=}Mo(OH)TPP + Py \longrightarrow [O{=}Mo(OH)(Py)TPP]^{\neq} \longrightarrow [O{=}Mo(Py)TPP]^+ \cdot OH^-. \quad (6)$$

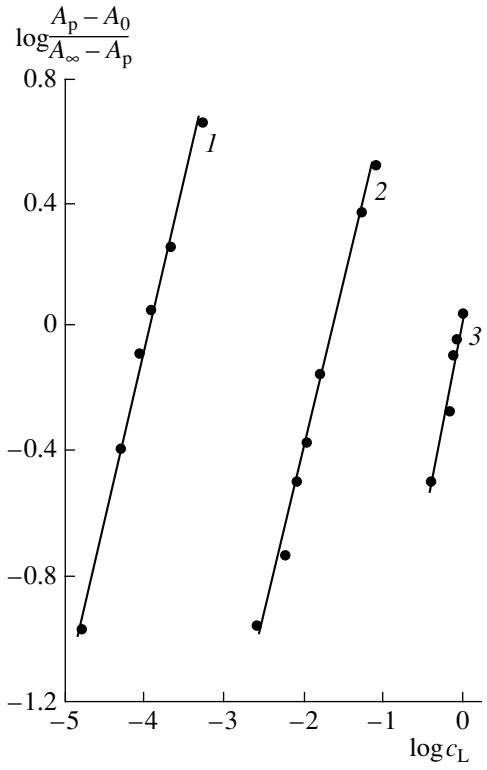

Fig. 4. The plot of $\log\frac{A_p - A_0}{A_\infty - A_p}$ vs. $\log c_L$ for O=Mo(OH)TPP reaction with Py in toluene at (*1*) first, (*2*) second, and (*3*) third stage (the correlation coefficient (ρ) is equal to 0.996, 0.995, and 0.977, respectively).

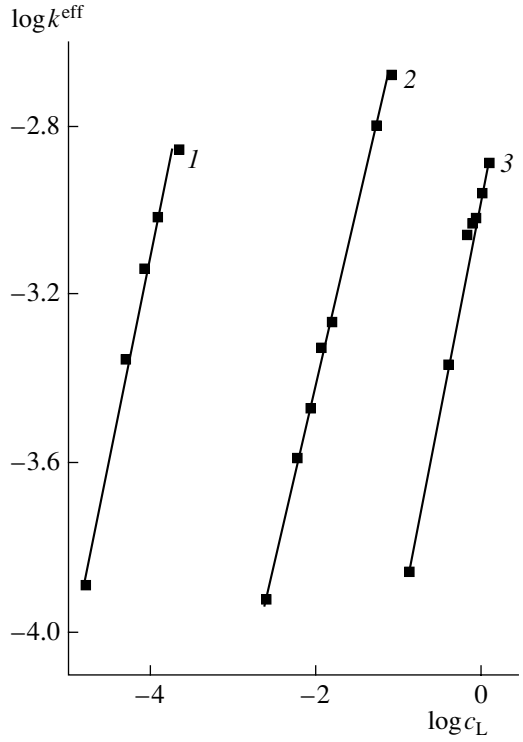

Fig. 5. The plot of $\log k_{eff}$ vs. $\log c_L$ for O=Mo(OH)TPP reaction with Py in toluene at 298 K at (*1*) first, (*2*) second, and (*3*) third state (ρ = 0.994, 0.999, and 0.995, respectively).

The second equilibrium bimolecular state of reaction between **I** and Py occurs at Py concentration 8.27×10^{-4}–1.29×10^{-1} mol/l. The equilibrium is established within 40 min. The stoichiometry of the reaction is confirmed by the plot $\log\frac{A_p - A_0}{A_\infty - A_p} - \log c_L$ (Fig. 4, *2*) ($n_2 = 1.04$). The equilibrium constant decreases by more than two orders of magnitude as compared with the first stage ($K_2 = 39.3 \pm 5.2$ l/mol). The second stage of the reaction is likely to occur at bidentate oxygen:

$$[Mo(Py)TPP]^+ \cdot OH^- + Py + H_2O \underset{}{\overset{K_2}{\rightleftharpoons}} [Mo(OH)(Py)_2TPP]^{2+} \cdot 2OH^-. \quad (7)$$

Rupture of a double bond requires sufficient energy, which is reflected in the equilibrium constant. The

Table 1. Effective rate constants (k^{eff}) of formally first-order reaction of O=Mo(OH)TPP with Py in toluene at 298 K ($c_{O=Mo(OH)TPP} = 1.11 \times 10^{-5}$ mol/l)

Stage 1		Stage 2		Stage 3	
$c_{Py} \times 10^5$, mol/l	$(k_1^{eff} \pm \delta k_1^{eff}) \times 10^4$, s^{-1}	$c_{Py} \times 10^3$, mol/l	$(k_2^{eff} \pm \delta k_2^{eff}) \times 10^4$, s^{-1}	$c_{Py} \times 10$, mol/l	$(k_3^{eff} \pm \delta k_3^{eff}) \times 10^4$, s^{-1}
1.65	1.3 ± 0.08	2.48	1.2 ± 0.1	1.29	1.4 ± 0.04
4.96	4.4 ± 0.4	5.79	2.6 ± 0.3	3.88	4.3 ± 0.1
8.27	7.2 ± 0.3	8.27	3.4 ± 0.4	6.47	8.7 ± 0.3
11.6	9.6 ± 0.8	10.7	4.7 ± 0.2	7.44	9.3 ± 0.2
20.7	14 ± 1.2	14.9	5.4 ± 0.2	8.27	9.6 ± 0.3
		51.7	16 ± 1.4	9.92	11 ± 0.07
		77.6	21 ± 2.1	11.6	13 ± 1.3

absorption spectrum of complex **I** at the second stage of a reaction changes more significantly: not only the decrease in the optical density is observed, but also a hypsochromic shift of the maximum of the band at 462.7 nm (to 457.6 nm).

The kinetic parameters of reaction (7), i.e., the effective rate constants k_2^{eff}, the true rate constants k_2, and the reaction order m_2 in c_{Py}, found in the same way as for reaction (3) (Fig. 5, *2*) are given in Tables 1, 2. The rate constant of reverse equilibrium reaction (7) is 4.65×10^{-4} s^{-1}. The first orders of the reaction in MP and Py concentration indicate bimolecular process, which follows associative mechanism, and indirectly confirm the nature of equilibrium (7) with participation of one Py molecule (Fig. 4, *2*).

At Py concentration 1.29×10^{-1}–1.16 mol/l, the third equilibrium stage of the reaction of **I** with Py is observed. The equilibrium is attained in 50 min. At this state, the electronic absorption spectrum of the reaction mixture shows a decrease in the optical density in the region of the band at 456 nm. When Py concentration is 7.44×10^{-1} mol/l and higher, the band at 457.6 nm almost disappears, while a new band appears with $\lambda_{\max}$ = 496.3 nm. The thermodynamic study was performed at wavelength 501 nm, when the optical density changes are the most pronounced. The equilibrium constant at the third stage $K_3 = 1.0 \pm 0.1$ mol/l, the number of interacting Py molecules $n_3 = 1.26$ (Fig. 4, *3*). The absorption spectrum of extra ligand formed at the third stage (Fig. 1, *2*) is similar to that of O=Mo(OH)TPP treated with an excess gaseous HCl, i.e., to the spectrum of $(Cl)_3$MoTPP [9]. Extra complex, formed in the course of the reaction with Py, is likely to be Mo(V) compound. The authors of [10] reported somewhat different (in the number and positions of the bands) electronic absorption spectrum of O=Mo^{IV}TPP in toluene ($\lambda_{\max}$, nm): 645, 590, 453, 397.

Table 1 presents effective rate constants k_3^{eff} determined for different initial Py concentrations, while Table 2 contains the values of the true rate constants k_3 and of the reaction order m_3 in c_{Py} determined from the data in Fig. 5. The rate constant of a reverse reaction is 1.20×10^{-3} s^{-1} (Table 2). The experimental kinetic equation is identical to those for stage one and stage two.

The above data show that the third stage of the reaction between molybdenum(V)porphyrin with Py is in fact displacement of the third OH^- group to the second coordination sphere stable in organic solvent toluene:

$$[\text{Mo(OH)(Py)}_2\text{TPP}]^{2+} \cdot 2\text{-}^{-} + \text{Py} \xrightleftharpoons{K_3} [\text{Mo(Py)}_3\text{TPP}]^{3+} \cdot 3\text{OH}^-. \quad (8)$$

The structure of the product of reaction (8) is confirmed by IR spectra of the initial complex O=Mo(OH)TPP and of the complex isolated at the third stage from a solution in Py by vacuum distillation of the later (Table 3). The spectrum of the initial complex **I** contains the absorption band at 625 cm^{-1} corresponding to the Mo=O bond and disappearing from the spectrum of the complex $[\text{Mo(Py)}_3\text{TPP}]^{3+} \cdot 3\text{OH}^-$. IR spectrum of the complex isolated at the third stage from a solution in Py contains new absorption bands due to vibrations of Py bonds, namely, at 412, 590, 700, 990, 1040, 1384, 1425, 1570 cm^{-1} [14]. The bands at 1384, 1425, and 1570 cm^{-1}, which correspond to vibrations of the C–C and C–N bonds in pyridine cycle, are shifted toward low-frequency region, probably, due to coordination of pyridine in the complex.

Table 2. Reaction order (m) in c_{Py}, true rate constants (k) of forward and reverse reactions of O=Mo(OH)TPP with Py

Reaction stage	m	k, s^{-1} mol^{-1} l (forward reaction)	k, s^{-1} (reverse reaction)
1	0.96	5.25	5.75×10^{-4}
2	0.83	1.83×10^{-2}	4.65×10^{-4}
3	1.03	1.19×10^{-3}	1.20×10^{-3}

The ratio of the stage equilibrium constants for analogous reaction with participation of W complex O=W(OH)TPP (1.3×10^4, 8.4×10^3, and 89 l/mol) previously studied in [17] shows that the reaction of W complex with Py occurs at bidentate oxygen O^{2-} only at the third stage. This fact agrees well with the suggested scheme of transformations for Mo complex. It is known [15, 18] that the W=O bond is noticeably stronger than the Mo=O bond in the metal coordination compounds. Therefore, the reactivity of the latter bond is also higher in the case of complex **I**: this bond is the reaction center already at the second stage of the reaction with Py.

With regard to the equilibrium constant of the reaction of displacement of a single-charged acido ligand to the second coordination sphere, the complexes (AcO)CrTPP [19], O=W(OH)TPP [17], and O=Mo(OH)TPP can be arranged in the following series:

$$\text{O=Mo(OH)TPP } (K = 9100) \approx \text{O=W(OH)TPP } (8400) > \text{(AcO)CrTPP } (2.8).$$

This series coincides with the series of the kinetic stability of the complexes at the M–$N_{\text{porphyrin}}$ bonds [20]. One can see that an increase in the formal charge of the metal cation is attended by an increase in the affinity of metalloporphyrin to both Py and a macrocycle.

The comparison of reactions of O=Mo(OH)TPP with different bases revealed the following conclusions. The equilibrium of the reaction of **I** with Py is characterized by a higher rate constant (K = 9100 l/mol) as compared to analogous parameter in the case of imidazole (**Im**) (480 l/mol, unpublished data of the authors) and hydrogen sulfide (83 l/mol [12]). This corresponds to the growing energy of protonation when going from Py

Table 3. Frequencies of the bands (cm^{-1}) in IR spectra of molybdenum(V)tetraphenylporphyrin before and after treatment with pyridine

No. of band	O=Mo(OH)TPP	$[Mo(Py)_3TPP]^{3+} \cdot 3OH^-$	Band assignment
		412	$\nu(Mo–N_{Py})$
1	447	447	$\nu(Mo–N)$
2	475	480 (w.ab.)	$\nu(Mo–O)$
		590	Vibrations of Py bonds
5	625		$\nu(Mo=O)$
		700	$\gamma(C–H)$ of pyridine
7	708	708	$\gamma(C–H)$ of benzene ring
9	758	758	The same
10	805	805	$\gamma(C–H)$ of pyrrole ring
14	930		$\nu(Mo–O)$
		990	$\delta(C–H)$ of pyridine
16	1020	1025	$\delta(C–H)$ of pyrrole ring, $\nu(C_3–C_4)$, $\nu(C–N)$
		1040	$\nu(C–C)$, $\nu(C–N)$ of pyridine
17	1075	1072	$\delta(C–H)$ of benzene ring
19	1180	1170	The same
23	1335	1325	$\nu(C–N)$
		1384	$\nu(C=C)$ of pyridine
		1425	$\nu(C=N)$ of pyridine
25	1445	1445	$\nu(C=N)$
26	1480	1470	$\nu(C=C)$ of benzene ring
27	1540	1540	Vibratioans of pyrrole ring
		1570	$\nu(C=C)$ of pyridine
29	1610	1600	$\nu(C=C)$ of benzene ring
	Unstudied region	2852	$\nu(C–H)$ of pyrrole ring
		2870	The same
		2922	$\nu(C–H)$ of benzene ring
		2960	The same

to H_2S (438 [21] and 520 kJ/mol[1], respectively). Hence, the stability of extra complexes $[O=Mo(Py)TPP]^+$ and O=Mo(SH)TPP changes in accordance with an increase in stability of the bond molybdenum–donor atom of the extra ligand. Among the investigated bases, Im has the minimum value of E (398 kJ/mol [21]). The equilibrium constant of the reaction of OH^- replacement by Im does not comply with this tendency, which can be explained by the presence in extra complex $[O=Mo(Im)_2TPP]^+$ of an additional Im molecule coordinated at the previous stage.

ACKNOWLEDGMENTS

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[1] Calculated by PM3 method by S.V. Zaitseva.

REFERENCES

1. Berezin, B.D. and Koifman, O.I., *Usp. Khim.*, 1980, vol. 49, no. 12, p. 2389.
2. Koroleva, T.A., Koifman, O.I., and Berezin, B.D., *Koord. Khim.*, 1981, vol. 7, no. 11, p. 1642.
3. Karmanova, T.V., Koifman, O.I., and Berezin, B.D., *Koord. Khim.*, 1983, vol. 9, no. 7, p. 919.
4. Izatt, R.M., Bradshaw, J.S., and Pawlak, K., *et al., Chem. Rev.*, 1992, vol. 92, no. 6, p. 1261.
5. Falk, J., *Porphyrins and Metalloporphyrins*, Amsterdam: Elsevier, 1964.
6. Ohta, N., Scheuermann, W., Nakamoto, K., *et al.*, *Inorg. Chem.*, 1979, vol. 18, no. 2, p. 457.
7. Fleischer, E.B. and Srivastava, T.S., *Inorg. Chim. Acta*, 1971, vol. 5, no. 2, p. 151.

8. Ledon, H. and Mentzen, B., *Inorg. Chim. Acta*, 1978, vol. 31, no. 1, p. L393.
9. Bains, M.S. and Davis, D.G., *Inorg. Chim. Acta*, 1979, vol. 37, no. 1, p. 53.
10. Tachibana, J. and Imamura, T., *Chem. Lett.*, 1990, no. 11, p. 2085.
11. Sanders, J.K.M., Kampos, N., Clyde-Watson, Z., *et al.*, *The Porphyrin Handbook.*, Kadish, K.M., Smith, K.M., and Guieard, R., Eds., San Diego–San Francisco: Academic, 1999, vol. 3, p. 1.
12. Tipugina, M.Yu., Lomova, T.N., and Ageeva, T.A., Abstracts of Papers, *VII Intern. Conf. "The Problems of Solvation and Complex Formation in Solutions,"* Ivanovo, 1998, p. 285.
13. Buchler, J.W. and Rochbock, K., *Inorg. Nucl. Lett.*, 1972, vol. 8, no. 12, p. 1073.
14. Gordon, A.J. and Ford, R.A., *A Handbook of Practical Data, Techniques, and References*, New York: Wiley, 1972.
15. Lomova, T.N., Volkova, N.I., and Berezin, B.D., *Zh. Neorg. Khim.*, 1985, vol. 30, no. 3, p. 626.
16. Scheidt, W.R, *The Porphyrins*, Dolphin, D.N.Y., Ed., New York: Academic, 1978, p. 463.
17. Tipugina, M.Yu. and Lomova, T.N., Abstracts of Papers, *IX Mezhd. konf. po khimii porfirinov i ikh analogov* (IX Int. Conf. on the Chemistry of Porphyrins and Their Analogs), Suzdal, 2003, p. 28.
18. Cheremisina, I.M., *Zh. Strukt. Khim.*, 1978, vol. 19, no. 2, p. 336.
19. Tipugina, M.Yu. and Lomova, T.N., *Zh. Neorg. Khim.*, 2002, vol. 47, no. 7, p. 1088 [*Russ. J. Inorg. Chem.* (Engl. Transl.), 2002, vol. 47, no. 7, p. 978].
20. Lomova, T.N., *Doctoral (Chem.) Dissertation*, Ivanovo: Inst. of the Chemistry of Nonaqueous Solutions, 1990.
21. Zaitseva, S.V., *Cand. Sci. (Chem.) Dissertation*, Ivanovo: Inst. of Solution Chemistry, 1999.