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# Kinetic Stability of Substituted Tetrapyrazinoporphyrazines in a System Nitrogen Base–Dimethylsulfoxide

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**Abstract**—The state of tetra(5-*tert*-butylpyrazino)porphyrazine, octaethyltetrapyrazinoporphyrazine, octaphenyltetrapyrazinoporphyrazine in DMSO medium was studied. It was found that the complexes formed with the proton transfer exhibit a relatively high stability. In strong basic media these complexes are kinetically unstable. The influence of the nature of cyclic and acyclic nitrogen-containing bases, as well as the influence of NH-acidity of the porphyrazine macrocycle on the rate and activation parameters of decomposition of the proton-transfer complexes of tetra(5-*tert*-butylpyrazino)porphyrazine, octaethyltetrapyrazinoporphyrazine, and octaphenyltetrapyrazinoporphyrazine was established.

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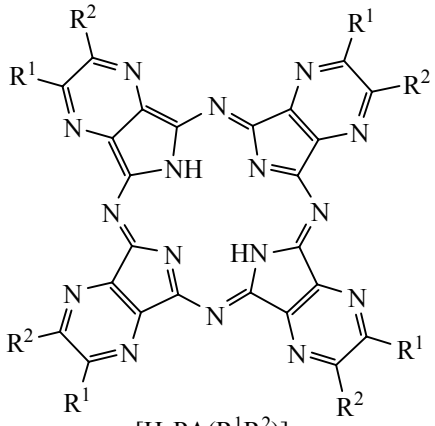
The successful practical application of porphyrazines in catalysis, biological and chemical monitoring, qualitative and quantitative analysis, as well as in various fields of medicine depends on the stability of their π-chromophore system in solution. To date, the stability of the porphyrazine type macrocycles was studied sufficiently in the proton-donor environments [1, 2]. Quantitative data on the stability in the proton-acceptor media are much poorer. The most complete information was obtained only on some β-substituted and β,β-benzofused porphyrazines [3–6]. It turned out that in the system of a nitrogen-containing base–benzene (or dimethyl sulfoxide) they exhibit the properties of dibasic NH-acids and in most cases form a kinetically unstable complexes with the proton transfer. The process of decomposition leading to the formation of low molecular weight colorless compounds obeys complex laws, and its kinetic parameters depend strongly on the electronic and geometric structure of the nitrogen base, as well as on the basicity and dielectric constant of the medium.

In order to identify further the factors influencing the stability of the macrocycles of the porphyrazine type, we examined the state of tetra(5-*tert*-butylpyrazino)porphyrazine [$H_2PA(t\text{-BuPyz})_4$], octaethyltetrapyrazinoporphirazine [$H_2PA\ (Et_2Pyz)_4$], and octaphenyltetrapyrazinoporphyrazine [$H_2PA\ (Ph_2Pyz)_4$] in the system a nitrogen base (B) – dimethyl sulfoxide (DMSO). As bases pyridine (Py), 2-methylpyridine (MePy), morpholine (Mor), piperidine (Pipy), *n*-butylamine ($BuNH_2$), and diethylamine ($Et_2NH$) were taken.

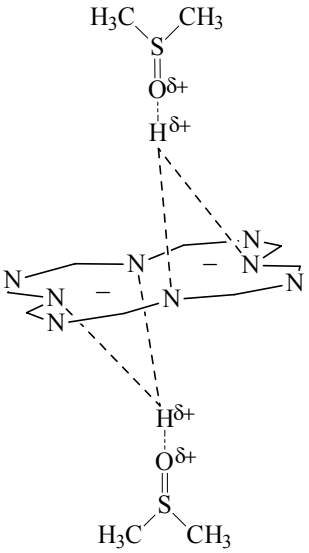


$[H_2PA(R^1R^2)]$

$[H_2PA(t\text{-BuPyz})_4]$, $R^1$ = *t*-Bu, $R^2$ = H; $[H_2PA(Et_2Pyz)_4]$, $R^1 = R^2$ = Et; $[H_2PA(Ph_2Pyz)_4]$, $R^1 = R^2$ = Ph.

Preliminary experiments showed that the electron absorption spectra of $H_2PA$ $(t\text{-BuPyz})_4$ and $H_2PA$ $(Et_2Pyz)_4$ in DMSO contained in the visible region an unsplit *Q*-band at λ 643 nm (Fig. 1) characteristic of $D_{4h}$ symmetry of the π-chromophore of the molecule, in contrast to the split *Q*-band in neutral solvents ($D_{2h}$ symmetry of the π-chromophore) [7, 8]. The increase in the effective symmetry of the macrocycle from $D_{2h}$

to $D_{4h}$ [9] means that the $H_2PA(t\text{-BuPyz})_4$ and $H_2PA(Et_2Pyz)_4$ in the presence of DMSO exhibit the properties of dibasic acids and form in the solution the kinetically stable complexes with proton transfer, the tetra(5-*tert*-butylpyrazino)porphyrazine [$H_2PA(t\text{-BuPyz})_4 \cdot 2DMSO$] and octaethyltetrapyrazinoporphyrazine [$H_2PA(Et_2Pyz)_4 \cdot 2DMSO$], respectively. According to [3, 10] the protons from the NH-groups in these complexes being associated with the oxygen atoms of the molecules of DMSO and intracyclic nitrogen atoms by hydrogen bonds [11] are located axially above and below the plane of the macrocycle, which ensures the high symmetry of the charge distribution [12]. It should be noted that a similar structure and stability over time exhibits the complex $H_2PA(PH_2Pyz)_4 \cdot 2$ DMSO [13].



$[H_2PA(R^1R^2) \cdot 2DMSO]$

Further studies showed that at the use of a base with weak proton-acceptor properties (pyridine, 2-methylpyridine) in the dimethylsulfoxide solution the complexes $H_2PA(t\text{-BuPyz})_4 \cdot 2DMSO$ and $H_2PA(Et_2Pyz)_4 \cdot 2DMSO$ retain their electronic absorption spectra unchanged with $\lambda = 643$ nm in the concentration range [Py] = [MePy] = 0.31–9.93 M at $T = 343$ K for ~ 70 h. In contrast, the addition of stronger bases (morpholine, *n*-butylamine, piperidine) lead to the destabilization of the complexes with proton transfer. Regardless of the nature of the base, a decrease in the spectral intensity of unsplit *Q*-band at λ 643 nm occurs with time (Fig. 2). At the same time, the green color of the solution is changed to colorless.

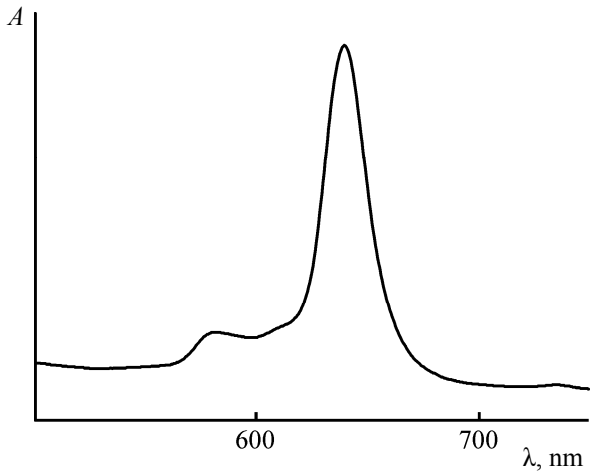



**Fig. 1.** The electron absorption spectrum of $H_2PA(t\text{-BuPyz})_4 \cdot [H_2PA(Et_2Pyz)_4]$ in DMSO at 298 K.

Kinetic studies showed that the reaction of degradation of the complexes $H_2PA(t\text{-BuPyz})_4 \cdot 2DMSO$ and $H_2PA(Et_2Pyz)_4 \cdot 2DMSO$ in the DMSO–morpholine (*n*-butylamine, piperidine) has the order equal to unity with respect to the proton transfer complex (Fig. 3) and close to unity (within the experimental error) with respect to the base (Fig. 4). A similar fact was established for the process of decomposition of the complex $H_2PA(PH_2Pyz)_4 \cdot 2DMSO$ [13]. Consequently, $k_{ef} = k[B] - d[H_2PA(R_1R_2) \cdot 2DMSO]/d\tau = k[H_2PA(R_1R_2) \cdot 2DMSO][B]$. Here $k_{ef}$ and $k$ are the effective and the second order reaction rate constants, respectively.

$$-d[H_2PA(R^1R^2) \cdot 2DMSO]/d\tau = k[H_2PA(R^1R^2) \cdot 2DMSO][B].$$

The instability of the proton-transfer complexes in the strongly basic media with high dielectric constant is due to the occurrence of competitive reactions of the proton attraction. Its possible mechanism may be represented by the following scheme:

$$H_2PA(R^1R^2) \cdot 2DMSO + B \xrightarrow{k_1} [HPA(R^1R^2) \cdot DMSO]^- + HB^+ + DMSO, \quad (1)$$

$$[HPA(R^1R^2) \cdot DMSO]^- + B \xrightarrow{k_2} [PA(R^1R^2)]^{2-} + HB^+ + DMSO, \quad (2)$$

$$[PA(R^1R^2)]^{2-} \xrightarrow{k_3} \text{Products of degradation.} \quad (3)$$

In the first and second stages the base molecules react with hydrogen atoms of $H_2PA(R_1R_2) \cdot 2DMSO$, and thanks to a more pronounced proton-acceptor quality they displace the DMSO molecules. The high basicity and high dielectric constant of the medium favors the formation of dianion form of tetra(5-*tert*-

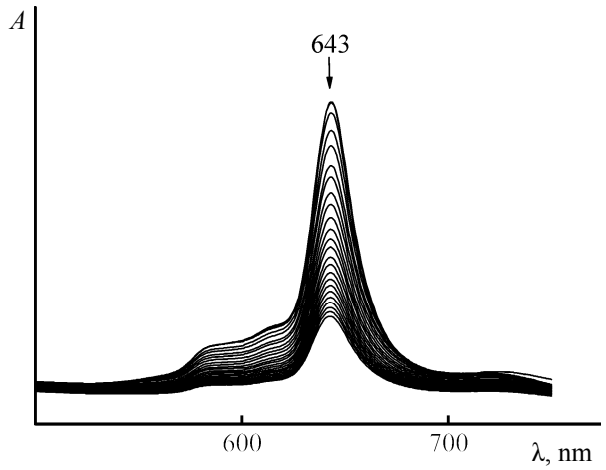



**Fig. 2.** Changes in the electron absorption spectra of $H_2PA$·($t$-BuPyz)$_4$·2DMSO [$H_2PA(Et_2Pyz)_4$·2DMSO] in the piperidine–DMSO system in the course of 50 min at [Pipy] 9.96 M and $T$ = 323 K.

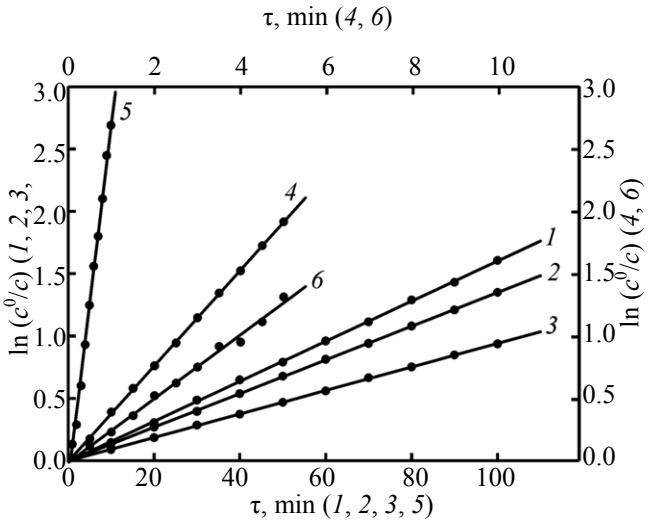



**Fig. 3.** Dependences of $\ln(C^0/C)$ on the reaction time of decomposition of $H_2PA$($t$-BuPyz)$_4$·2DMSO at the concentrations (M): [Mor] = (*1*) 8.86, [$BuNH_2$] = (*2*) 8.85, [Pipy] = (*3*) 9.96 in DMSO at (*1, 3*) 333 K) and (*2*) 338 K and on the reaction time of decomposition of $H_2PA(Et_2Pyz)_4$·2DMSO at the concentrations (M): [Mor] = (*4*) 9.96, [$BuNH_2$ ] = (*5*) 6.32, [Pipy] = (*6*) 5.06 in DMSO at (*4, 6*) 323 and (*5*) 318 K.

butylpyrazino)porphyrazine, octaethyltetrapyrazinoporphyrazine, and octaphenyltetrapyrazinoporphyrazine that correspond to the symmetry group $D_{4h}$ and spectrally not differ from the proton-transfer complexes. Due to the lack of effective compensation of excess negative charge in the macrocycle the dianions $[PA(R_1R_2)]^{2-}$ are losing their kinetic stability and undergo spontaneous decomposition with the formation of low molecular weight colorless products. The decrease in the concentration of $H_2PA(R_1R_2)$·2DMSO in the presence of a very large excess of the nitrogen bases occurs without the appearance of the intermediate spectral form [$HPA(R_1R_2)$·DMSO] in the reacting system (Fig. 2). This fact suggests that $k_1 < k_2$.

The results of the experiment (Table 1) show that among all studied bases, the maximum rate of decomposition of complexes $H_2PA$($t$-BuPyz)$_4$·2DMSO and $H_2PA(Et_2Pyz)_4$·2DMSO is observed in the presence of piperidine and *n*-butylamine, which have relatively high proton-acceptor ability and greatly facilitate the competitive reaction for the proton according to Eqs. (1) and (2). At replacing piperidine (p$K_a$ = 11.23 [14]) and *n*-butylamine (p$K_a$ = 10.60 [14]) by less basic morpholine (p$K_a$ = 8.70 [14]) the rate of degradation of the $H_2PA$($t$-BuPyz)$_4$·2DMSO and $H_2PA(Et_2Pyz)_4$·2DMSO complexes, judging from the values of $k^{298}$, decrease against the background of the growing $E_a$ and $\Delta S^{\neq}$ of the process (Table 1).

Despite the structural similarity of the complexes $H_2PA(R_1R_2)$·2DMSO in the DMSO–$BuNH_2$ (Pipy, Mor) complexes, the complexes $H_2PA$($t$-BuPyz)$_4$·2DMSO and $H_2PA(Et_2Pyz)_4$·2DMSO have higher kinetic stability than the complex $H_2PA(PH_2Pyz)_4$·2DMSO. Thus, the transition from close by the reactivity $H_2PA$($t$-BuPyz)$_4$·2DMSO and $H_2PA(Et_2Pyz)_4$·

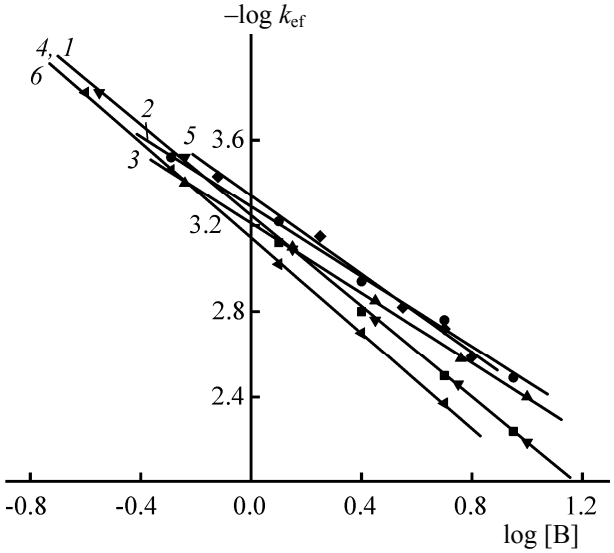



**Fig. 4.** Dependences of log $k$, log $k_{ef}$ on log [B] for the reaction of decomposition of $H_2PA$ ($t$-BuPyz)$_4$·2DMSO in the presence of morpholine (*1*), *n*-butylamine (*2*) and piperidine (*3*) in DMSO at 318 (*2*) and 323 K (*1* and *3*), and for the reaction of decomposition of $H_2PA(Et_2Pyz)_4$·2DMSO in the presence of morpholine (*4*), *n*-butylamine (*5*) and piperidine (*6*) in DMSO at 318 (*5*) and 323 K (*4*, *6*).

**Table 1.** Kinetic parameters of decomposition reactions of complexes $H_2PA(t\text{-BuPyz})_4\cdot 2DMSO$ and $H_2PA(Et_2Pyz)_4\cdot 2DMSO$ in the system nitrogen base–DMSO

| $H_2PA(R^1R^2)\cdot 2DMSO$ | $c^0_{aq}$, M | $T$, K | $k_{ef}\times 10^{3a}$, $s^{-1}$ | $k\times 10^4$, l $mol^{-1}$ $s^{-1}$ | $E_a$, kJ $mol^{-1}$ | $-\Delta S^{\neq a}$, J $mol^{-1}$ $K^{-1}$ |
|---|---|---|---|---|---|---|
| $H_2PA(t\text{-BuPyz})_4\cdot 2DMSO$ | | | Morpholine | | | |
| | 8.86 | 298 | 0.30 | 0.30 | 94 | 5 |
| | | 323 | 5.80 | 5.90 | | |
| | | 333 | 16.00 | 16.20 | | |
| | | 343 | 44.80 | 45.30 | | |
| | | | *n*-Butylamine | | | |
| | 8.85 | 298 | 0.63 | 0.90 | 64 | 99 |
| | | 318 | 3.20 | 5.00 | | |
| | | 328 | 6.75 | 10.60 | | |
| | | 338 | 13.50 | 21.15 | | |
| | | | Piperidine | | | |
| | 9.96 | 298 | 0.40 | 0.65 | 76 | 63 |
| | | 323 | 4.00 | 6.35 | | |
| | | 333 | 9.40 | 14.90 | | |
| | | 343 | 20.70 | 32.85 | | |
| $H_2PA(Et_2Pyz)_4\cdot 2DMSO$ | | | Morpholine | | | |
| | 9.96 | 298 | 0.45 | 0.40 | 85 | 32 |
| | | 323 | 6.40 | 5.70 | | |
| | | 333 | 16.00 | 14.30 | | |
| | | 343 | 40.90 | 36.60 | | |
| | | | *n*-Butylamine | | | |
| | 6.32 | 298 | 0.45 | 0.80 | 68 | 89 |
| | | 318 | 2.55 | 4.45 | | |
| | | 328 | 5.65 | 9.80 | | |
| | | 338 | 11.80 | 20.50 | | |
| | | | Piperidine | | | |
| | 5.06 | 298 | 0.60 | 1.00 | 62 | 107 |
| | | 323 | 4.30 | 7.30 | | |
| | | 333 | 8.50 | 14.30 | | |
| | | 343 | 16.20 | 27.20 | | |

[a] Values of $k_{ef}$ at 298 K are calculated using the Arrhenius equation. The error in the determination of $k_e$ does not exceed 5%, $E_a$ and $\Delta S^{\neq}$ 12%.

2DMSO to $H_2PA(PH_2Pyz)_4\cdot 2DMSO$ the $k^{298}$ value increases, while $E_a$ and $\Delta S^{\neq}$ of the process are significantly reduced (Tables 1, 2). A further increase in the stability of the π-chromophore system of the $H_2PA(PH_2Pyz)_4\cdot$ 2DMSO complex is observed when it is dissolved in dimethylsulfoxide with the addition of diethylamine. The lower reactivity of $Et_2NH$ ($pK_a$ = 10.93 [14]) compared to close in basicity $BuNH_2$ (Table 2) is due to the effect of a stronger spatial screening of the unshared electron pair of the nitrogen atom by the bulky alkyl substituents in the latter, resulting in the hampering of interaction between $H_2PA(PH_2Pyz)_4\cdot$ 2DMSO and $Et_2NH$ according to the reactions (1) and (2), therefore the kinetic stability of the complex with the proton transfer increases.

In contrast to diethylamine, the addition of a weak nitrogen base (pyridine, 2-methylpyridine) into the dimethylsulfoxide solution does not have a destabilizing effect on the $H_2PA(PH_2Pyz)_4\cdot 2DMSO$ complex, as the weakly expressed proton-acceptor ability and the high conformational rigidity of pyridine and 2-methylpyridine, as well as the appearance of electrostatic repulsion of the π-electron systems of interacting molecules do not allow them to compete with DMSO for the proton.

The complexes $H_2PA(t\text{-BuPyz})_4\cdot 2DMSO$ and $H_2PA\cdot(Et_2Pyz)_4\cdot 2DMSO$ do not decompose over time not only in the DMSO–Py (MePy), but also in the DMSO–$Et_2NH$. These data suggest that the increase in the rate

**Table 2.** Kinetic parameters of decomposition reactions of $H_2PA(PH_2Pyz)_4$·2DMSO in the system nitrogen base–DMSO [13]

| Base, B | $c^0_{aq}$, M | $k^{298}_{ef}\times10^4$, $s^{-1}$ | $k\times10^4$, l $mol^{-1}$ $s^{-1}$ | $E_a$, kJ $mol^{-1}$ | $-\Delta S^{\neq a}$, J $mol^{-1}$ $K^{-1}$ |
|---|---|---|---|---|---|
| Morpholine | 3.21 | 2.58 | 0.75 | 47 | 322 |
| *n*-Butylamine | 0.63 | 1.71 | 2.48 | 28 | 325 |
| Diethylamine | 4.82 | 0.28 | 0.04 | 62 | 340 |
| Piperidine | 1.26 | 3.14 | 2.32 | 44 | 320 |

of decomposition of the complexes in going from $H_2PA(t\text{-BuPyz})_4$·2DMSO and $H_2PA(Et_2Pyz)_4$·2DMSO to $H_2PA(PH_2Pyz)_4$·2DMSO is associated with increased acidity of the macrocycle [15] that underlies the proton-transfer complexes.

## EXPERIMENTAL

Tetra(5-*tert*-butylpyrazino)porphyrazine and octaethyltetrapyrazinoporphyrazine were synthesized by techniques [7, 16]. Dimethyl sulfoxide was kept for 24 h over calcined $MgSO_4$ and CaO, and then distilled under reduced pressure (2–3 mm Hg, bp 50°C). Nitrogen bases were subjected to double purification according to [17]. To carry out kinetic studies, in the temperatrure-controlled cell of the spectrophotometer U-2001/U-2010 UV/Vis was placed freshly prepared solution of $H_2PA(t\text{-BuPyz})_4$ or $H_2PA(Et_2Pyz)_4$ with a constant concentration in DMSO and added variable amount of amines. The rate of decomposition of the proton-transfer complexes $H_2PA(t\text{-BuPyz})_4$·2DMSO and $H_2PA(Et_2Pyz)_4$·2DMSO were determined by the decrease in absorbance of the solution at a wavelength of λ 643 nm. The current and final concentration of the complexes were determined by the formula (4).

$$c = c^0(A_\tau - A_\infty)/(A_0 - A_\infty). \quad (4)$$

Here $A_0$, $A_\tau$, and $A_\infty$ are optical densities of solutions at the initial time, at time τ, and after the reaction completion ($\tau_\infty$); $C^0$ and $C$ are initial and current concentrations of $H_2PA$ complexes ($t$-BuPyz)$_4$2DMSO or $H_2PA(Et_2Pyz)_4$·2DMSO. All measurements were performed under the conditions of the pseudo-first order reaction, so the effective rate constant of degradation of $H_2PA(t\text{-BuPyz})_4$·2DMSO and $H_2PA(Et_2Pyz)_4$·2DMSO were calculated with the formula (5).

$$k_{ef} = (1/\tau)\ln[(A_0 - A_\infty)/(A_\tau - A_\infty)]. \quad (5)$$

The errors in the kinetic parameters were determined by the Student method.

## ACKNOWLEDGMENTS

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