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Kinetic Stability of Tetra(1,2,5-thiadiazolo)porphyrazine in the System Nitrogen-Containing Base–Dimethyl Sulfoxide

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Abstract—The behavior of tetra(1,2,5-thiadiazolo)porphyrazine in dimethyl sulfoxide has been studied, and fairly high stability of the resulting proton-transfer complex has been revealed. The complex is kinetically unstable in strongly basic media. The effects of the nitrogen-containing base and NH acidity of the porphyrazine macrocycle on the rate and activation parameters of decomposition of the proton-transfer complex have been estimated.

Keywords: tetra(1,2,5-thiadiazolo)porphyrazine, proton-transfer complex, decomposition, kinetics, DMSO

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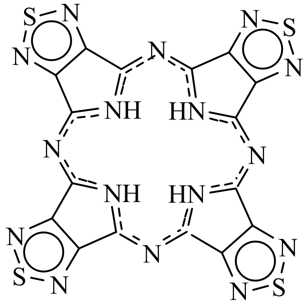
Fused porphyrazines are characterized by unusual structure and unique properties which underlie their wide applications as highly efficient and selective catalysts, chemosensors, liquid crystals, and photosensitizers. Comprehensive study of factors responsible for the stability of the π-chromophore system of porphyrazines in various media is necessary to ensure their successful practical application and extend the range of their useful properties. Up to now, the stability of porphyrin macrocycles in proton-donor media has been studied in sufficient detail [1], whereas quantitative data on their stability in proton-acceptor media are considerably scarcer. Most exhaustive information was obtained only for some substituted phthalocyanines [2] and tetrapyrazinoporphyrazine [3]. It was found that these compounds in the system nitrogen-containing base–dimethyl sulfoxide undergo decomposition to form low-molecular-weight colorless compounds. The decomposition process is fairly complicated, and its kinetic parameters strongly depend on the macrocycle structure, nature of the nitrogen base, and dielectric permittivity and basicity of the medium.

The goal of the present work was to further reveal factors determining the stability of porphyrazine macrocycles. For this purpose, we examined the behavior of tetra(1,2,5-thiadiazolo)porphyrazine [$H_2PA(SN_2)_4$] in the system nitrogen-containing base (B)–dimethyl sulfoxide (DMSO). As nitrogen bases we selected morpholine (Mor) and *n*-butylamine ($BuNH_2$).



[$H_2PA(SN_2)_4$]

Preliminary experiments showed that the electronic absorption spectrum of $H_2PA(SN_2)_4$ in benzene contains in the visible region two well resolved Q_x and Q_y bands with their maxima at λ_I 650 and λ_{II} 636 nm, respectively (Fig. 1a). Unlike benzene, the *Q* band in spectrum recorded in DMSO is not split (Fig. 1b). These findings indicate increase of the π-chromophore symmetry from D_{2h} to D_{4h} as a result of change of the energy of the frontier π-molecular orbitals [4] and show that $H_2PA(SN_2)_4$ behaves as a dibasic NH acid toward DMSO. The proton-transfer complex $H_2PA(SN_2)_4 \cdot 2DMSO$ thus formed remains unchanged with time. The electronic absorption spectrum of $H_2PA \cdot (SN_2)_4$ in DMSO did not change over ~65 h at 323 K (Fig. 1b). Analogous kinetic stability was observed for

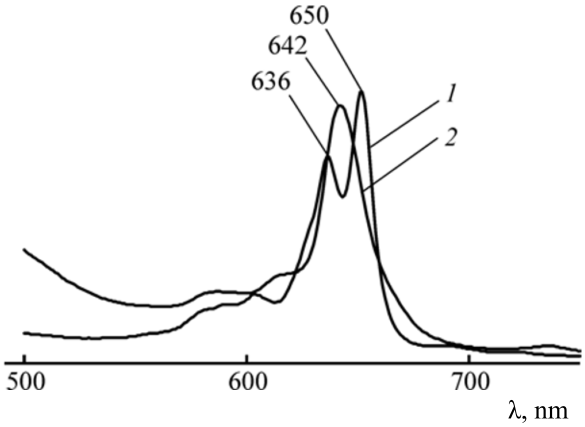


Fig. 1. Electronic absorption spectra of (*1*) $H_2PA(SN_2)_4$ in benzene at 298 K and (*2*) $H_2PA(SN_2)_4\cdot 2DMSO$ in DMSO at 298 K.

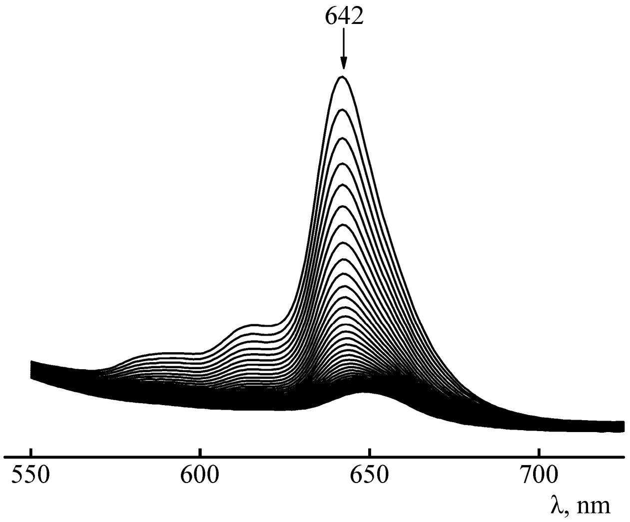
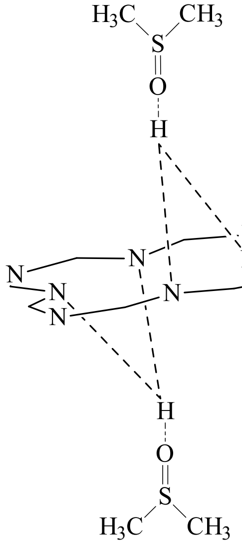


Fig. 2. Variation of the electronic absorption spectrum of $H_2PA(SN_2)_4\cdot 2DMSO$ in DMSO in the presence of morpholine over a period of 30 min; [Mor] = 2.89 M, 303 K.

proton-transfer complexes formed by tetra(5-*tert*-butyl-3-nitro)phthalocyanine [2] and substituted tetrapyrazinoporphyrazines in DMSO [3, 5]. According to [6], the NH protons in these complexes are linked through hydrogen bonds to the oxygen atoms of DMSO molecules and inner nitrogen atoms [7] and are oriented axially above and below the macrocycle plane, which ensures highly symmetrical charge distribu-tion [8]. Analogous structure may be expected for the complex $H_2PA(SN_2)_4\cdot 2DMSO$ in DMSO.



Further study has shown that addition of morpholine or *n*-butylamine (to a concentration of more than 0.14 or 0.05 M, respectively) to a solution of $H_2PA(SN_2)_4$ in DMSO reduces the intensity of the unsplit *Q* band at λ 642 nm (Fig. 2). Simultaneously, the solution loses its color. In the range of base concentrations [Mor] = 4.52–10.98 or [$BuNH_2$] = 1.94–9.63 M in DMSO, the decomposition of $H_2PA(SN_2)_4\cdot 2DMSO$ accompanied by rupture of the π-chromophore system becomes so rapid that its rate cannot be measured by conventional spectrophotometric methods.

Our kinetic studies have shown that the decomposition of $H_2PA(SN_2)_4\cdot 2DMSO$ in DMSO–morpholine (*n*-butylamine) is of first order in the substrate (Fig. 3) and of nearly first order in the base (Fig. 4). Therefore,

$$k_{\mathrm{ef}} = k\,[\mathrm{B}],$$

$$-\partial[\mathrm{H_2PA(SN_2)_4\cdot 2DMSO}]/\partial\tau = k[\mathrm{H_2PA(SN_2)_4\cdot 2DMSO}][\mathrm{B}].$$

Here, k_{ef} and k are the effective and second-order rate constants, respectively.

A probable mechanism of the decomposition of the complex $H_2PA(SN_2)_4\cdot 2DMSO$ in DMSO in the presence of morpholine or butylamine may be represented by the following scheme:

$$\mathrm{H_2PA(SN_2)_4\cdot 2DMSO + B} \underset{k_{-1}}{\rightleftharpoons} [\mathrm{HPA(SN_2)_4\cdot DMSO}]^- + \mathrm{HB^+ + DMSO}, \qquad (1)$$

$$[\mathrm{HPA(SN_2)_4\cdot DMSO}]^- + \mathrm{B} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{PA(SN_2)_4}]_2^- + \mathrm{HB^+ + DMSO}, \qquad (2)$$

$$[\mathrm{PA(SN_2)_4}]_2 \xrightarrow{k_3} \text{Decomposition products.} \qquad (3)$$

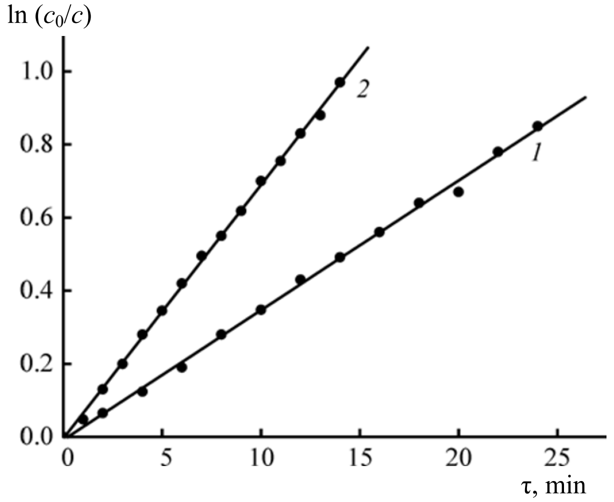


Fig. 3. Plot of ln (c_0/c) versus time for the decomposition of $H_2PA(SN_2)_4·2DMSO$ in DMSO in the presence of (*1*) morpholine, [Mor] = 0.58 M (303 K) and (*2*) *n*-butylamine [$BuNH_2$] = 0.51 M (298 K).

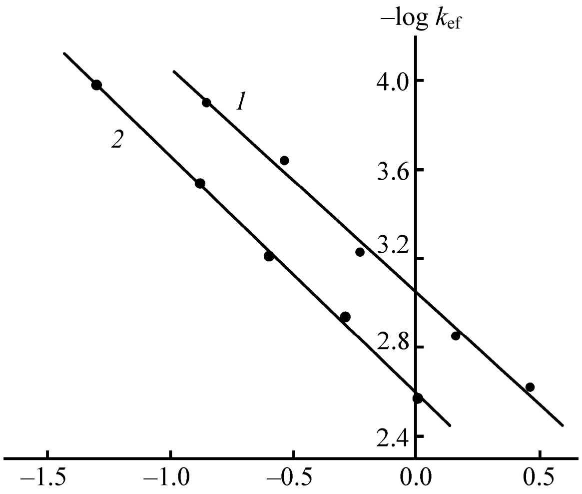


Fig. 4. Plots of log k_{ef} versus log[B] for the decomposition of $H_2PA(SN_2)_4·2DMSO$ in DMSO in the presence of (*1*) morpholine at 303 K and (*2*) *n*-butylamine at 298 K.

In the first and second steps, nitrogen base molecules react with the hydrogen atoms in $H_2PA(SN_2)_4·2DMSO$ and replace DMSO molecules due to their higher proton-acceptor power. The high basicity and dielectric permittivity of the medium favor formation of tetra(1,2,5-thiadiazolo)porphyrazine dianion which also has D_{4h} symmetry and is therefore spectrally indistinguishable from $H_2PA(SN_2)_4·2DMSO$. Because of the lack of efficient compensation of excess negative charge in the macrocycle, the dianion $[PA(SN_2)_4]^{2-}$ loses its kinetic stability and spontaneously decomposes to give low-molecular-weight colorless products. In the presence of a very large excess of base decrease in the concentration of $H_2PA(SN_2)_4·2DMSO$ is not accompanied by appearance of a spectrally detectable amount of intermediate $[HPA(SN_2)_4·DMSO]^-$ (Fig. 2). Therefore, we can assume $k_1 < k_2$, $k_1 > k_{-1}$, and $k_2 > k_{-2}$.

According to the data in Table 1, the rate of the decomposition of $H_2PA(SN_2)_4·2DMSO$ attains its maximum value in the presence of *n*-butylamine which is a fairly strong proton acceptor, so that the competition for proton according to Eqs. (1) and (2) is essentially facilitated. In going from *n*-butylamine (pK_a 10.60 [9]) to less basic morpholine (pK_a 8.70 [9]) the rate of decomposition of $H_2PA(SN_2)_4·2DMSO$ (k^{298}) decreases in parallel with the increase of E_a and $\Delta S^{\neq}$ (Table 1). Analogous pattern was observed for the proton-transfer complexes derived from tetra(5-*tert*-butylpyrazino) porphyrazine [$H_2PA(t\text{-}BuPyz)_4·2DMSO$], octaethyltetrapyrazinoporphyrazine [$H_2PA(Et_2Pyz)_4·2DMSO$] and octaphenyltetrapyrazinoporphyrazine [$H_2PA(Ph_2Pyz)_4·2DMSO$] in DMSO–morpholine (*n*-butylamine) [3].

Analysis of the kinetic data (Tables 1, 2) shows that the complex $H_2PA(SN_2)_4·2DMSO$ is the least kinetically stable in the series of proton-transfer complexes formed by substituted tetrapyrazinoporphyrazines. The k^{298} value increases by factors of ~20 and 30 for morpholine and *n*-butylamine, respectively, in the series $H_2PA(t\text{-}BuPyz)_4·2DMSO \approx H_2PA(Et_2Pyz)_4·2DMSO < H_2PA(Ph_2Pyz)_4·2DMSO < H_2PA(SN_2)_4·2DMSO$. This is not surprising, taking into account that 1,2,5-thiadiazole fragments in the porphyrazine macrocycle are stronger electron acceptors than pyrazine fragments [10, 11]. Therefore, it seems quite probable that $H_2PA·(SN_2)_4$ as stronger NH acid forms a more polar proton-transfer complex with DMSO, and this complex relatively readily decomposes with degradation of the π-chromophore according to Eqs. (1)–(3).

EXPERIMENTAL

Tetra(1,2,5-thiadiazolo)porphyrazine was synthesized according to the procedure described in [12]. Dimethyl sulfoxide was kept for 24 h over calcined $MgSO_4$ and CaO and was then distilled under reduced pressure (2–3 mm, bp 50°C). Morpholine and *n*-butylamine were purified as described in [13]. For kinetic measurements, a freshly prepared solution of

Table 1. Kinetic parameters[a] of the decomposition of the proton-transfer complex $H_2PA(SN_2)_4{\cdot}2DMSO$ in the system nitrogen

c_0, mol/L	T, K	$k_{ef} \times 10^4$, s^{-1}	$k \times 10^4$, L mol^{-1} s^{-1}	E_a, kJ/mol	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}	c_0, mol/L	T, K	$k_{ef} \times 10^4$, s^{-1}	$k \times 10^4$, L mol^{-1} s^{-1}	E_a, kJ/mol	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
					Morpholine						
0.14	298	0.83	5.96	61	124	1.44	298	9.51	6.60	59	112
	303	1.26	9.00				303	14.10	9.79		
	313	2.68	19.10				313	32.10	22.30		
	323	5.77	41.20				323	60.40	41.90		
0.29	298	1.47	5.05	67	102	2.89	298	15.80	5.45	62	99
	303	2.29	7.90				303	23.80	8.24		
	313	6.23	21.50				313	57.80	20.00		
	323	11.90	41.00				323	109.00	37.70		
0.58	298	4.10	7.07	55	133						
	303	5.91	10.20								
	313	13.40	23.10								
	323	22.80	39.31								
					n-Butylamine						
0.05	298	1.05	26.42	49	165	0.25	298	6.20	26.99	47	156
	308	2.00	50.71				308	11.60	50.49		
	318	3.64	90.82				318	20.35	88.45		
0.13	298	2.90	24.20	53	143	0.51	298	11.55	23.56	50	141
	308	6.50	54.05				308	22.80	46.47		
	318	11.05	92.05				318	41.20	84.05		
						1.01	298	26.75	26.49	45	151
							308	51.70	51.20		
							318	83.10	82.27		

[a] The k_{ef} values at 298 K for morpholine were calculated using the Arrhenius equation. The error in the determination of k_{ef} did not exceed 5%, and in the determination of E_a and $\Delta S^{\neq}$, 12%.

Table 2. Kinetic parameters of the decomposition of proton-transfer complexes of tetrapyrazinoporphyrazines in the system nitrogen base–DMSO[a] [3, 5]

Complex	Base	$k^{298} \times 10^4$, L mol^{-1} s^{-1}	E_a, kJ/mol	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
$H_2PA(t\text{-}BuPyz)_4{\cdot}2DMSO$	Morpholine	0.30	94	5
	n-Butylamine	0.90	64	99
$H_2PA(Et_2Pyz)_4{\cdot}2DMSO$	Morpholine	0.40	85	32
	n-Butylamine	0.80	68	89
$H_2PA(Ph_2Pyz)_4{\cdot}2DMSO$	Morpholine	0.75	47	322
	n-Butylamine	2.48	28	325

[a] $[H_2PA(t\text{-}BuPyz)_4{\cdot}2DMSO] = 1.18 \times 10^{-5}$ M, $[H_2PA(Et_2Pyz)_4{\cdot}2DMSO] = 1.24 \times 10^{-5}$ M, $[H_2PA(Ph_2Pyz)_4{\cdot}2DMSO] = 1.2 \times 10^{-5}$ M.

$H_2PA(SN_2)_4$ in DMSO with a required concentration was placed into a spectrophotometric cell of an U-2001/U-2010 UV/Vis spectrophotometer, which was maintained at a constant temperature, and a required amount of the nitrogen base was added. The rate of the decomposition of $H_2PA(SN_2)_4{\cdot}2DMSO$ was determined by the decrease of the optical density of the reaction solution at λ 642 nm. The current and final concentrations of the complex were calculated by formula (4).

$$c = c_0(A_\tau - A_\infty)/(A_0 - A_\infty). \quad (4)$$

Here, A_0, A_τ, and A_∞ are, respectively, the optical density of the reaction solution at the initial moment, time τ, and by the end of the process (τ_∞); c_0 and c are the initial and current concentrations of $H_2PA(SN_2)_4 \cdot 2DMSO$. All experiments were carried out under pseudofirst-order conditions, and the effective rate constant of the decomposition of $H_2PA(SN_2)_4 \cdot 2DMSO$ was calculated by formula (5).

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

The accuracy of the determination of kinetic parameters was estimated according to Student.

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REFERENCES

1. Berezin, B.D., *Coordination Compounds of Porphyrins and Phthalocyanine*, New York: Wiley, 1981.
2. Petrov, O.A., Osipova, G.V., and Kuz'mina, E.L., *Russ. J. Gen. Chem.*, 2011, vol. 81, no. 6, p. 1211. DOI: 10.1134/S1070363211060247.
3. Osipova, G.V., Petrov, O.A., and Efimova, S.V., *Russ. J. Gen. Chem.*, 2013, vol. 83, no. 3, p. 562. DOI: 10.1134/S1070363213030262.
4. *Phthalocyanines: Properties and Applications*, Leznoff, C.C. and Lever, A.B.P., Eds., New York: VCH, 1996, vol. 4, p. 19.
5. Petrov, O.A., Stuzhin, P.A., and Ivanova, Yu.B., *Russ. J. Phys. Chem. A*, 2008, vol. 82, no. 2, p. 201. DOI: 10.1007/s11504-008-2010-1.
6. Kokareva, E.A., Petrov, O.A., and Khelevina, O.G., *Russ. J. Gen. Chem.*, 2009, vol. 79, no. 11, p. 2440. DOI: 10.1134/S1070363209110267
7. Mamaev, V.M., Gloriozov, I.P., and Orlov, V.V., *Izv. Vyssh. Uchebn. Zaved., Ser. Khim. Khim. Tekhnol.*, 1982, vol. 25, no. 11, p. 1317.
8. Gurinovich, G.P., Sevchenko, A.N., and Solov'ev, K.N., *Spektroskopiya khlorofilla i rodstvennykh soedinenii* (Spectroscopy of Chlorophyll and Related Compounds), Minsk: Nauka i Tekhnika, 1968.
9. Albert, A. and Serjeant, E., *Ionization Constants of Acids and Bases*, London: Methuen, 1962.
10. Stuzhin, P.A., *J. Porphyrins Phthalocyanines*, 2003, vol. 7, no. 12, p. 813.
11. Stuzhin, P.A., *Doctoral (Chem.) Dissertation*, Ivanovo, 2004.
12. Stuzhin, P.A., Bauer, E.M., and Ercolani, C., *J. Inorg. Chem.*, 1998, vol. 37, p. 1533.
13. Tietze, L.-F. and Eicher, T., *Reactions and Syntheses in the Organic Chemistry Laboratory*, Mill Valley, California: University Science Books, 1989.