# **CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY** =

# Stability of Benzotriazolyl-Substituted Phthalocyanines with Respect to Thermal Oxidative Decomposition

S. A. Znoiko<sup>a</sup>, V. E. Maizlish<sup>a</sup>, G. P. Shaposhnikov<sup>a</sup>, N. Sh. Lebedeva<sup>b,c</sup>, and E. A. Mal'kova<sup>b</sup>

<sup>a</sup>Ivanovo State University of Chemistry and Technology, Ivanovo, 153000 Russia

<sup>b</sup>G. A. Krestov Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, 153045 Russia <sup>c</sup>Ivanovo Institute of the State Fire Prevention Service, Ministry of Emergency Situations, Ivanovo, 153040 Russia

> *e-mail: znoykosa@yandex.ru* Received February 3, 2012

**Abstract**—The thermal oxidative decomposition of benzotriazolyl-substituted phthalocyanines and their copper complexes is investigated by means of thermogravimetric, elemental, and spectroscopic analysis. It is shown that the nature of peripheral substituents exerts the greatest effect on the thermal stability of the compounds.

*Keywords*: benzotriazolyl-substituted phthalocyanines, thermal oxidative decomposition, thermal stability. **DOI:** 10.1134/S0036024413030345

### INTRODUCTION

Phthalocyanines and their metal complexes are an extremely promising class of organic compounds for practical application [1-3], since they have high thermal stability and inherent spectroscopic properties due to the unique structure of their multicircuit conjugated aromatic system. The presence of substituents in phthalocyanine molecules gives rise to new valuable properties and broadens the area of their application, but can influence their thermal stability. This is particularly important with benzotriazolyl-substituted phthalocyanines, since there were no data on the effect of heterocyclic substituents (particularly the benzotriazole moiety) on the thermal stability of phthalocyanines at the time we were designing our investigation. Additional interest was also generated by the compounds investigated in this work having thermotropic mesomorphism (a  $Cr \rightarrow Mes$  phase shift at 99-212°C) [4, 5], further demonstrating the need to study their behavior at high temperatures.

#### **EXPERIMENTAL**

The investigated compounds (1a–4a, 6a) were synthesized by the interaction between the corresponding substituted phthalonitriles and copper acetate at 200– 220°C for 2 h [4]. The metal-free phthalocyanines (3b, 5b–7b) were synthesized by heating the corresponding substituted phthalonitriles in the presence of urea at 200–220°C for 2 h. The compounds were purified by column chromatography. The purity of the compounds was estimated by the constancy of log $\varepsilon$  (the molar extinction coefficient). Thermogravimetric investigations were performed in air using a thermoanalytical setup that consisted of a 1000D derivatograph, an instrumentation amplifier with gain factor of 500; a five-channel analog-to-digital converter and a PC [6]. The heating rate was 5 K/min. A sample of compound **7b** was investigated under a nitrogen atmosphere on a Perkin–Elmer DCS 7 (heating rate, 10 K/min).

Electronic absorption spectra from solutions of the investigated compounds in organic solvents (chloroform, DMF) at concentrations of  $10^{-4}$ – $10^{-6}$  M were recorded on a Hitachi U-2001 spectrophotometer at ~20°C in the wavelength range of 250–900 nm; the IR spectra were recorded on an Avatar 360 FT–IR ESP in the area of 400–4000 cm<sup>-1</sup> using pellets of KBr. The <sup>1</sup>H NMR spectra of 5% sample solutions using 0.1% TMS as an internal standard were recorded on a Brucker DRX-500. Elemental analysis was performed using a Flash EA 1112 CHNS–O Analyzer.

## **RESULTS AND DISCUSSION**

The results from our study of the thermal oxidative stability of benzotriazolyl-substituted phthalocyanines in the presence of atmospheric oxygen are presented in Table 1; our thermograms, in Figs. 1 and 2. The negligible mass loss of investigated samples study was registered on the TG curves upon heating to 200°C. The electronic absorption and IR spectra of the investigated samples recorded before the beginning of the experiment and after heating to 200°C were identical. As a consequence, the observed changes are not associated with the decomposition processes of phthalocyanine molecules.





The next stage,  $200^{\circ}$ C to  $350-400^{\circ}$ C, is characterized by a substantial change in mass and two peaks on the DTG and DTA curves (Fig. 1). The 20-30%reduction in the mass of the sample (Table 1) corresponds approximately to the elimination of the four benzotriazole substituents from the phthalocyanine molecule. An additional reference of the progress of thermal decomposition by IR spectroscopy and elemental analysis supports this assumption. For tetra-4-(1-benzotriazolyl)tetra-5-(4'-(quinoxalyl-2')phenoxy)phthalocyanine (**7b**), it was found by thermogravimetric analysis (TGA) that the first exo peak was registered in the DTA curve at 290°C; i.e., it was at this point that the thermal decomposition of this compound began (Fig. 1b). The 23.6% reduction in sample mass occurred in the temperature range of  $290-404^{\circ}$ C, corresponding to the removal of the four benzotriazole substituents according to mass, and is in agreement with our theoretical calculations of the mass of benzo-triazole substituents (Table 1).

After sample **7b** was heated at  $290^{\circ}$ C for 10 min, it was found that 94% of the obtained substance was soluble in chloroform, benzene, and DMF (X1); the character of its electronic absorption spectrum (EAS) (Fig. 2, curve 4) was analogous to those of the spectral curve of tetra-4-(4'-quinoxalyl-2'-phenoxy)phthalocyanine (Fig. 2, curve 2). We may therefore assume that this stage of thermal decomposition is more likely related to the elimination of the four benzotriazole substituents. The elemental analysis data of XI are also

No.	R	$\Delta m, \%$	$\Delta T$ , °C	$T_{\rm exo}$ , °C
1a	SPh	31.9 (29.0)	360-371	366
2a	OPh	33.4 (29.0)	427-455	431
<b>3</b> a	OC H (4' Ph)	27.5 (26.6)	410-430	413
<b>3</b> b	$OC_6 H_4(4 - FII)$	28.3 (28.0)	460-510	503
<b>4</b> a	$OC_6H_4(4'-t-Bu)$	29.9 (28.3)	407-413	412
5b	$OC_6H_4(4'-C(Ph)_3)$	21.4 (20.7)	544-580	577
6a		29.3 (28.6)	450-497	494
6b		30.3 (28.6)	480-530	520
7b		25.1 (23.6)	456-615	542

Table 1. Thermal oxidative decomposition of benzotriazolyl-substituted phthalocyanines and their copper complexes

Note:  $\Delta m$  is the theoretically calculated value of mass loss at 300–400°C. The experimentally obtained values are in parentheses.  $\Delta T$  is the temperature range corresponding to the maximum mass loss of the sample, °C;  $T_{exo}$  is the temperature of the maximum exo effect.



Fig. 1. Thermograms: (a) copper tetra-4-(1-benzotriazolyl)tetra-5-phenoxyphthalocyanine (2a) and (b) tetra-4-(1-benzotriaz-olyl)tetra-5-(4'-(quinoxalyl-2')-phenoxy)phthalocyanine (7b).

**Table 2.** Elemental analysis data on the product (**X**) obtained by heating tetra-4-(1-benzotriazolyl)tetra-5-(4'-(quinoxalyl-2')-phenoxy)phthalocyanine (**7b**) at  $290^{\circ}$ C

Compound	Empirical for- mula	N, %	C, %
X1	_	15.83	74.25
X2	_	18.69	70.12
X	_	16.88	77.35
Tetra-4-(1-benzotriaz- olyl)tetra-5-(4'-(quinox- alyl-2')-phenoxy)phthalo- cyanine ( <b>7b</b> )	$C_{112}N_{28}H_{62}O_4$	21.06	72.25
Tetra-4-(1-benzotriaz- olyl)phthalocyanine	$C_{56}N_{20}H_{30}$	28.56	68.57
Tetra-4-(quinoxalyl-2- phenoxy)phthalocyanine	$C_{88}N_{16}H_{50}O_4$	16.08	75.85

close to those for tetra-4-(4'-quinoxalyl-2'-phenoxy)phthalocyanine. The remainder of the heated sample (X2, ~6%) was soluble in DMF and retained its phthalocyanine structure (long-wavelength absorption bands at 710 nm in DMF and at 812 nm in concentrated  $H_2SO_4$  were observed in EAS).

To confirm our assumption of the removal of the benzotriazole fragments at the second stage, a sample of the compound **7b** exposed to heating at 290°C under an inert atmosphere (nitrogen) was investigated by electronic absorption, IR and <sup>1</sup>H NMR spectroscopy, and elemental analysis. The results are presented in Figs. 2 and 3 and Table 2. The solubility of the sample heated at the abovementioned temperature in chloroform and benzene was retained; hence, the oxo heteryl fragment that ensures solubility in these solvents was not eliminated. A 9 nm hypsochromic shift of the Q-band is therefore observed in EAS, and the ratio between the Q-band and its vibrational satellite



**Fig. 2.** EAS in DMF: (1) compound **7b**; (2) tetra-4-(4'-quinoxalyl-2'-phenoxy)phthalocyanine; (3) compound **7b** after heating at 290°C (in air); (4) compound **7b** after heating at 290°C (nitrogen).

changes (Fig. 2, curve 3). Consequently, the EAS of the heated sample (X) is identical to that of tetra-4-(4'-(quinoxalyl-2'-phenoxy)phthalocyanine (Fig. 2, curve 2) and differs from that of the initial compound 7b (Fig. 2, curve 1). According to our elemental analvsis data, the sample of compound 7b heated at 290°C contained nitrogen and carbon corresponding approximately to the percentage content of these elements in tetra-4-(4'-(quinoxalyl-2'-phenoxy)phthalocyanine (Table 2, X). The disappearance of the valence vibration band of the N=N bond in benzotriazole (1040- $1050 \text{ cm}^{-1}$ ) in the IR spectrum and the signal at 8.71 ppm in the <sup>1</sup>H NMR spectrum (the proton labeling for molecules of the compounds is given in Figs. 3a and 3b) implies that benzotriazole moieties are subject to elimination. We may thus conclude that the decomposition of this compound proceeds with the participation of 1-benzotriazole fragments at the first stage.

Further heating to 360–540°C leads to the thermal oxidative decomposition of the phthalocyanine mac-



**Fig. 3.** <sup>1</sup>H NMR spectra of tetra-4-(1-benzotriazolyl)tetra-5-(4'-(quinoxalyl-2')-phenoxy)phthalocyanine (**7b**): (a) initial; (b) after heating at 290°C.

RUSSIAN JOURNAL OF PHYSICAL CHEMISTRY A Vol. 87 No. 3 2013

rocycle, which in the case of copper complexes yields copper oxide. In the case of metal-free compounds, thermal oxidation is accompanied by the formation of gaseous products.

Among the investigated copper phthalocyanines, copper tetra-4-(1-benzotriazolvl)-tetra-5-phenvlsulfanylphthalocyanine (1a) has the least thermal stability. Replacing bridged sulfur atoms with oxygen atoms (2a) raises the temperature of the maximum exo effect by 65°C. This is probably due to the difference between the C–O and C–S bond strengths (a result of the low C-S bond energy [7]) and the easier oxidation of the thiobridge owing to the lower electronegativity of sulfur atom. The high thermal stability of complex 6a is probably due to the bulky 2-naphthol fragments, which lie outside the phthalocyanine macrocycle plane and are turned at an angle of  $60^{\circ}$  to it, shielding the phthalocyanine core from oxygen molecules most efficiently. This raises the temperature of the maximum exo effect. Analogous regular trends in the substituent's influence were noticed earlier when analyzing the stability of benzotriazolyl-substituted phthalocyanines [8].

The thermal oxidative decomposition of most of the studied metal-free phthalocyanines takes place at higher temperatures than for the corresponding metal complexes. As can be seen from the data presented in Table 1, their thermal stability depends substantially on the nature of the substituent introduced in the *ortho*-position to the 1-benzotriazolyl fragment. The temperature of the maximum exo effect of phthalocyanines—ligands thus rises in the following series (Table 1):

#### 3b < 6b < 7b < 5b.

It can seen from the presented series that both the annelation and the introduction of bulky substituents in the *para*-position to phenoxy groups leads to an increase in the thermal stability of the compounds (Table 1). Compound **5b** containing the bulkiest triphenymethyl fragments in the *para*-positions to phenoxy groups have the highest thermal stability.

#### REFERENCES

- K. M. Kadish, K. M. Smith, and R. Guilard, *The Porphyrin Handbook* (Acad. Press, Elsevier Science (USA), New York, 2003), Vol. 15.
- G. P. Shaposhnikov, V. P. Kulinich, and V. E. Maizlish, in *Achievements of Porphyrin Chemistry*, Ed. by O. A. Golubchikov (NII Khimii SPbGU, St. Petersburg, 1999), Vol. 2, p. 190 [in Russian].
- G. P. Shaposhnikov, V. E. Maizlish, V. P. Kulinich, et al., Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol. 48 (7), 22 (2005).
- S. A. Znoiko, V. E. Maizlish, G. P. Shaposhnikov, et al., Zhidk. Krist. Praktich. Ispolz., Nos. 3–4 (13–14), 30 (2007).
- S. A. Znoiko, V. E. Maizlish, G. P. Shaposhnikov, et al., Zhidk. Krist. Praktich. Ispolz., No. 1 (27), 24 (2009).
- N. Sh. Lebedeva, S. P. Yakubov, A. N. Kinchin, and A. I. V'yugin, Russ. J. Phys. Chem. A 79, 827 (2005).
- 7. B. D. Berezin and D. B. Berezin, *Course of Modern Organic Chemistry*, The Manual for Higher School (Vysshaya Shkola, Moscow, 1999) [in Russian].
- N. A. Pavlycheva, N. Sh. Lebedeva, A. I. V'yugin, et al., Russ. J. Phys. Chem. A 82, 1847 (2008).