ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 6, pp. 1211–1215. © Pleiades Publishing, Ltd., 2011.
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Kinetic Stability of Tetra(3-nitro-5-*tert*-butyl)phthalocyanine in the System Nitrogen-Containing Base–DMSO

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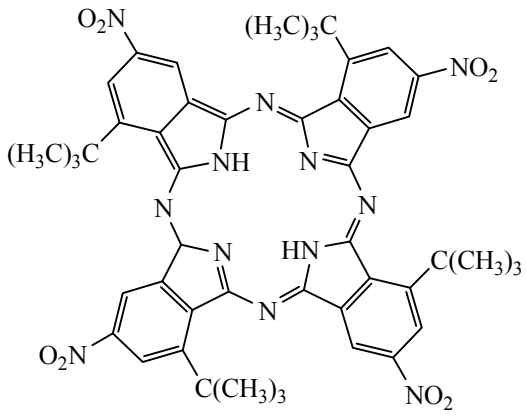
Received May 25, 2010

Abstract—The state of tetra(3-nitro-5-*tert*-butyl)phthalocyanine in DMSO medium was studied. Sufficiently high stability of the obtained proton transfer complex is established, and its structure is suggested. It is shown that this complex is kinetically unstable in the highly basic media. Effect of the nature of cyclic and acyclic nitrogen-containing bases on the rate and activation parameters of destruction of the proton transfer complex of tetra(3-nitro-5-*tert*-butyl)phthalocyanine was found.

DOI: 10.1134/S1070363211060247

Stability of macrocycles of the porphyrin type in solution is one of the most important properties which in many cases determines more or less rigid limitations of their practical use in catalysis, bio- and chemical monitoring, extraction, qualitative and quantitative analysis, and also in various fields of medicine. In connection with that the attention of researchers is attracted by the problems related to the investigation of stability of porphyrins and their aza-substituted analogs in the proton-donor media [1, 2]. Quantitave data on their stability in the proton-acceptor media are scarce. Most complete information was obtained only for β-tetrahaloporphyrazines [3–7]. It occurred that in the nitrogen-containing base–benzene (DMSO) system they behave as two-basic NH-acids and form proton transfer complexes which in the majority of cases after some time decompose to give the low molecular colorless products. The destruction process is governed by complex kinetic rules, and its rate and activation parameters depend on the basicity of the medium, on its permittivity, and also on the specific features of electronic and geometrical structure of nitrogen-containing base.

With the purpose of further elucidating the factors affecting the stability of β-substituted and β,β-benzofused porphyrazines (phthalocyanines) the state of tetra(3-nitro-5-*tert*-butyl)phthalocyanine [$H_2Pc(NO_2)_4(t\text{-}Bu)_4$ in the nitrogen-containing base (B)–DMSO system was studied. Pyridine, 2-methylpyridine, morpholine, piperidine, *n*-butylamine, and diethylamine were chosen as bases.



$[H_2Pc(NO_2)_4(t\text{-}Bu)_4]$

In the preliminary experiments it was found that the electron absorption spectrum of $H_2Pc(NO_2)_4(t\text{-}Bu)_4$ in DMSO contains in the visible region a non-split *Q*-band at λ = 677 nm (Fig. 1a) characteristic of D_{4h} symmetry of π -chromophore of molecule unlike the split *Q*-band in neutral solvents (D_{2h}-symmetry of π-chromophore) (Fig. 1b). The increase in the effective symmetry of the porphyrazine macrocycle from D_{2h} to D_{4h} originating from the change in the energy of the frontier π-molecular orbitals [8] means that $H_2Pc(NO_2)_4(t\text{-}Bu)_4$ exhibits the properties of the two-basic NH-acid with respect to DMSO and indicates the formation of proton transfer complex of tetra(3-nitro-5-*tert*-butyl)phthalocyanine $H_2Pc(NO_2)_4(t\text{-}Bu)_4 \cdot 2DMSO$.

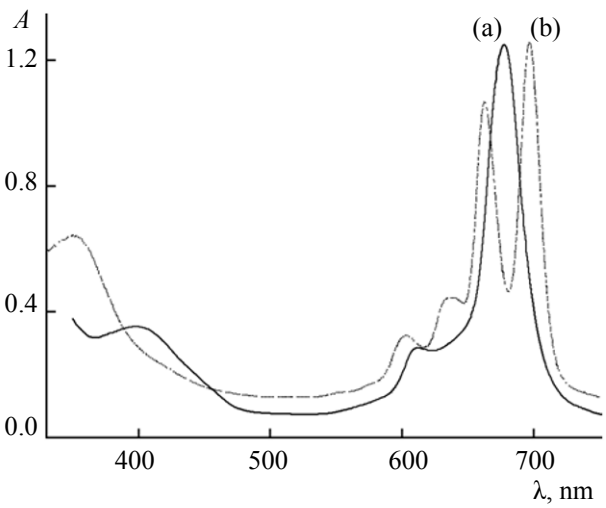


Fig. 1. Electron absorption spectra of (a) $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ in DMSO at 298 K and (b) $H_2Pc(NO_2)_4(t\text{-}Bu)_4$ in benzene at 298 K.

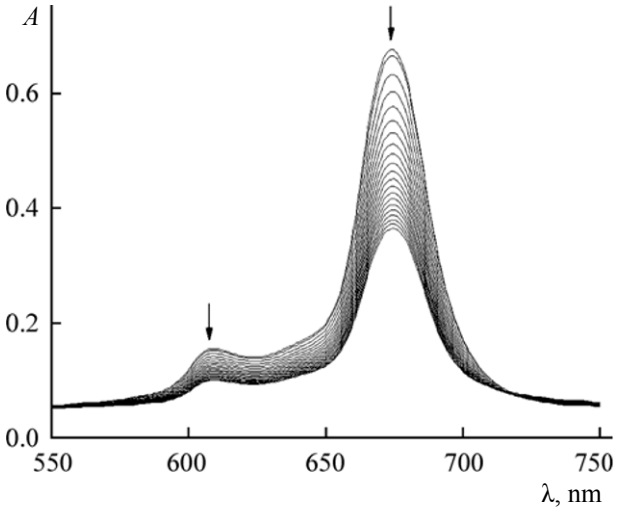
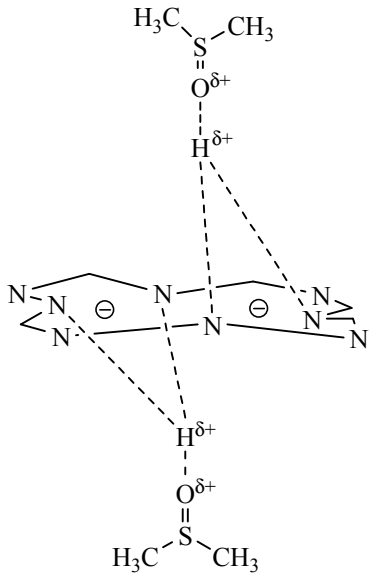


Fig. 2. Alterations in the electron absorption spectra of $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ in *n*-butylamine–DMSO system in the course of 45 min at $C(BuNH_2)$ 5.05 M and T = 338 K.

According to [3, 6, 7] in the complexes of β-substituted and ββ-fused porphyrazines with DMSO the protons of NH-groups bound with the pyrrole and pyrrolenine nitrogen atoms as well as with the oxygen atom of DMSO molecule by means of hydrogen bonds [9] are located above and below the plane of macroring on the fourth order symmetry axis what provides high symmetry of charge distribution [10]. It must be expected that $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ exhibiting sufficiently high kinetic stability has the same structure. Its electron absorption spectrum in DMSO does not alter within ~180 h (T = 333K) (Fig. 1a).



$[H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO]$

Further studies showed that if the sufficiently weak bases such as pyridine and 2-methylpyridine are added to DMSO solution of the complex $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ it preserves the electron absorption spectrum with λ = 677 in the concentration range [Py] = [MePy] = 0.31–12.10 M at T = 328K within 70 h. Analogous fact was observed while using morpholine instead of pyridine or 2-methylpyridine. Unlike that, additives of stronger bases such as *n*-butylamine and piperidine lead to destabilization of $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$. Independent of the nature of bases after some time a decrease is observed in the intensity of the non-split *Q*-band with λ = 677 nm (Fig. 2) accompanied by the discoloration of the green solution (Fig. 2).

Kinetic studies showed that the reaction of destruction of $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ in the DMSO–*n*-butylamine (piperidine) system is described by the first order equation with respect to the proton transfer complex (Fig. 3).

$$-d[H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO]/d\tau = k_e[H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO].$$

Here k_e is the effective rate constant.

The reaction order with respect to the nitrogen-containing base was found graphically as the slope in the coordinates $\log k_e = f(\log [B])$ (Fig. 4). It occurred to be close to 1. Hence $k_e = k[B]$. Hence it follows that:

$$-d[H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO]/d\tau = k[H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO][B],$$

where k is the real rate constant.

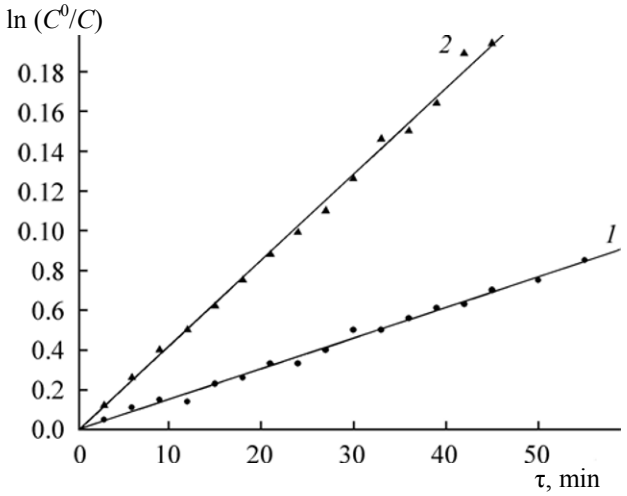


Fig. 3. Dependence of ln (C^0/C) on time in the reaction of destruction of $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ at the concentrations (M): (*1*) [$BuNH_2$] 6.32, (*2*) [Pipy] 5.05 in DMSO at (*1*) 338 K and (*2*) 343 K.

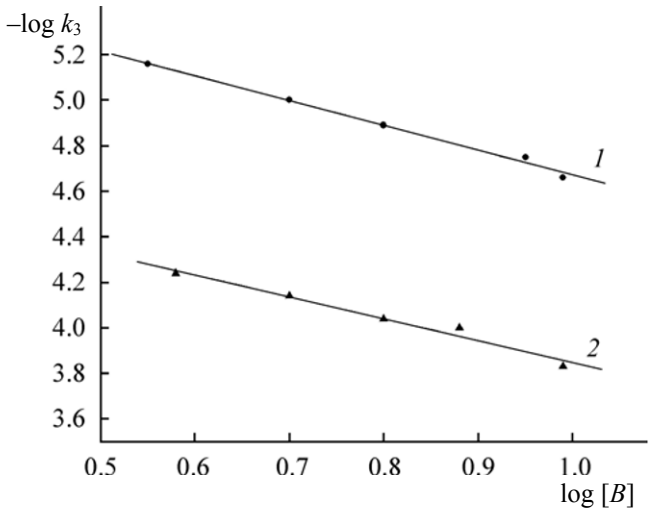


Fig. 4. Dependence of log k on log [B] for the reaction of destruction of $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ in the presence of (*1*) *n*-butylamine and (*2*) piperidine at (*1*) 328 K and (*2*) 343 K.

On the basis of the data obtained the probable mechanism of destruction of $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ under the action of $BuNH_2$ or piperidine may be presented by the following scheme:

$$H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO + B \xrightarrow{k_1} [HPc(NO_2)_4(t\text{-}Bu)_4\cdot DMSO]^- + HB^+ + DMSO, \quad (1)$$

$$[HPc(NO_2)_4(t\text{-}Bu)_4\cdot DMSO]^- + B \xrightarrow{k_2} [Pc(NO_2)_4(t\text{-}Bu)_4]_2^- + HB^+ + DMSO, \quad (2)$$

$$[Pc(NO_2)_4(t\text{-}Bu)_4]^{2-} \xrightarrow{k_3} \text{Destruction priducts.} \quad (3)$$

On the first and the second stages of the process the molecules of base react with hydrogen atoms of $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ and due to more expressed proton-acceptor properties displace DMSO molecules. At the same time the high basicity and permittivity of the medium favors the formation of dianionic form of tetra(3-nitro-5-*tert*-butyl)phthalocyanine which corresponds to the same D_{4h} symmetry group and does not differ spectroscopically from the proton transfer complex. Due to the absence of the effective compensation of the excess negative charge on the macroring $[Pc(NO_2)_4(t\text{-}Bu)_4]^{2-}$ the dianion becomes kinetically unstable and undergoes spontaneous decomposition to form the low molecular colorless products. The decrease in the concentration of $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ in the presence of the significant excess of nitrogen-containing base proceeds with the preservation of clear isobestic points without the appearance of the intermediate spectral form $[HPc(NO_2)_4(t\text{-}Bu)_4\cdot DMSO]^-$ (Fig. 2). This fact permits to suggest that $k_1 < k_2$.

Results of the experiments show (see the table) that the highest rate of decomposition of $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ is observed in the presence of piperidine which exhibits sufficiently high proton-acceptor ability and has sterically available nitrogen atom [11] which significantly facilitates the competing reaction with the proton according to Eqs. (1) and (2).

While using *n*-butylamine (pK_a 10.60 [12]) instead of piperidine (pK_a 11.23 [12]) the rate of destruction of $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ according to k^{298} value decreases ~2 times (see the table) despite the close basicity value of these amines. At the same time E_a and $\Delta S^{\neq}$ do not alter significantly. More significant differences were observed in going from *n*-butylamine to diethylamine (pK_a 10.93 [12]). In DMSO-Et_2NH system $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ complex does not decompose while handling. It seems quite possible that the decreased reactivity of diethylamine compared to *n*-butylamine is caused by the effect of stronger shielding of the unshared electron pair of nitrogen with bulky alkyl substituents. Therefore the interaction between $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ and diethylamine seems hardly probable. The key role of sterical factor was found previously in the investigation of stability of β-tetrahaloporphyrazine complexes with DMSO in the

Kinetic parameters of the reaction of destruction of complex $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ in the system nitrogen-containing compound–DMSO

C_B^0, M	T, K	$k_e\times10^4$,[a] s^{-1}	$k\times10^6$, l mol^{-1} s^{-1}	E_a, kJ mol^{-1}	$-\Delta S^{\neq}$,[a] J mol^{-1} K^{-1}
		Piperidine			
3.79	298	0.015	0.4	69	132
	323	0.13	3.4		
	333	0.27	7.1		
	343	0.58	15.3		
5.05	298	0.021	0.42	66	140
	323	0.17	3.4		
	333	0.33	6.5		
	343	0.72	14.3		
6.32	298	0.022	0.35	70	126
	323	0.2	3.2		
	333	0.38	6.0		
	343	0.92	14.6		
7.58	298	0.028	0.37	68	131
	323	0.23	3.0		
	333	0.5	6.6		
	343	0.99	13.1		
9.85	298	0.042	0.43	67	131
	323	0.34	3.5		
	333	0.75	7.6		
	343	1.47	14.9		
		n-Butylamine			
3.54	298	0.007	0.18	60	170
	328	0.07	1.85		
	338	0.14	3.70		
	348	0.25	6.60		
5.05	298	0.010	0.18	62	160
	328	0.10	1.90		
	338	0.20	3.70		
	348	0.37	6.70		
6.32	298	0.014	0.20	59	167
	328	0.13	1.90		
	338	0.26	3.75		
	348	0.45	6.55		
8.85	298	0.018	0.18	62	155
	328	0.18	1.80		
	338	0.35	3.60		
	348	0.66	6.70		
9.86	298	0.026	0.23	57	169
	328	0.22	1.99		
	338	0.41	3.71		
	348	0.74	6.70		

[a] k_e values at 298 K were calculated by means of the Arrhenius equation. Error of k_e evaluation is not more 5%, of E_a and $\Delta S^{\neq}$ 12%.

presence of *n*-butylamine and diethylamine. The rate of competing reaction with proton leading to the formation of the unstable porphyrazine dianion decreased significantly on the background of the growth of E_a of the process while using diethylamine instead of *n*-butylamine [3, 5].

Further studies showed that the decrease of K_a by five orders of magnitude in the series piperidine → morpholine → methylpyridine → pyridine also favors the kinetic stability of $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ complex because sufficiently weak proton acceptors can not compete with DMSO molecule in the reaction with proton. Due to that $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ complex is kinetically stable in DMSO–pyridine (methylpyridine, morpholine) systems.

EXPERIMENTAL

Tetra(3-nitro-5-*tert*-butyl)phthalocyanine was synthesized according to the procedure [13]. DMSO was kept for 24 h over the calcined magnesium sulfate and CaO and then distilled in a vacuum (2–3 mm Hg, bp 50°C). Nitrogen-containing compounds were twice purified according to [14]. While performing the kinetic measurements freshly prepared $H_2Pc(NO_2)_4\cdot(t\text{-}Bu)_4$ solution in DMCO was placed in the themperature-controlled cell of U-2001 spectrophotometer and the varied amount of nitrogen-containing base was added to it. The rate of destruction of the proton-transfer complex $H_2Pc(NO_2)_4(t\text{-}Bu)_4$ was evaluated from the decrease in the optical density of solution at λ = 677 nm. Current and final concentrations of complex were calculated by the formula:

$$C = C^0(A_\tau - A_\infty)/(A_0 - A_\infty), \quad (4)$$

where A_0, A_τ, and A_∞ are optical densities of the solutions at the beginning, at the current time τ, and after completion of the reaction (τ_∞), C^0, and C are the initial and the current concentrations of $H_2Pc(NO_2)_4\cdot(t\text{-}Bu)_4\cdot 2DMSO$ complex. All measurements were carried out under the conditions of the pseudofirst order. Therefore the effective rate constant of destruction of $H_2Pc(NO_2)_4(t\text{-}Bu)_4\cdot 2DMSO$ was calculated by the formula:

$$k_e = (1/\tau)\ln[(A_0 - A_\infty)/(A_\tau - A_\infty)]. \quad (5)$$

ACKNOWLEDGMENTS

The work was carried out with the financial support of Russian Fundation for Basic Research (project code 10-03-003950a).

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