Journal of Thermal Analysis and Calorimetry, Vol. 81 (2005) 451–455

THERMAL OXIDATIVE DESTRUCTION OF COBALT(II)PHTHALOCYANINES WITH OXYGEN CONTAINING SUBSTITUENTS

N. Sh. Lebedeva[1*], *N. A. Pavlycheva*[1], *V. P. Kulinich*[2], *G. P. Shaposhnikov*[2] *and E. V. Parfenyuk*[1]

[1]Institute of Solution Chemistry, Russian Academy of Sciences, 1 Akademicheskaya Street, 153045 Ivanovo, Russia
[2]State University of Chemistry and Technology, 7 Fridrif Engels Street, 153460 Ivanovo, Russia

Processes of thermooxidizing destruction of series of oxygen containing cobalt(II)phthalocyanines were studied by thermogravimetry and IR and electronic absorption spectroscopy. These processes have several stages including dehydration, oxidation, desulphonation (decarboxylation) of peripheral substituents of cobalt(II)phthalocyanines, destruction of phthalocyanine macrocycle and oxidation until the highest oxides. The temperature of beginning of the process of thermal oxidative destruction decreases in the following order: $Co(4\text{-}PhSO_3H)_4Pc > Co(4\text{-}COO^-)_4(5\text{-}SO_3^-)_4(Ba^{2+})_4Pc > Co(4\text{-}Br)_4(5\text{-}SO_3H)_4Pc > Co(4\text{-}Cl)_4(5\text{-}SO_3H)_4Pc > Co(4\text{-}COOH)_4(5\text{-}SO_3H)_4Pc$.

Keywords: *macrocycle, metallophthalocyanines, thermogravimetry, thermooxidizing destruction*

Introduction

Phthalocyanines (Pc) and their metal complexes are characterized by unique physical-chemical properties. Potential possibility of application of Pc and MPc as chemical sensors [1], catalysis [2], liquid crystals, drugs for inactivation of bacteria and viruses, in photodynamic therapy etc. causes increased interest to this class of compounds. Due to the great scientific and practical applications of MPc, the information about thermal oxidative stability is of a great importance [3–5]. Attempts of the investigation of thermal oxidative destruction process of MPc containing different functional substituents were undertaken repeatedly. However, contradictory conclusions were obtained. Complexity of investigation of solid crystal samples of MPc and their molecular complexes is associated with an ability of these macroheterocyclic compounds to exist in different polymorphous modifications. In the present time a few polymorphous forms (α, β, γ) have been found and characterized by spectral method [6].

The information about influence of heating on intraphase polymorphous transition from α to more stable β-modification is also contradictory. Elshereaty and El-Ghaffar [7] determined the activation energy of the intrapolymorphous transition $\alpha \to \beta$ for CuPc. From the point of view of these authors, exothermic peaks on the DTA curve at 438–503 K correspond to this process. It should be noted [7] that at the used heating rate (15 K min^{-1}) a complete transition from α- to β-form must be realized during 4–10 min while accordingly to the results reported in [3], the $\alpha \to \beta$ transition was registrated after heating during 2 h at 553 K. For another MPc much more time is required (≈5–6 h). From IR spectra of alkyl substituted MPc it has been found that crystal sample of sublimated zinc(II)-tetra-*tert*-butylphthalocyanine ($Zn(t\text{-}Bu)_4Pc$) contains both crystal forms (α and β). The heating of this sample with the rate of 5 K min^{-1} up to destruction temperature of $Zn(t\text{-}Bu)_4Pc$ (523 K) does not lead to significant changes of the modification percentage. The endothermic and exothermic effects on the DTA curve are associated with defects of crystal lattice of the studied sample. Interpretation of the data on the thermal oxidative stability of MPc containing oxygen is more difficult because the heating of MPc can promote not only intraphase polymorphous transition but also can lead to ‘cross-linking’ of MPc molecules. In particular, an analysis of the thermal stability of $Cu(4\text{-}COOH)_4Pc$ [4] showed that at 643 K decarboxylation occurs which is accompanied by formation of polymer phthalocyanine structures. The exothermic peak on the DTA curve was observed for this process. On the contrary, according to the data reported in [8], the decarboxylation of $Cu(4\text{-}COOH)_4Pc$ begins at 558 K and is accompanied by the endothermic effect on the DTA curve. The studies of conductivity of crystal samples of $Cu(4\text{-}COOH)_4Pc$ [7] showed that the reaction of decarboxylation occurs at 453 K. On the one hand, such contradictory date testify about complexity of the systems under study. On the other hand, this demonstrates a necessity of complex study based on application of a few experimental methods. The aim of this work is to study the process of the thermal oxidative destruction of some O-containing cobalt(II)phthalocyanines (CoPc) synthesized earlier [9, 10] by method of thermogravimetric analysis and IR and electron absorption spectroscopy.

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[*] Author for correspondence: nsl@isc-ras.ru

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Experimental

Materials and methods

Thermogravimetric measurements were made with thermoanalytical apparatus containing derivatograph 1000D (MOM, Hungry), software apparatus package, computer. Thermogravimetric measurements were made in air atmosphere. All the experiments were triplicate. Derivatograph at a heating rate of 5 K min^{-1}.

Infrared spectra of CoPc and heating sample were recorded on Perkin-Elmer 'Spectrum BX' spectrometer in 4000–400 cm^{-1} region. The samples for measurements were prepared according to standard procedure as KBr discs.

Electron absorption spectra of CoPc in DMF and DMSO were recorded on spectrophotometer Specord M40 (Germany).

Cobalt(II)phthalocyanines

Cobalt(II)-tetra-4-sulfophenylphthalocyanine (Co(4-PhSO$_3$H)$_4$Pc) (**I**), cobalt(II)-tetra-4-brom-tetra-5-sulfophthalocyanine (Co(4-Br)$_4$(5-SO$_3$H)$_4$Pc) (**II**), cobalt(II)-tetra-4-chloro-tetra-5-sulfophthalocyanine (Co(4-Cl)$_4$(5-SO$_3$H)$_4$Pc) (**III**), cobalt(II)-tetra-4-carboxy-tetra-5-sulfophthalocyanine (Co(4-COOH)$_4$(5-SO$_3$H)$_4$Pc) (**IV**), barium salt cobalt(II)-tetra-4-carboxy-tetra-5-sulfophthalocyanine (Co(4-COO$^-$)$_4$(5-SO$_3^-$)$_4$(Ba^{2+})$_4$Pc) (**V**) were synthesized and purified in accordance with recommendation [9, 10].

Results and discussion

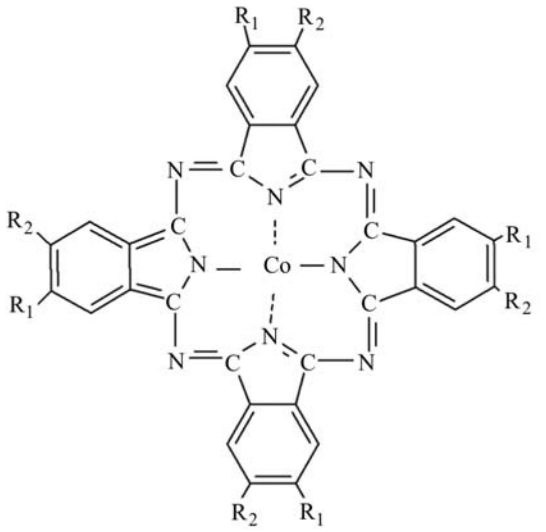
The results of the study on the thermal oxidative destruction of CoPc are presented in Table 1. The thermogravimetric curve for Co(4-PhSO$_3$H)$_4$Pc), Co(4-Br)$_4$(5-SO$_3$H)$_4$Pc, Co(4-Cl)$_4$(5-SO$_3$H)$_4$Pc, Co(4-COOH)$_4$(5-SO$_3$H)$_4$Pc, Co(4-COO$^-$)$_4$(5-SO$_3^-$)$_4$(Ba^{2+})$_4$Pc are shown in Figs 1–5, respectively.

During the first step (283–523 K) mass losses from 9 to 20% were registered for the samples studied. The electron absorption spectra of CoPc solutions before thermogravimetric analysis and after heating of the samples to corresponding temperature (Table 1, step I) show that the registered changes do not deal with CoPc destruction process. It is likely that this step is associated with the losses of H_2O, CO_2 molecules adsorbed by CoPc from the air. The percentage of the adsorbed substances in the samples increases in the following order:

$$\text{Co(4-Br)}_4\text{(5-SO}_3\text{H)}_4\text{Pc} \leq \text{Co(4-PhSO}_3\text{H)}_4\text{Pc} \leq \text{Co(4-Cl)}_4\text{(5-SO}_3\text{H)}_4\text{Pc} < \text{Co(4-COOH)}_4\text{(5-SO}_3\text{H)}_4\text{Pc} \leq \text{Co(4-COO}^-\text{)}_4\text{(5-SO}_3^-\text{)}_4\text{(Ba}^{2+}\text{)}_4\text{Pc}$$

The second step reflects the beginning of the thermal oxidative destruction process of CoPc. The samples of CoPc were heated to corresponding temperatures (Table 1, step II) and analyzed by the spectral method. The mass loss (%) during the second step decreases in the following order:

$$\text{Co(4-Br)}_4\text{(5-SO}_3\text{H)}_4\text{Pc} \geq \text{Co(4-Cl)}_4\text{(5-SO}_3\text{H)}_4\text{Pc} > \text{Co(4-PhSO}_3\text{H)}_4\text{Pc} > \text{Co(4-COOH)}_4\text{(5-SO}_3\text{H)}_4\text{Pc} > \text{Co(4-COO}^-\text{)}_4\text{(5-SO}_3^-\text{)}_4\text{(Ba}^{2+}\text{)}_4\text{Pc}$$



I $R_1=R_2=C_6H_4SO_3H$ **III** $R_1=Cl$, $R_2=SO_3H$

II $R_1=Br$, $R_2=SO_3H$ **IV** $R_1=COOH$, $R_2=SO_3H$

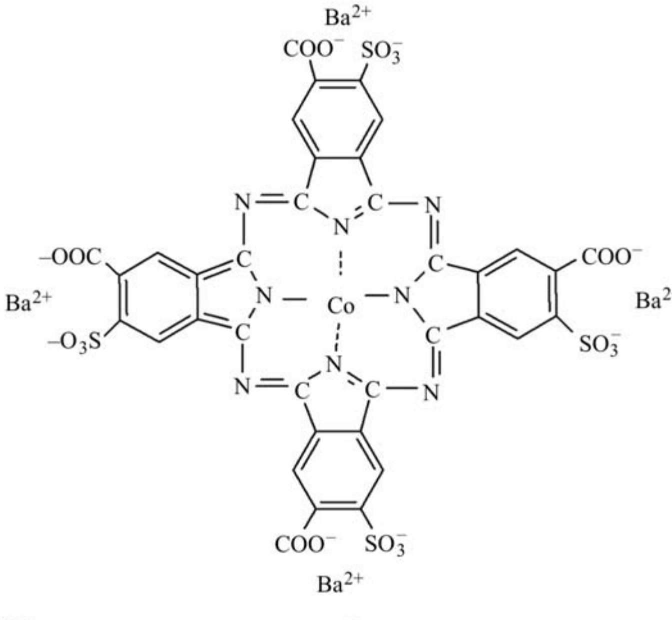


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Table 1 Thermal oxidative destruction of cobalt(II)phthalocyanine

CoPc	Step	Temperature range/K	Mass loss of sample/%	T_{max}/K
Co(4-PhSO$_3$H)$_4$Pc	I	291–423	9.6	828
	II	523–683	23.5*	
	III	683–793	20.9*	
	IV	793–893	45.2*	
Co(4-Br)$_4$(5-SO$_3$H)$_4$Pc	I	287–423	8	898
	II	493–573	24.8*	
		573–670	7*	
	III	670–833	34.9*	
	IV	833–903	22.3*	
Co(4-Cl)$_4$(5-SO$_3$H)$_4$Pc	I	285–423	11.2	758
	II	483–623	28.4*	
	III	623–703	21.1*	
	IV	703–863	37.9*	
Co(4-COOH)$_4$(5-SO$_3$H)$_4$Pc	I	291–443	16	823
	II	483–613	18.6*	
	III	613–758	37.9*	
	IV	758–913	33.1*	
Co(4-COO$^-$)$_4$(5-SO$_3^-$)$_4$(Ba^{2+})$_4$Pc	I	287–493	18.1	863
	II	503–653	9.5*	
	III	653–773	11.8*	
	IV	773–903	46.5*	

*These values were corrected to amount of the corresponding cobalt(II)phthalocyanine

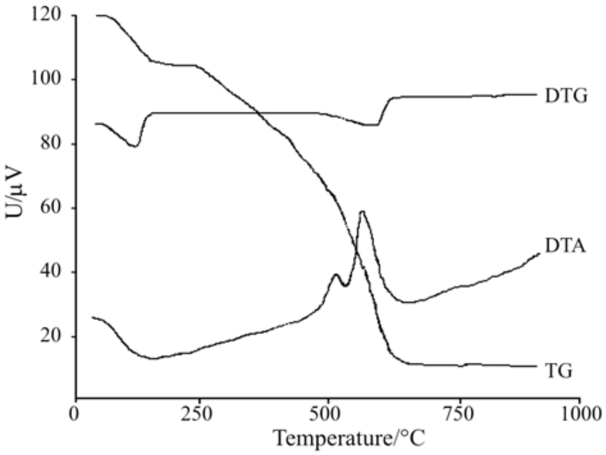

Fig. 1 Thermal oxidative destruction of Co(4-PhSO$_3$H)$_4$Pc

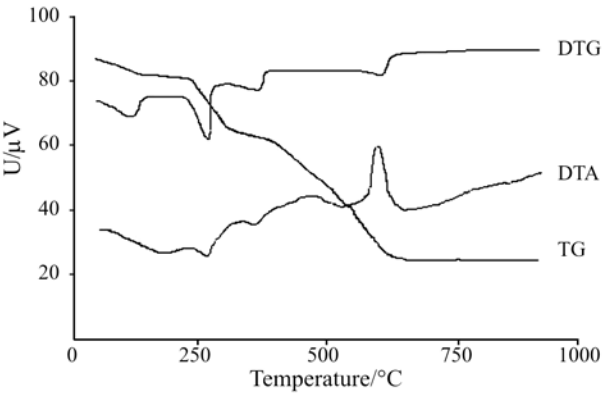

Fig. 2 Thermal oxidative destruction of Co(4-Br)$_4$(5-SO$_3$H)$_4$Pc

Comparison of the IR spectra of Co(4-Br)$_4$(5-SO$_3$H)$_4$Pc, Co(4-Cl)$_4$(5-SO$_3$H)$_4$Pc and Co(4-PhSO$_3$H)$_4$Pc heated to corresponding temperatures with the IR spectra of initial substances demonstrates the following total characteristic features: (*i*) coincidence of a large number of the bands is observed; (*ii*) resolution of the spectra on the whole is kept; (*iii*) however, the band 1617 cm^{-1} disappears completely. The IR spectrum of Co(4-PhSO$_3$H)$_4$Pc, heated to 683 K is similar to the spectrum of the initial sample. However, the intensities of OH (1210–1220 cm^{-1}) [11] and C–S (613–635 cm^{-1}) stretching vibrations decrease significantly. Obviously, such spectral changes reflect decrease of amount of sulfo-groups. But complete loss of sulfo-groups is not observed because very intensive band (1180–1210 cm^{-1}) assigned to the anhydride (S=O) vibrations [12] is kept. No additional bands in the spectrum of the heated Co(4-PhSO$_3$H)$_4$Pc assigned to polymer MPc molecules in low- and high-frequency regions were found. Lower solubility of Co(4-PhSO$_3$H)$_4$Pc after thermal treatment and some changes in its absorption spectrum in DMF (shift of *Q* band to short-wave region ($\Delta\lambda$=8 nm) and bathochromic shift of Sore band) can be explained both by decrease of amount of peripheral O-containing substitutes and formation of polymer structures of MPc [12, 13]. The exothermic peaks on the DTA curve are not also characteristic because they include effects of dehydration and formation of anhydrides. Moreover, the DTA curve reflects changes of heat capacity of the sample.

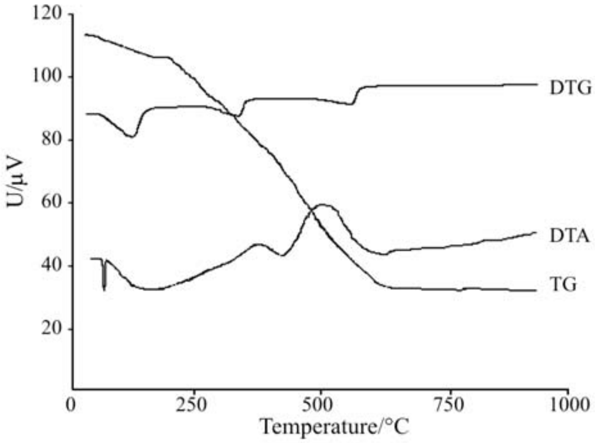

Fig. 3 Thermal oxidative destruction of Co(4-Cl)$_4$(5-SO$_3$H)$_4$Pc

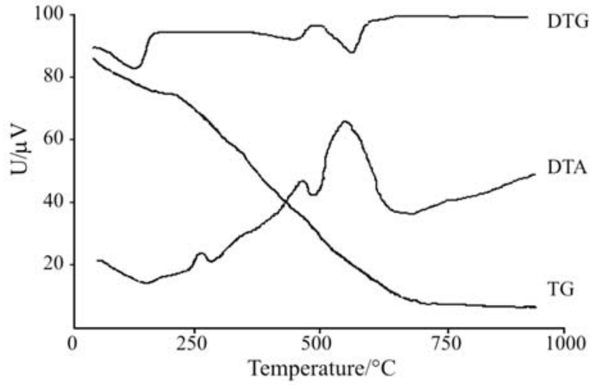

Fig. 4 Thermal oxidative destruction of Co(4-COOH)$_4$(5-SO$_3$H)$_4$Pc

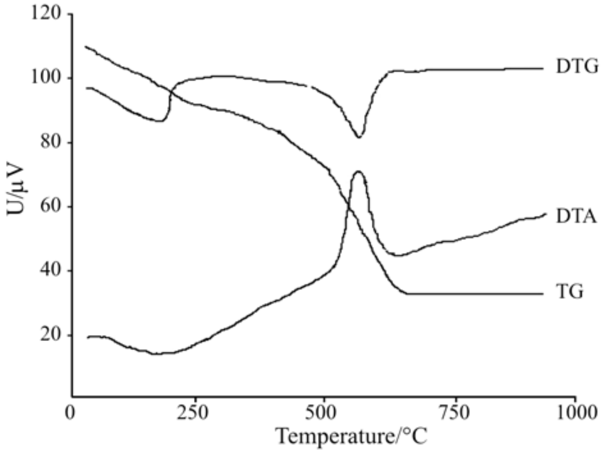

Fig. 5 Thermal oxidative destruction of Co(4-COO$^-$)$_4$(5-SO$_3^-$)$_4$(Ba^{2+})$_4$Pc

Pronounced IR spectral changes were registered for halogen substituted CoPc. In the IR spectrum of Co(4-Br)$_4$(5-SO$_3$H)$_4$Pc heated to 670 K the band at 604 cm^{-1} assigned to (C–Br) vibrations disappears. In comparison with Co(4-PhSO$_3$H)$_4$Pc, the intensity of the anhydride ν(S=O) band at 1180–1210 cm^{-1} [12] decreases and a band appears at 929 cm^{-1}. Probably the greatest mass loss during the second step of the thermal oxidative destruction of Co(4-Br)$_4$(5-SO$_3$H)$_4$Pc and the registered spectral changes are associated with dehalogenation and desulfonation processes of the corresponding CoPc. The kind of the DTG curve reflecting different rates of losses of gaseous products confirms this supposition. The enthalpy change for the loss of these gaseous products (523–573 K) is to be 253 kJ mol^{-1}. This value is very close to the value reported for the energy of C–Br bond being equal 276 kJ mol^{-1} [14]. The mass loss of 25% which corresponds to amount (mass%) bromine atoms in Co(4-Br)$_4$(5-SO$_3$H)$_4$Pc molecule is indirect evidence of the dehalogenation process at the 523–573 K range. The absorption spectra in the visible region for Co(4-Br)$_4$(5-SO$_3$H)$_4$Pc solutions heated to 670 K are similar to those for MPc. However, in comparison with the initial solutions, the long-wave *Q* band of Co(4-Br)$_4$(5-SO$_3$H)$_4$Pc solutions exhibits blue shift of 2 nm.

The heating of Co(4-Cl)$_4$(5-SO$_3$H)$_4$Pc to 623 K results in essential IR changes also. Like for Co(4-Br)$_4$(5-SO$_3$H)$_4$Pc, after heating of Co(4-Cl)$_4$ (5-SO$_3$H)$_4$Pc samples the intensities of the ν(C=S) band at 612 cm^{-1}, (S=O) vibrations at 1400 cm^{-1} and 1110–1200 cm^{-1} [6, 11, 12] decrease and a new band appears at 1514 cm^{-1}. The comparison of the obtained results allows to conclude that oxidation of peripheral substituents of Co(4-Cl)$_4$ (5-SO$_3$H)$_4$Pc molecules occurs at the second step. The process of the loss of the gaseous products at the thermal oxidative destruction proceeds with constant rate (monotonous DTG curve). Consequently, no complete dehalogenation of Co(4-Cl)$_4$(5-SO$_3$H)$_4$Pc occurs at the given step (483–623 K).

Pronounced changes occur in Co(4-COOH)$_4$ (5-SO$_3$H)$_4$Pc spectrum in the visible region after heating to 613 K. The *Q* band shifts to short-wave region and Sore band shifts to long-wave region. The IR spectrum of Co(4-COOH)$_4$(5-SO$_3$H)$_4$Pc after heating has lesser resolution as compared to the spectrum of initial Co(4-COOH)$_4$(5-SO$_3$H)$_4$Pc. It should be noted disappearances of the band at 694 cm^{-1} ((C–S) vibrations), 2840–2310 cm^{-1} assigned to OH groups in carboxyl substituents [12] and significant decrease of the intensities of the ν(C=O) band at 1720 cm^{-1} [12], the ν(S=O) band at 1400 and 1197 cm^{-1}, the band at 1092 cm^{-1}. New bands appear at 973 and 1519 cm^{-1}. The kind of DTA curve of Co(4-COOH)$_4$(5-SO$_3$H)$_4$Pc at the 483–613 K range is unusual. The DTA curve has a few extrema. Thus, on the basis of the obtained data it may be concluded that the processes of dehydration of carboxyl substituents, anhydride formation and partial decarboxylation and desulfonation take place.

Salt formation of the peripheral O-containing substituents with metal ions Co(4-COO$^-$)$_4$(5-SO$_3^-$)$_4$(Ba^{2+})$_4$Pc changes the thermal oxidation process completely. The second step (503–603 K) of the thermal oxidation of barium salt of $Co(4\text{-}COOH)_4(5\text{-}SO_3H)_4Pc$ is accompanied by insignificant mass loss (up to 10%). The DTA curves are monotonous at this step. The IR spectrum of $Co(4\text{-}COO^-)_4(5\text{-}SO_3^-)_4(Ba^{2+})_4Pc$ are not changed on principle after heating in comparison with the initial $Co(4\text{-}COO^-)_4(5\text{-}SO_3^-)_4(Ba^{2+})_4Pc$: (*i*) the intensities of the bands at 766 cm^{-1} (vibrations associated with deformation of macrocycle [6]) and at 1374 cm^{-1} (vibrations assigned to a state of central metal ion in MPc molecule [6]) decrease; (*ii*) the band at 766 cm^{-1} exhibits a shift of 10 cm^{-1} to low-frequency region and the band at 1374 cm^{-1} exhibit the shift of 10 cm^{-1} to high-frequency region. It is interesting to note that for all another cobalt(II)phthalocyanine studied the greatest shift of bands is observed at 1180–1190 and 1711–1738 cm^{-1} which are assigned to valent and deformation vibrations of O-containing peripheral substituents of cobalt(II)phthalocyanines.

The results obtained testify about absence of the processes of decarboxylation and desulfonation of the barium salt of cobalt(II)phthalocyanines at the 503–603 K range and allow make supposition about process of phase transformations affecting on state of metal ion and peripheral substituents. It is not intraphase polymorphous $\alpha\rightarrow\beta$ transformation because the bands that are sensitive to crystal structure of MPc (No. 11, 12, 14, 15, 19, 22 according to [6]), except the bands 8 and 9, do not undergo significant changes. The presence of the thermo induced intraphase transformation of the barium salt $Co(4\text{-}COOH)_4(5\text{-}SO_3H)_4Pc$ associated with change of energy of crystal lattice and state of peripheral O-containing substituents is confirmed by increasing solubility of $Co(4\text{-}COO^-)_4(5\text{-}SO_3^-)_4(Ba^{2+})_4Pc$ after heating. The electron absorption spectra of water-alkaline solutions of the initial sample and after heating that were treated by HCl previously, testify about different ability of $Co(4\text{-}COO^-)_4(5\text{-}SO_3^-)_4(Ba^{2+})_4Pc$ to aggregate.

The third and fourth steps may be attributed to breaking of phthalocyanine macrocycle and formation of the highest oxides (Figs 1–5, exo-effects). The breaking of phthalocyanine macrocycle (step III) has confirmed by the methods of electron absorption and vibration spectroscopy: at heating to the corresponding temperatures a typical spectrum of cobalt(II)phthalocyanine is not reproduced.

Generalization of the obtained results allows to conclude that the process of the thermal oxidative destruction of the studied cobalt(II)phthalocyanine have a few steps, including dehydration, oxidation, desulfonation (decarboxylation) of peripheral substituents of phthalocyanine, destruction of phthalocyanine macrocycle and oxidation up to the highest oxides.

The temperature of beginning of the process of thermal oxidative destruction decreases in the following order:

$$Co(4\text{-}PhSO_3H)_4Pc > Co(4\text{-}COO^-)_4(5\text{-}SO_3^-)_4(Ba^{2+})_4Pc > Co(4\text{-}Br)_4(5\text{-}SO_3H)_4Pc > Co(4\text{-}Cl)_4(5\text{-}SO_3H)_4Pc > Co(4\text{-}COOH)_4(5\text{-}SO_3H)_4Pc$$

Acknowledgements

This work was supported by Russian Academy of Sciences. The program of fundamental studies of Presidium of RAS ‘Directional synthesis of compounds with prescribed properties and creation of functional materials on their basis’ and Russian Science Support Foundation.

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Received: December 28, 2004
In revised form: February 28, 2005

DOI: 10.1007/s10973-005-6639-2