Instructions for use

N₄-COMPLEXES AND HIGH-MOLECULAR COMPOUNDS ON THEIR BASIS AS ELECTROCATALYSTS OF PROCESSES INVOLVING OXYGEN-CONTAINING PARTICLES*

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Abstract

To the most active catalysts for the molecular oxygen electroreduction and sulfur dioxide electrooxidation reactions belong heat-treated (800°C) tetra (p-methoxyphenyl) porphyrin of cobalt, CoTMPP. Application for these purpose of the metalless complex, H₂TMPP, does not yield a catalyst for these reactions. The products obtained by heat treatment of CoTMPP and H₂TMPP in inert atmospher in the temperature range 30–800°C were studied by pyrolytic mass-spectrometry, IR- and EPR-spectroscopy, thermal, X-ray diffraction and elementary analyses. Pyrolysis of the porphyrin system leads to its partial decomposition and consolidation resulting in formation a secondary structure with a higher degree of condensation. Since metal affects the strength of the bond of the substituents with macroring, the kind of metal defines the resulting structure. The role of cobalt in pyrolysis of the porphyrin system consists in that it promotes formation of an active new structure.

As is known, a vital problem in the field of electrochemical power sources is development of anodes and cathodes without precious metals for acid media. This problem can be solved by developing radically new types of inorganic and organic electrocatalysts. In recent years great interest has been shown in the use of metalloporphyrins and their derivatives (Fig. 1) for acceleration of a number of important reactions.[1] The chemical stability of these complexes in acid media, however, proves to be insufficient. We proposed a method of preparing active and stable catalysts for the molecular oxygen electroreduction reaction in real power sources with the use of high temperature (800°C) treatment of the above-mentioned complexes in inert atmosphere.[2] By this means we obtained oxygen electrodes whose char-
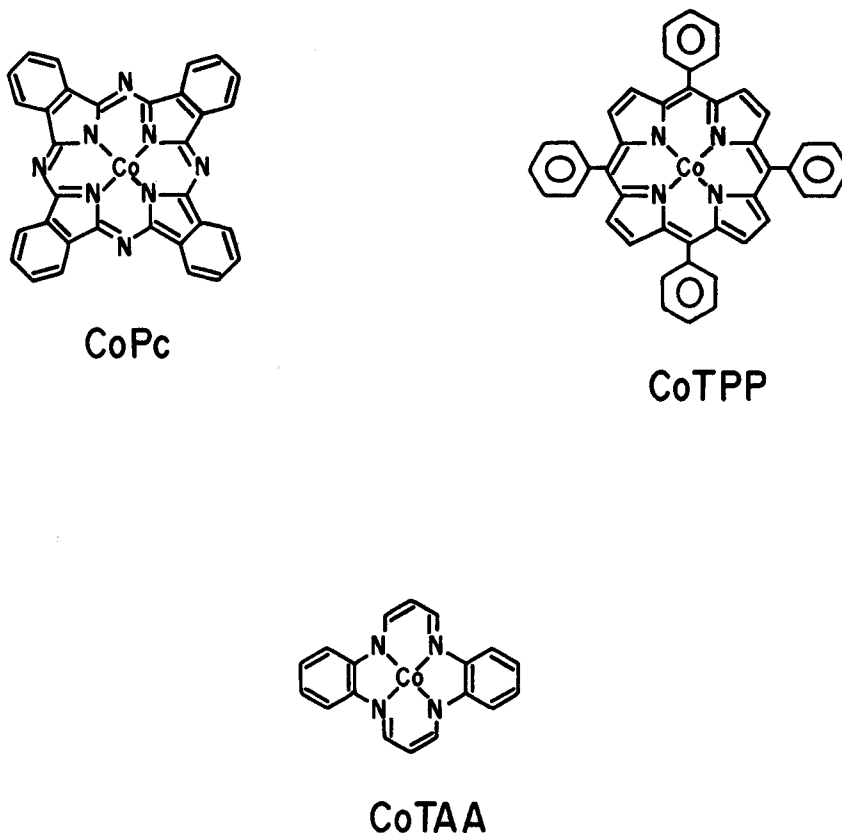

CoPc

CoTPP

CoTAA

Fig. 1. Structural formulas of N_4-complexes.

acteristics in 2,25 M sulfuric acid remained unchanged during a year. The most active complex is tetra (p-methoxyphenyl)porphyrin of cobalt. Application for these purpose of the metalless tetra(p-methoxyphenyl)porphyrin does not yield a catalyst for oxygen electrodes. Fig. 2 shows the polarization curves of oxygen reduction in 0,05 M sulfuric acid on cobalt tetra(p-methoxyphenyl)porphyrin (1), on the product obtained by its heat treatment (2) and on the product of the heat treatment of metalless tetra(p-methoxy-phenyl)porphyrin (3). The lower curves are for oxygen electroreduction on a rotating pyrographite disk coated with a thin film of organic complex, the upper curves are the corresponding dependences of the limiting current of hydrogen peroxide oxidation on a platinized platinum ring. As can be seen from these curves and as shown by calculations, oxygen electroreduction on initial cobalt porphyrin proceeds only to hydrogen peroxide, which in the potential range examined does not undergo further transformations
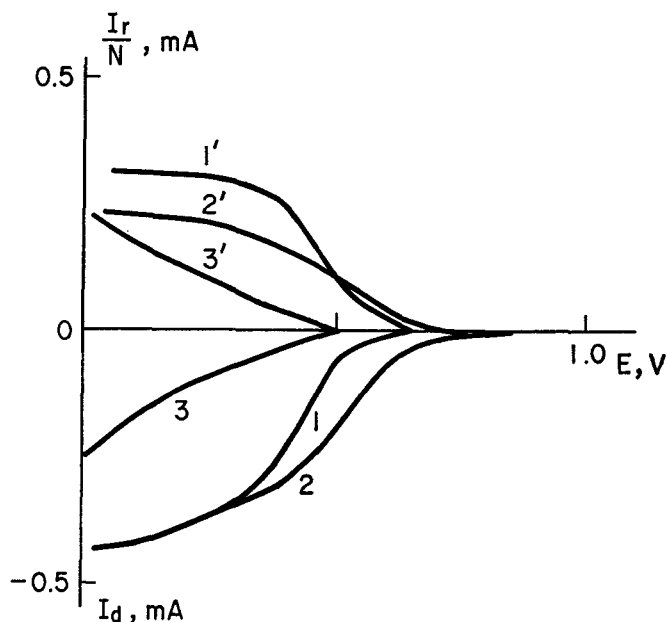
Fig. 2. Polarization curves of oxygen reduction on cobalt tetra (p-methoxy-phenyl) porphyrin (1), heat-treated at 800°C combalt tetra (p-methoxy phenyl)porphyrin (2) and tetra (p-methoxyphenyl) porphyrin (3) and corresponding dependences of the limiting currents of hydrogen peroxide oxidation (1'-3') on the ring from platinized platinum in 0.05 M H_2SO_4 at the rate of rotation of the electrode 960 rpm.

(is not reduced and does not decompose catalytically). On heat-treated cobalt porphyrin oxygen electroreduction begins at more positive potentials and, as shown by calculations, along with the oxygen electroreduction process to hydrogen peroxide, there occurs a direct reaction of oxygen electroreduction to water without intermediate hydrogen peroxide formation. The hydrogen peroxide formed in a consequent reaction, just as in the case of the nonheat-treated complex, does not undergo further transformations. The activity of heat-treated metalless prophyrin (curves 3 and 3') is very low. A similar effect is observed for the sulfur dioxide electrooxidation reaction (Fig. 3). The reaction rate increases by an order of magnitude when passing from cobalt tetra(p-methoxyphenyl)porphyrin to its heat treatment product (Fig. 3 curves 1 and 2). Heat treatment of the complex without metal tetra(p-methoxyphenyl)porphyrin, however, does not yield a catalyst for sulfur dioxide electrooxidation (Fig. 3 curve 3').

It follows from numerous studies of the oxygen reaction carried out so far on metalloporphyrin that it is on the metal central ion that the electro-
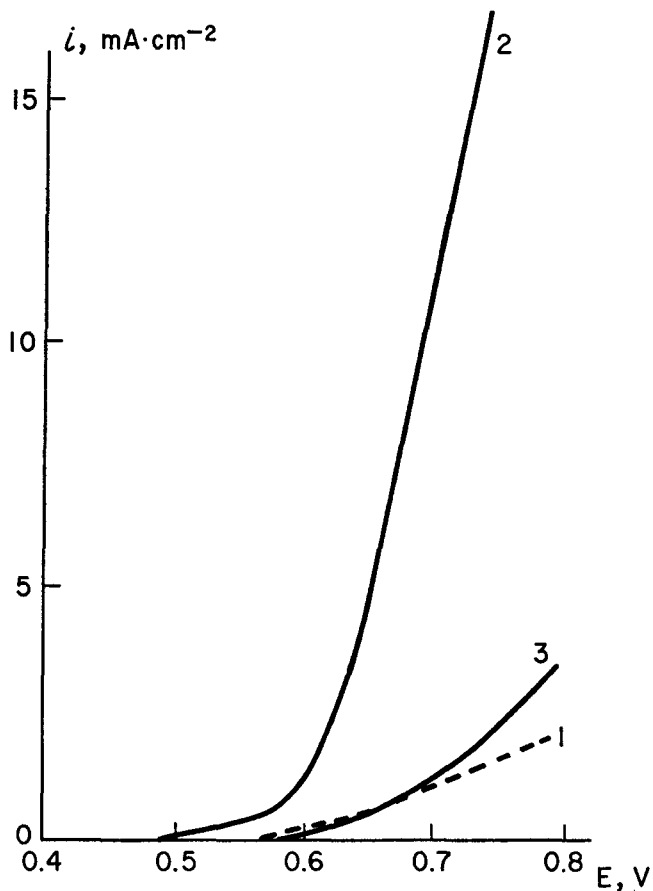
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Fig. 3. Sulfur dioxide electrooxidation on cobalt tetra(p-methoxy phenyl)porphyrin (1), heat-treated at 800°C cobalt tetra- (p-methoxyphenyl) porphyrin (2) and tetra (p-methoxyphenyl) porphyrin (3) in 0.5 M H_2SO_4.

catalytic process occurs. And what is the role of metal in the case of pyrolyzed complexes?

We studied the products obtained by heat treatment in inert atmosphere in the temperature range $30 \sim 800°C$ of tetra (*p*-methoxyphenyl) porphyrin and its complex with cobalt by means of pyrolytic mass-spectrometry, IR- and EPR-spectroscopy, thermal, X-ray diffraction and elementary analyses.[3]

As shown by the TG, DTA and DTG curves, at temperatures over 130°C an endothermic process takes place on both compounds involving a drastic weight loss, with further temperature increase to 400°C the weight
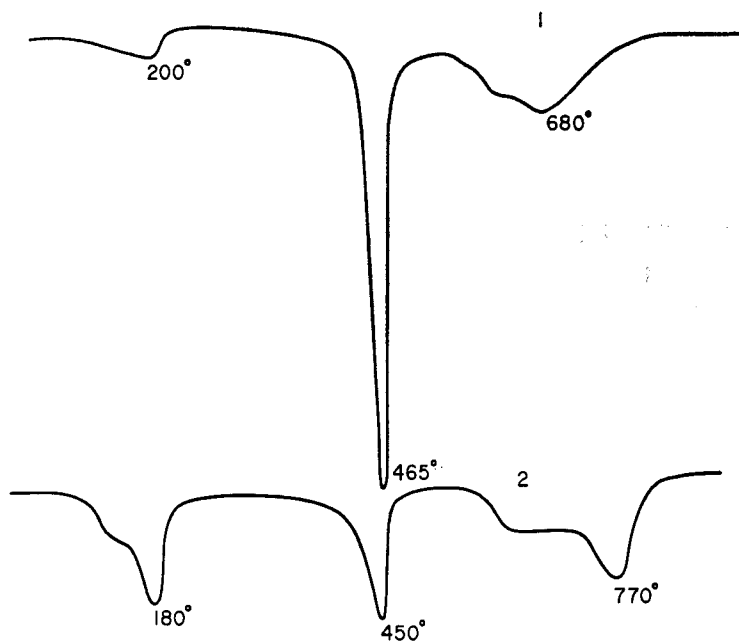
Fig. 4. DTG curves for metalless (1) and cobalt complexes (2) of tetra
(p-methoxyphenyl)porphyrin.

loss occurs slowly.   In the temperature range 400∼470°C the DTG and DTA
curves show a sharp peak.   A weight decrease is also observed in th tem-
perature range in the vicinity of 700°C (Fig. 4).   The general structure of
the IR spectra bands (Fig. 5) remains unchanged in the treatment temperature
range 30∼400°C.   At temperatures above 400°C the structure of the bands
disappears completely.   Comparison of the X-ray patterns obtained at dif-
ferent temperatures shows that for the complex without metal the strength
of the main reflexes decreases with increasing temperature much slower than
for a cobalt complex.   The peaks corresponding to crystalline structure disap-
pear completely at the temperature about 700°C for both complexes.   At
temperatures over 400°C cobalt shows up as a separate phase — cubic β-
cobalt.

The investigation of the paramagnetic properties of these compounds
as a function of the heat treatment temperature included analysis of the
shape and width of the EPR spectrum as well as of the concentration of
paramagnetic centers (p. m. c.).   Fig. 6 shows the EPR spectra of the metal-
less complex and its heat treatment product at 680°C.   For the heat-treated
complex the single line with g-factor close to that of a free electron increases
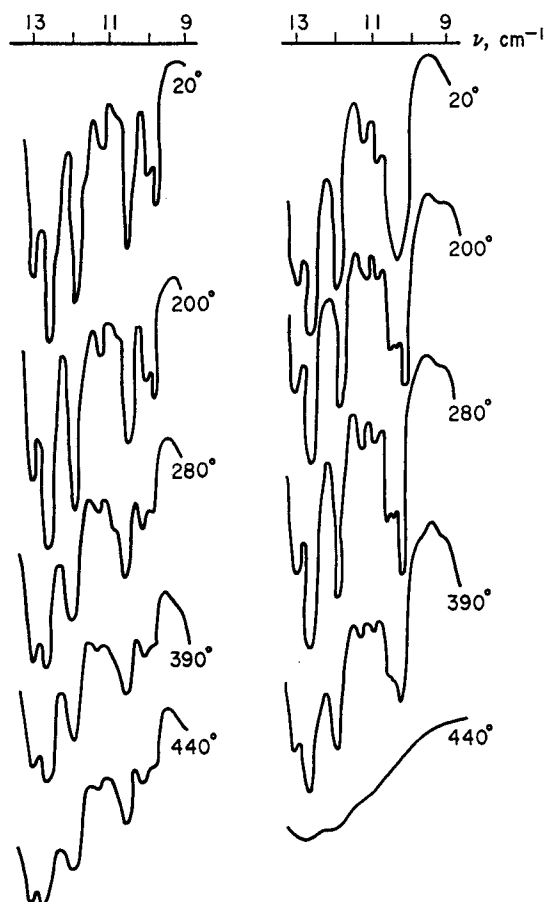
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Fig. 5. IR spectra of metalless (1) and cobalt complexes of tetra-
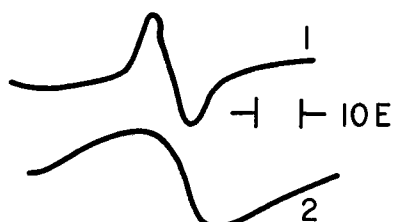(p-methoxyphenyl)porphyrin at different temperatures.

Fig. 6. EPR spectra of metalless tetra(p-methoxyphenyl)-
porphyrin (1) and the product of its heat treatment
at 680°C (2).

TABLE 1.   Parameters of the EPR spectra of metalless
H_2TMPP and its heat treatment products

Sample	p. m. c. concentration, cm^{-3}	$\Delta H, E$
1. H_2TMPP	2×10^{17}	4, 0
2. H_2TMPP heated at 280°C	$2, 3 \times 10^{17}$	4, 0
3. H_2TMPP heated at 390°C	$9, 9 \times 10^{17}$	5, 0
4. H_2TMPP heated at 680°C	$1, 7 \times 10^{18}$	9, 0

in width and intensity. The p. m. c. concentration increases by an order of magnitude after heat treatment of the metalless complex at 680°C (Table 1). The EPR spectra for the heat treatment products of cobalt porphyrin show more complicated changes (Fig. 7). Superfine structure components (s. f. c.) appear in the initial spectrum of this compound, corresponding to the interaction of the unpaired spins of the central ion — bivalent cobalt. In the case of heat-

Fig. 7. EPR spectra of CoTMPP (a) and its heat treatment products at temperatures: b——280°C (magnetic field sweep 200 E), b'——280°C (500 E), c ——390°C, d——680°C. Dashed line ——680°C and treatment in 0,5 M H_2SO_4.

treated complexes the s. f. c. become smeared and a broad signal appears, whose intensity and ΔH depend on pyrolysis temperature. It is interesting to note that after treatment of the pyrolysis product of cobalt porphyrin at 680°C in 0.5 M sulfuric acid containing hydrogen peroxide and a partly removal of cobalt from it, the EPR signal (Fig. 7, dashed line) decreases in intensity and at the same time broadens. This leads to the conclusion that the p. m. c. concentration does not change when cobalt is removed. Comparison of the EPR spectra of the heat treatment products of metalless and cobalt complexes shows that due to the presence of the metal ion in the complex the structural changes begin at earlier pyrolysis stages. For the product of the heat treatment of metalless complex at 280°C no marked changes were found neither in the p. m. c. concentration, nor in the ΔH signal value (Table 1). The EPR spectrum of the heat treatment product of the cobalt complex already has a broad signal, which points to structurization of the sample.
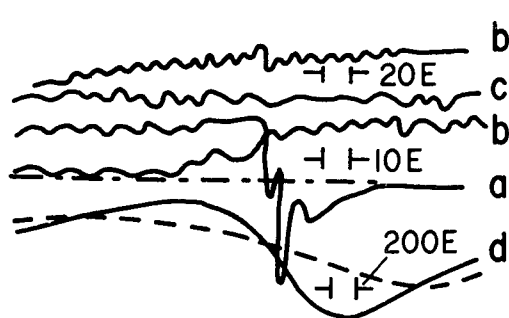
The volatile pyrolysis products were examined by pyrolytic mass-spectrometry. The technique of measurement implied direct introduction of destruction products into the ionization chamber of the mass-spectrometer, rapid removal of the products formed and practically complete absence of secondary reactions. At each moment of time the intensity of peaks in the mass-spectrum, corresponding to definite destruction products, is proportional to the rate of separation of these products, and the total ionic current (TIC) is proportional to the rate of total separation of pyrolysis products. Fig. 8 shows the curves of the variation of the total ionic current with temperature increasing from 30 to 800°C. For both samples the curves of the variation of the TIC have several maxima. It follows from the mass-spectra obtained at the pyrolysis temperature in the range from 30 to 150°C that the maxima on these curves in the low temperature range correspond to evaporation of low-molecular impurities. These are benzene (m/e 78), pyridine (m/e 79), acetic acid (m/e 60), *etc.* Apparently, here the porphyrin complexes themselves and the intermediate products of their formation also undergo evaporation.

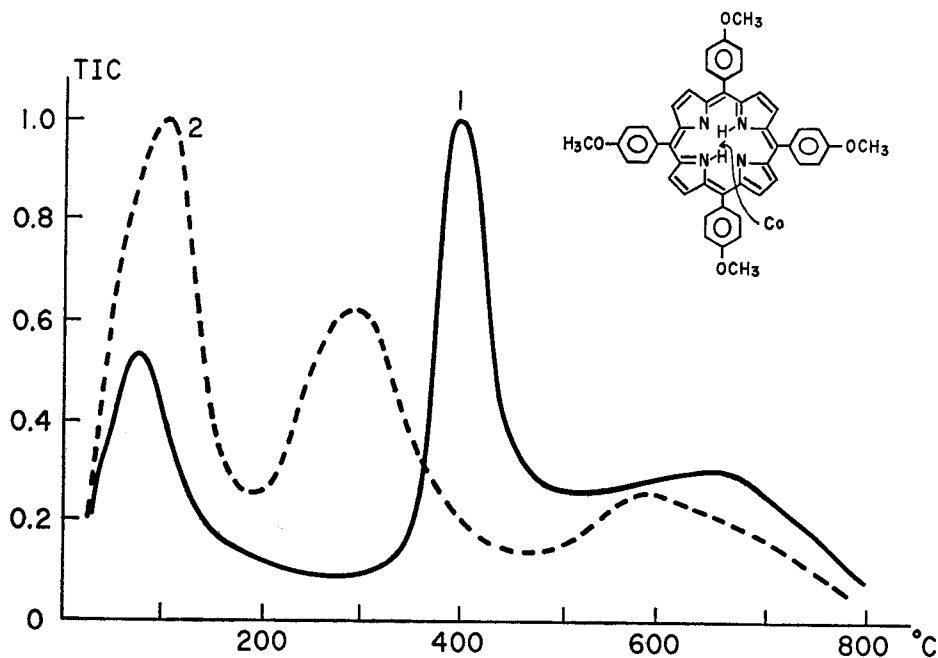The peaks of the TIC curves in the temperature region 395°C for the

Fig. 8. Variation of the total ionic current (TIC) as a function of temperatures for H$_2$TMPP (1) and CoTMPP (2).

metalless complex and 300°C for the complex with cobalt are due to decom-
position of the components being examined. It is characteristic that for both
complexes the qualitative composition of the destruction products is much
the same. It is possible to single out three main groups of the decomposition
products:
1. Fragments formed from methoxyphenyl groups,
2. Fragments formed during splitting of the porphyrin system,
3. Small fragments formed during breaking of pyrrole rings.
The composition of the destruction products shows that the splitting out
of methoxyphenyl groups is accompanied by formation of anisole (m/e 108),
phenol (m/e 94), benzene (m/e 78) and also methane (m/e 16) and form-
aldehyde (m/e 30). Fig. 9 shows the dependences on the pyrolysis tempera-
ture of the peak intensities of the ions with m/e 94, 107 and 108 correspond-
ing to formation of phenol and anisoles. The small width of the peaks
indicates that the system underwent rearrangement fast enough. Inclusion
of metal into the porphyrin system lowers the decomposition temperature
considerably. The activation energy of phenol formation calculated from
corresponding thermograms is equal to 40 and 18 kcal/mole for metalless
and cobalt complexes, respectively. A lower activation energy and decreased
temperature of splitting out of methoxyphenyl groups in metal-containing
porphyrin as compared to metalless porphyrin indicates that the bonds of
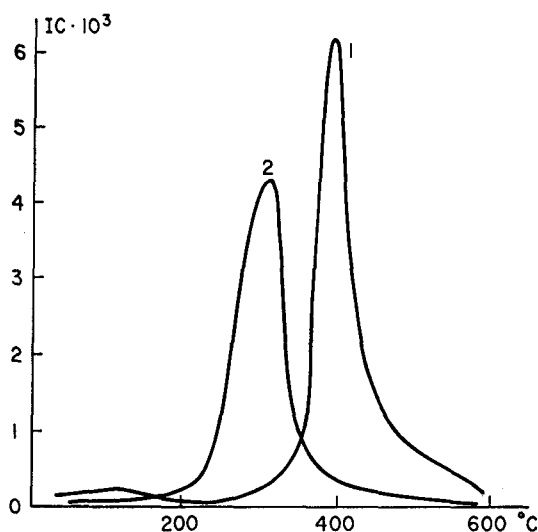
Fig. 9. Dependence of the total intensity (IC) of the peaks
of the ions with m/e 94, 107, 108 on temperature for
H₂TMPP (1) and CoTMPP (2).

these groups with the macroring are somewhat weakened.

The separation of products corresponding to large fragments of the porphyrin macroring proper (m/e 219, 239, 186, 187) occurs in the same temperature range (395 and 300°C) (Table 2). These fragments include one or several pyrrole rings, phenyl, hydrooxy- or methoxyphenyl groups. For the cobalt complex the yield of these products is much lower than for the metalless sample. Thus inclusion of metal leads to weakening of the bonds of substituents with the macroring and to strengthening of the bonds in the macroring itself.

Among the low-molecular fragments of the porphyrin system we identified some fragments of pyrrole ring — nitriles (m/e 41, 53) and imines (m/e 29, 43, 57, 55).

At higher pyrolysis temperatures (over 500°C) upon completion of the processes of splitting out and decomposition of methoxyphenyl groups as well as of the splitting of the porphyrin ring, the fragments of the porphyrin system undergo consolidation. This is evidences by appearence of fragmented ions with m/e 128, 141, 142, 154, 165, 178, 191, characteristic

TABLE 2. Relative intensity of the peaks of ions of main fragments formed during destruction of H_2TMPP and CoTMPP (with respect to the integral total current), %

	Type of fragments	Masses of characteristic ions	H_2TMPP	CoTMPP
1.	Impurities and low-molecular products		50	39
2.	Phenols	94, 107, 108	8,11	11,84
3.	Anisoles	121, 122	2,41	0,78
4.	Pyridine	79	1,47	1,32
5.	Methoxyphenyl-containing fragments of the porphyrin system	186, 187	1,30	0,02
6.	Fragments of the porphyrin system	219	0,10	0,01
	—— ″ ——	239	0,02	—
7.	Condensed polycyclic systems	128, 141, 142, 143, 144, 154, 155, 156	1,64	0,32
	—— ″ ——	178, 191, 192, 165	0,27	0,13
8.	Pyrrols	67, 80, 81	3,41	1,14
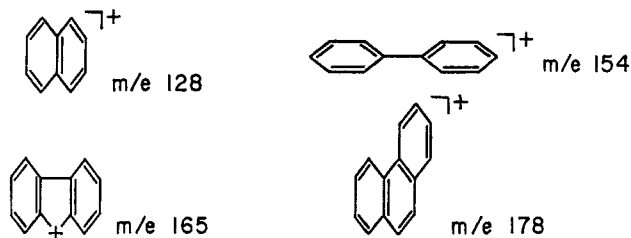
of polycyclic compounds. In this temperature region also present are ions of aromatic compounds with m/e 77, 78, 91 as well as ions characteristic of nitrogen-containing compounds with m/e 67, 81, 30, 41 and 53. No metal-containing ions were found in the mass-spectra of pyrolysis products.

Thus, thermolysis of the porphyrin system leads to its rearrangement and consolidation to form a more condensed structure. In the first decomposition stage methoxyphenyl substituents undergo intensive splitting out and destruction. If metal is present in the complex the process occurs at a lower temperature. Rearrangment of the system is accompanied by metal segregation into a separate phase. During this process methoxyphenyl substituents are partly split out and partly incorporated into the polycyclic structures formed. The structure resulting form the molecule rearrangement should be, probably, determined by the kind of metal, *i. e.* by redistribution of the electronic density in the porphyrin system caused by metal. Since metal affects the strength of the bond of the substituents with macroring, the kind of metal defines the resulting structure. Thus, on the basis of the investigations carried out by us, we consider that the role of cobalt in pyrolysis of the porphyrin system consists in that it promotes formation of an active new structure, which we call a high-molecular compound based on cobalt porphyrins.

References

1) M. R. Tarasevich and K. A. Radyushkina, Progress in Surface and Membrane Science, 14, 175 (1981).

2) V. S. Bagotzky, M. R. Tarasevich, K. A. Radyushkina, O. A. Levina and S. I. Andruseva, J. Power Sources, 2, 233 (1977).

3) E. S. Brodsky, K. A. Radyushkina and G. A. Kalinkevich *et al*, J. Appl. Chem. (USSR), 55, 2070 (1982).