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THERMAL OXIDATIVE DESTRUCTION OF COMPLEXES OF HETEROCYCLIC N-OXIDES WITH Zn(II)TETRA-PHENYLPORPHYRIN

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Thermogravimetry, differential thermal analysis and differential scanning calorimetry were applied for investigation of molecular complexes of heterocyclic N-oxide with zinc(II)tetraphenylporphyrin. The kinetic characteristics of the process of the thermal oxidative destruction for individual compounds and their molecular complexes have been calculated. The obtained results indicate that the complex formation of ZnTPhP with heteroaromatic N-oxides leads to an increase of the thermal stability both the metalloporphyrin and the ligands. It has been shown that the stability of the molecular complexes of ZnTPhP with heteroaromatic N-oxides depends on basicity of the coordinated ligand.

Keywords: *complexes of heterocyclic N-oxides with Zn(II)tetraphenylporphyrin, kinetics, thermal oxidative destruction*

Introduction

Heterocyclic N-oxides are of great practical interest due to their biological properties. Some of them show carcinogenic, herbicidal, analgesic, antifungal, stimulating growth of plant activity [1–4]. Heterocyclic N-oxides due to their structural peculiarities (high donor ability of N→O group and its steric accessibility) play an important role in metabolic processes in living organisms and have practical industrial and pharmaceutical significance. Because complex formation of metalloporphyrins with bioactive ligands plays key roles in nature, the studies of these processes are of a great importance. But notwithstanding obvious significance, such studies are very rare. No the works devoted to thermochemical investigations of specific intermolecular interactions of metalloporphyrins with heterocyclic N-oxides were found. The aim of this work is to study the process of thermal oxidative destruction of molecular complexes of zinc(II)tetra-phenylporphyrin (ZnTPhP) with pyridine and quinoline N-oxides and their styryl derivatives.

Experimental

Materials

Ligands: (L)

4-NPyO	4-nitropyridine N-oxide
4-DPyO	4-(4-dimethylaminostyryl)pyridine N-oxide
4-MPyO	4-(4-methoxystyryl)pyridine N-oxide
QO	Quinoline N-oxide
2-MeQO	2-methylquinoline N-oxide
4-MeQO	4-methylquinoline N-oxide
4-ClQO	4-chloroquinoline N-oxide
2-StQO	2-styrylquinoline N-oxide
2-DQO	2-(4-dimethylaminostyryl)quinoline N-oxide

Complexes

All the heterocyclic N-oxides studied were synthesized and purified by known procedures [5–7]. The complexes were prepared by mixing of equimolar amounts of ZnTPhP and N-oxide solutions in acetone. Complex of ZnTPhP·4-NPyO was synthesized by mixing of equimolar amounts of ZnTPhP and N-oxide solutions in mixture of chloroform and hexane. The detailed description of the preparation of these complexes and their identification has been reported in [8].

Application of synthetic symmetrically substituted metalloporphyrin without peripheral substitutes allowing specific interactions with heterocyclic N-oxides enables to estimate an influence of nature of N-oxide on physico-chemical characteristics of molecular complexes. Thermogravimetry was applied to obtain kinetic characteristics of the thermal oxidative destruction of the molecular complexes of ZnTPhP with some heterocyclic N-oxides. The thermal stability of the complexes in argon were estimated by differential scanning calorimetry (DSC).

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Methods

TG and DTA analysis

The study of thermal oxidative destruction of the molecular complexes of ZnTPhP with heterocyclic N-oxides were performed in air atmosphere using the thermoanalytical unit (consisting of TG and DTA devices) [9]. For obtaining the thermal characteristics of the above processes, the samples were heated with the heating rate 5 K min^{-1}, at air flow. The results of the TG experiments were the basis of determination of the temperature limits of the postulated stages of processes in question and mass losses within these limits.

Differential Scanning Calorimetry (DSC)

The thermal destruction of the molecular complexes in inert atmosphere was studied using DuPont 2100 Thermal Analyst, DSC 910 unit. Measurements were carried-out in argon atmosphere, at flow and heating rates 50 mL min^{-1} and 5 K min^{-1}, respectively.

Treatment of the experimental data

Kinetic parameters of thermal oxidative process were calculated according to well-known procedures (Coats and Redfern [10], Sestak and Berggren [11]). The first procedure allows calculation of the activation energy (E_a) and the order of reaction. The procedure of calculation proposed by Sestak and Berggren allows to obtain all kinetic parameters E_a, ln(A) of the thermal oxidative process and determine limiting stage of the process.

Thirty-two expressions of $f(\alpha)$ (a mathematical function whose form depends on the reaction type [12, 13]) were used for calculation according the procedure proposed by Sestak and Berggren.

In the present work more simple method of calculation of the apparent activation energy using DTG data was also applied [14].

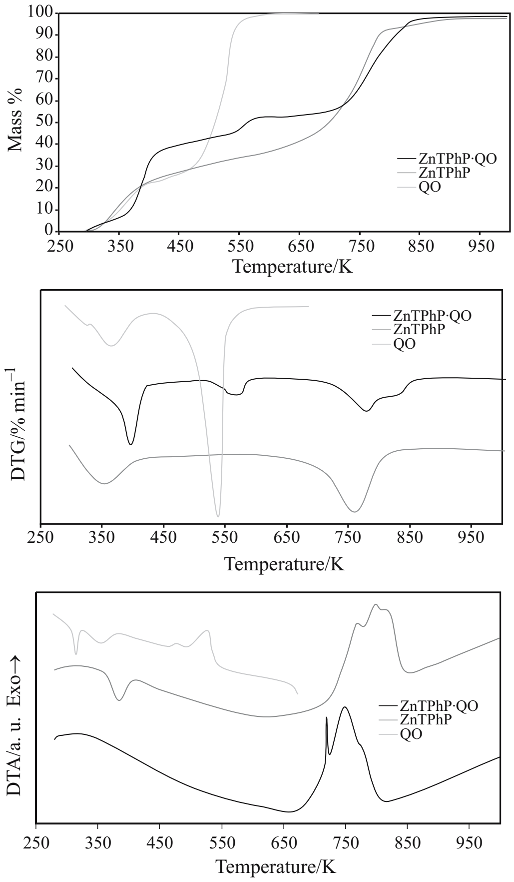

Fig. 1 Diagrams of the thermal oxidative destruction of QO, ZnTPhP, ZnTPhP·QO. TG, DTG and DTA curves

Results and discussion

As an example, typical thermoanalytical curves of the thermal oxidative destruction for molecular complex ZnTPhP·QO, QO and ZnTPhP are presented in Fig. 1. The kind of TG and DTG curves testify about mass losses of the sample under study at the 522–590 K range. But no changes is observed on the DTA curve. Comparison of the curves for the molecular complex

Table 1 The temperature ranges of stages of thermal oxidative destruction of the complexes studied

Substance	I stage	II stage	III stage	IV stage	V stage	VI stage	VII stage
	Temperature range/K						
ZnTPhP·2-DQO	291–453	453–498	498–532	532–685	685–806		
ZnTPhP·4-MeQO	289–430	430–511	511–576	576–700	700–799		
ZnTPhP·2-StQO	295–340	340–397	397–543	543–583	583–696	696–764	764–821
ZnTPhP·4-ClQO	294–444	444–512	512–555	555–702	702–835		
ZnTPhP·4-DPyO	291–472	472–522	522–573	573–674	674–746	746–796	
ZnTPhP·4-MPyO	294–395	395–445	445–513	513–539	539–566	566–700	700–802
ZnTPhP·4-NPyO	291–468	468–716	716–845				
ZnTPhP·QO	294–416	416–522	522–590	590–717	717–796		
ZnTPhP·2-MeQO	292–451	451–539	539–690	690–760			

Table 2 The kinetic characteristics of the thermal oxidation of the complexes

Substance	Nº stage	E_a/kJ mol^{-1}	ln A	n	r^2	$f(\alpha)$	Model	Method of calculation
ZnTPhP·2-DQO	I	42.62			0.971	(1–α)	F1	[14]
		23.82	9.4		0.928			[11]
		28.20		1	0.963			[10]
	III	360.04			0.989	(1–α)	F1	[14]
		183.47	46.1		0.920			[11]
		270.10		1	0.964			[10]
	V	294.81			0.990	(1–α)	F1	[14]
		201.16	33.8		0.988			[11]
		207.5		1	0.992			[10]
ZnTPhP·2-StQO	II	75.51			0.985	(1–α)	F1	[14]
		70.10	25.5		0.980			[11]
		80.79		1	0.987			[10]
	IV	451.12			0.942	(1–α)	F1	[14]
		400.98	89.0		0.957			[11]
		418.03		1	0.989			[10]
	VI	242.94			0.984	(1–α)	F1	[14]
		186.77	33.1		0.991			[11]
		292.25		1	0.982			[10]
	VII	580.68			0.970	(1–α)	F1	[14]
		208.17	33.0		0.781			[11]
		322.25		1	0.992			[10]
ZnTPhP·4-MeQO	I	36.42			0.964	(1–α)	F1	[14]
		29.35	12.0		0.973			[11]
		58.58		1	0.934			[10]
	III	187.05			0.982	(1–α)	F1	[14]
		148.06	35.8		0.952			[11]
		155.73		1	0.980			[10]
	V	242.93			0.978	(1–α)	F1	[14]
		213.29	36.2		0.979			[11]
		248.32		1	0.988			[10]
ZnTPhP·4-ClQO	I	34.02			0.972	(1–α)	F1	[14]
		26.71	11.1		0.969			[11]
		40.32		1	0.981			[10]
	III	185.26			0.983	(1–α)	F1	[14]
		256.91	66.3		0.938			[11]
		272.21		1	0.994			[10]
	V	299.71			0.992	(1–α)	F1	[14]
		164.08	27.6		0.961			[11]
		207.92		1	0.975			[10]
ZnTPhP·4-NPyO	I	40.14			0.979	(1–α)	F1	[14]
		21.22	8.8		0.971			[11]
		32.45		1	0.936			[10]
	III	223.88			0.966	(1–α)	F1	[14]
		179.73	29.2		0.974			[11]
		206.52		1	0.979			[10]
	I	40.17			0.966	(1–α)	F1	[14]
		24.72	10.1		0.967			[11]
		31.04		1	0.942			[10]

Table 2 Continued

Substance	№ stage	E_a/kJ mol^{-1}	ln *A*	*n*	r^2	*f*(α)	Model	Method of calculation
ZnTPhP·4-NPyO	III	166.28	39.3		0.973	(1–α)	F1	[14]
		162.07			0.957			[11]
		178.18		1	0.990			[10]
	V	169.38	37.0		0.976	(1–α)	F1	[14]
		208.18			0.982			[11]
		239.52		1	0.988			[10]
	VI	643.10	66.8		0.991	(1–α)	F1	[14]
		414.15			0.969			[11]
		436.16		1	0.988			[10]
ZnTPhP·4-MPyO	I	109.2	24.6		0.962	(1–α)	F1	[14]
		68.59			0.931			[11]
		74.08		1	0.976			[10]
	III	165.33	39.8		0.971	(1–α)	F1	[14]
		141.99			0.958			[11]
		154.51		1	0.985			[10]
	VI	139.29	40.3		0.975	(1–α)	F1	[14]
		160.35			0.975			[11]
		164.62		1	0.987			[10]
	V	304.41	102.2		0.980	(1–α)	F1	[14]
		453.83			0.972			[11]
		411.49		1	0.942			[10]
	VII	149.16	34.7		0.966	(1–α)	F1	[14]
		206.18			0.935			[11]
		208.32		1	0.992			[10]
ZnTPhP·QO	I	55.37	17.5		0.971	(1–α)	F1	[14]
		46.36			0.908			[11]
		59.13		1	0.987			[10]
	III	127.3	34.3		0.984	(1–α)	F1	[14]
		143.66			0.969			[11]
		180.97		1	0.993			[10]
	V	281.13	45.6		0.959	(1–α)	F1	[14]
		275.44			0.948			[11]
		275.65		1	0.989			[10]
ZnTPhP·2-MeQO	I	34.87	10.6		0.973	(1–α)	F1	[14]
		26.38			0.901			[11]
		37.61		1	0.906			[10]
	II	127.27	14.8		0.986	(1–α)	F1	[14]
		49.55			0.869			[11]
		73.05		1	0.983			[10]
	IV	202.03	49.5		0.978	(1–α)	F1	[14]
		280.75			0.964			[11]
		290.08		1	0.989			[10]

and the initial reagents allows to propose that breaking up of the molecular complex (endothermic effect) and formation and losses of gaseous products (exothermic effect) occur during this stage of the thermal oxidative destruction. The destruction of Zn^{2+} complexes with 5,6-benzoquinoline N-oxide has been studied in [15]. According to the results of this work, scheme of the thermal oxidative destruction of these complexes is the following: $MX_2\cdot$4-BenzqnQ$\xrightarrow{473-573K}MX_2\cdot$·2-BenzqnQ$\xrightarrow{578-678K}MX_2\xrightarrow{873K}$MO. Our calculations of the mass losses during the thermal oxidative destruction of the ZnTPhP·QO complex at the 522–590 range showed that they are equal to 17.7% while the amount of QO (mass%) in the complex is equal to

Table 3 The average kinetic characteristics of thermal oxidative destruction of metallocomplexes of macroheterocyclic compounds

Substance	I stage		II stage		III stage		IV stage		V stage		VI stage		VII stage	
	E_a/kJ mol^{-1}	ln*A*	E_a/kJ mol^{-1}	ln*A*	E_a/kJ mol^{-1}	ln*A*	E_a/kJ mol^{-1}	ln*A*	E_a/kJ mol^{-1}	ln*A*	E_a/kJ mol^{-1}	ln*A*	E_a/kJ mol^{-1}	ln*A*
ZnTPhP·2-DQO	26	9			227	46			204	34				
ZnTPhP·2-StQO			75	26			410	89			268	33	265	33
ZnTPhP·4-MeQO	33	12			152	36			246	36				
ZnTPhP·4-ClQO	37	11			265	61			186	28				
ZnTPhP·4-NPyO	31	9			215	29								
ZnTPhP·4-DPyO	28	10			164	39			224	37	426	67		
ZnTPhP·4-MPyO	71	25			154	40	163	40	433	102			207	35
ZnTPhP·QO	54	18			151	34			276	46				
ZnTPhP·2-MeQO	33	11	83	15			285	50						

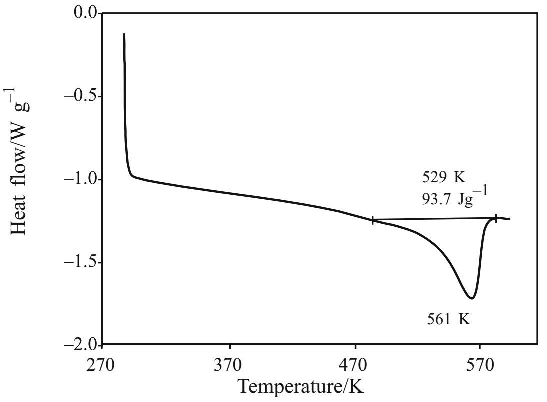

Fig. 2 DSC curve of ZnTPhP·QO

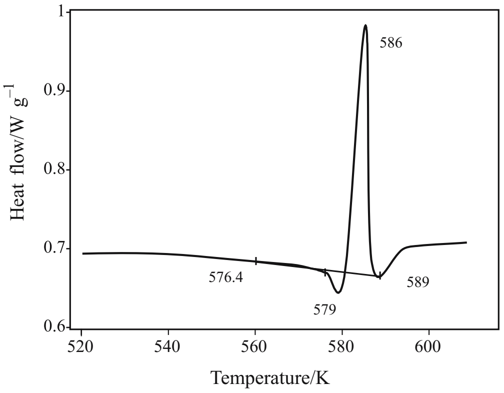

Fig. 3 DSC curve of ZnTPhP·2-StQO

17.63%. Thus, it may be proposed that the destruction of the complex occurs according to the following scheme: ZnTPhP·QO$\xrightarrow{522-590\ K}$ZnTPhP.

The process of the thermal oxidative destruction of QO (Fig. 1) indicates that the molecular ligand is oxidized. It is interesting to note that the losses of energy due to destruction of the complex are compensated completely by the energy evolving during combustion of QO. In order to determine the enthalpy of destruction of the ZnTPhP·QO complex, the contribution associated with the oxidation of QO must be eliminated. Therefore, the process of the thermal destruction of the ZnTPhP·QO complex was studied by DSC method in argon atmosphere (Fig. 2). As can be seen from Fig. 2, the process of destruction of the complex occurs at the 493–576 K range. This process is accompanied by significant heat effect. It should be noted that the thermal oxidative destruction of ZnTPhP after removal of the ligand starts at 717 K while pyrolysis of the initial ZnTPhP starts at 635 K. According to literature [16] and owing data, the first stage of the thermal oxidation is coordination of oxygen on central metal ion of the porphyrin. Therefore it is obvious that axial coordination of quinoline N-oxide on ZnTPhP prevents the coordination of O_2 on the reaction center of the metalloporphyrin. It is likely that after removal of QO (>590 K) the coordination of O_2 is difficult. It should be noted that besides the destruction temperatures of the initial ZnTPhP and after destruction of the molecular complex, kinetic characteristics of the process of the thermal oxidation are also changed significantly (Tables 1, 2 and 3). Stability of quinoline N-oxide in the complex with ZnTPhP is also much greater.

The process of the thermal oxidative destruction of the molecular complexes of ZnTPhP with alkyl substituted N-oxides (4-MeQO and 2-MeQO) is similar to that described for ZnTPhP·QO. It starts at 451 and 511 K for ZnTPhP·2-MeQO and ZnTPhP·4-MeQO, respectively. The mass change on the second stage corresponds to the complete removal of the ligands. The molecular complex formation provides higher stability of ZnTPhP as well as the alkyl derivatives of N-oxide. Unusual thermal destruction is observed in the case of the ZnTPhP·4-ClQO complex. For this complex, as in previous cases, the TG and DTG curves exhibit separate stage at the 512–555 K range which is not observed for the ligand and the metalloporphyrin. But the experimentally determined mass loss (4.7%) is not equal to the theoretical amount of N-oxide (21%) in the ZnTPhP·4-ClQO complex. It is interesting to note that the dehalogenation of the initial 4-ClQO occurs at significantly lower temperature (395 K). Thus, the obtained data demonstrate that the complex formation of the heterocyclic N-oxides with ZnTPhP leads to essential increasing of stability of the ligands in the thermal oxidative destruction process. The pyrolysis of the ligands starts during the destruction of the molecular complex. In argon atmosphere the destruction of ZnTPhP·4-ClQO is not associated with dehalogenation.

The thermal oxidative destruction of the ZnTPhP·2-StQO complex starts at 543 K. Up to a temperature of 583 K the mass loss of 12% was registered. It is not equal to theoretical amount of 2-StQO in the complex (26.7%). Thus, no complete destruction of the ligand occurs at the given stage. It should be noted that the mass fraction of styryl group in the ZnTPhP·2-StQO complex is 11.13%. In the case of the initial 2-styrylquinoline N-oxide, its thermal oxidative destruction starts at 483 K and is accompanied by the pronounced mass losses and exothermic effect on the DTA curve. The mass loss is 17.6%. It is not equal to amount (mass%) of styryl group in the N-oxide.

The interpretation of DSC curves for complex ZnTPhP·2-StQO is not simple. The DSC curve for the ZnTPhP·2-StQO complex exhibits a few peaks. We suggest that the first peak reflects endothermic process of destruction of the complex (T_{max}~579 K).

The second peak (T_{max}~586 K) is exothermic and corresponds to destruction of the N-oxide. It should be noted that the first and the second processes are overlapping. The kind of the DSC curve confirms this supposition (after the first peak the curve does not return on the baseline) (Fig. 3).

The destruction of the molecular complex of ZnTPhP with 2-(4-dimethylaminostyryl)quinoline N-oxide starts at 498 K. This process is also characterized by the pronouced mass losses and exothermic effect on the DTA curve. The mass loss on this stage (498–532 K) is 11.5%. The kind of TG curve indicates that the similar process of the thermal oxidation of the initial 2-DQO is observed at the 488–533 K range. The experimentally determined mass loss of this process of 15.5% is not equal to theoretical mass of 2-DQO in the complex. The DSC curve of ZnTPhP·2-DQO, as in the case of the complex with styryl N-oxide, exhibits two peaks: an endothermic effect at T_{start}= 549 K and an exothermic effect at T=557 K. The stage associated with the thermal destruction of ZnTPhP after destruction of the ZnTPhP·2-DQO complex starts at higher temperature and is characterized by higher energy barrier than that for the initial ZnTPhP.

The fusion process of 4-NPyO starts at 429 K. The endothermic effect on the DTA curve as well as absence of any changes on the mass losses curve testifies about it. According to literature data [17], the melting point of 4-NPyO is within 432–433 K.

At 519 K for 4-NPyO an intensive exothermic peak is observed on the DTA curve. The corresponding mass losses are 67.8%. These results indicate that at T=435 K the destruction of the N-oxide starts. The comparison of the results obtained for ZnTPhP·4-NPyO and 4-NPyO indicates that the effects associated with the destruction of 4-NPyO do not registered on the thermogramm of the molecular complex up to 716 K. This fact is difficult to explain taking into account that the thermal destruction of the ZnTPhP·4-NPyO complex in argon atmosphere occurs at 462 K (an intensive and wide exothermic peak).

The pyrolysis of the ZnTPhP·4-NPyO complex starts at higher temperature than of ZnTPhP. As in the case of the complexes of ZnTPhP with quinoline N-oxides, this may be due to difficult coordination of oxygen on the central metal ion in the presence of the ligand.

The destruction of 4-DPyO starts at a temperature of 497 K. The pronounced mass losses and the peaks on the DTG and DTA curves testify about this process. A separate stage of the thermal oxidative destruction is registered at the 533–610 K range. It is interesting to note that this stage on the DTA curve is characterized by a few small peaks.

For the ZnTPhP·4-DPyO complex, peaks on the DTA and DTG curves at the 522–573 K range and small mass losses (less than 11%) testify about the destruction of the complex. It is interesting that in argon atmosphere the destruction of this complex starts at 466 K. The pyrolysis of the ZnTPhP·4-DPyO complex starts at a temperature of 635 K. This indicates that the complex is more stable to the thermal oxidative destruction in comparison with ZnTPhP.

The thermal oxidative destruction of the ZnTPhP·4-MPyO complex starts at 513 K. The beginning of this process is accompanied by small exothermic effect on the DTA curve. Next stage of the thermal oxidation is registered at the 700–802 K range. It is characterized by an exothermic effect on the DTA curve and some mass losses. This may be due to pyrolysis of the porphyrin. As in the previous case, the increase of stability of the complex in comparison with 4-MPyO (417–439 K) and the porphyrin (635–790 K) is observed.

The physico-chemical parameters of the molecular complexes studied are presented in Table 4. The styryl derivatives of N-oxides are not included because it is impossible to separate heat effects associated with the destruction of the complex and the gaseous products. According to the data in Table 4, the stability of the molecular complexes of ZnTPhP estimated from temperatures of maximum of an endothermic peaks on the DSC curves increases in the following order: 4-NPyO<2-MeQO<4-ClQO<QO<4-MeQO (1), while the energy stability (Q) (Table 4) increases in the order: ClQO<2-MeQO<4-MeQO<QO (2).

Table 4 Characteristics of thermal decomposition of complexes of ZnTPhP for chosen ligands

L	T_{max}/K	Q/kJ mol^{-1}
4-NPyO	462	12.18
2-MeQO	531	61.86
4-ClQO	547	50.67
QO	561	85.7
4-MeQO	573	67.03

Conclusions

Thus, our results indicate that the complex formation of ZnTPhP with heteroaromatic N-oxides leads to an increase of the thermal stability both the metalloporphyrin and the ligands. It has been shown that the stability of the molecular complexes of ZnTPhP with heteroaromatic N-oxides depends on basisity of the coordinated ligand.

References

1 K. Takekawa, S. Kitamura, K. Sugihara and S. Ohta, Xenobiotica, 31 (2001) 11.

2 A. G. Anisimov, T. O. Volkova, A. A. Chekmasova and V. P. Andreev, XIII All-Russian Symposium ‘Structure and Functions of Karyon’ (2000) 258.

3 T. O. Volkova and N. N. Nemova, Molecular mechanisms of leukemia cell apoptosis, Since, Moscow, 2006.

4 A. G. Anisimov and V. P. Andreev, Biological Activity of Some Heteroaromatic N-Oxide Derivatives, IWRFRI, St.-Petersburg, (1999) 117.

5 E. Ochiai, J. Org. Chem., 18 (1953) 534.

6 V. P. Andreev, A. V. Ryzhakov and S. V. Tekanova, Chemistry of Heterocycles, (1995) 518.

7 G. D. Titzky and M. K. Turovskaya, Certificate of authorship 1599366, USSR, 1990.

8 V. P. Andreev, Ya. P. Nizhnik, D. G. Bezruchko and A. K. Morozov, Russ. J. Gen. Chem., 75 (2005) 1379.

9 N. Sh. Lebedeva, S. P. Yakubov, A. N. Kinchin and A. I. V’yugin, Russ. J. Phys. Chem., 79 (2005) 827.

10 A. W. Coats and J. P. Redfern, Nature., 201 (1964) 68

11 J. Sestak and G. Berggren, Thermochim. Acta, 3 (1971) 1.

12 J. J. Zhang, L. G. Ge, X. L. Zhang, Y. J. Dai, H. L. Chen and L. P. Mo, J. Therm. Anal. Cal., 58 (1999) 269.

13 M. Samtani, D. Dollimore and K. S. Aleksander, Thermochim. Acta, 392–393 (2002) 135.

14 A. F. Zatsepin and A. A. Fotiev, Russ. J. Neorg. Chem., 18 (1973) 2883.

15 A. K. Srivastava, A. Srivastava and P. C. Jain, Thermochim. Acta, 132 (1988) 297.

16 N. S. Enikolopyan. Porphyrins: Spectroscopy, Electrochemistry, Applications, Science, Moscow, 1986.

17 L. Pentimalli, Gazz. Chim. Ital., 93 (1963) 1093.

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