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The Synthesis and Properties of Polymeric Azaporphin Compounds

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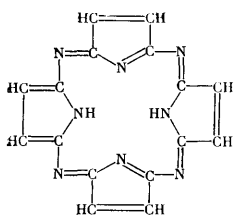
Data on the synthesis and principal properties of polymers with a conjugation system containing repeating azaporphin macrorings are surveyed and described systematically. An account is given of the change in properties on passing from metal-free polymers and their metal complexes, on the one hand, to the corresponding low-molecular-weight analogues, on the other. The bibliography includes 135 references.

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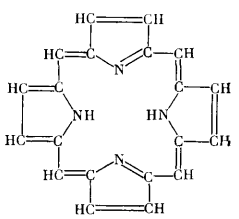
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I. INTRODUCTION

The cyclic systems (I), consisting of four pyrrole rings linked together in the α-positions by nitrogen atoms, are called azaporphins† or porphyrazines, in contrast to porphins (II), which have a similar structure but the rings are linked by methylidyne groups:



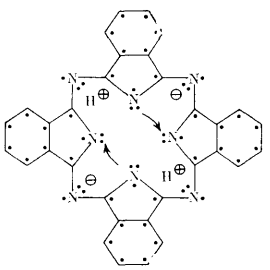
(I)



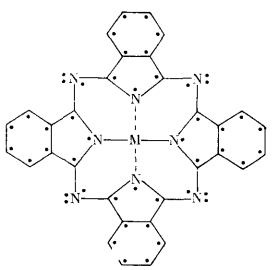
(II)

The pyrrole rings, which constitutes the basis of the azaporphin macroring, can be condensed with aromatic or heteroaromatic rings. Depending on the type of the latter, one can distinguish tetrabenzo-, tetranaphthalo-, tetrathiopheno-, and tetrafurano-azaporphins (tetrafuranoporphyrazines)[1,2]. Azaporphins whose pyrrole rings contain (usually in the 3- and 4-positions) various substituents—for example, octaphenyl-, dipropyl-, and octamethyl-porphyrazines, are known[2]. By analogy with porphins[3], such compounds could be usefully referred to also as azaporphyrins: octaphenyl-, dipropyl-, and octamethyl-azaporphyrins.

Despite the wide variety of porphyrazines, most investigations, among which those of Linstead, Vartanyan, and Berezin are the most important, were devoted to tetrabenzazaporphins, which are usually referred to as phthalocyanines. The structure and formulae of the metal-free phthalocyanine (III) and copper-phthalocyanine (IV) are given below‡:



(III)



(IV)

As can be seen from formula (III), as a result of internal dissociation the two protons of the imino-group of the azaporphin are subjected to the symmetrical electric field set up by the lone electron pairs of the nitrogen atoms[4,5]. These electrons are not localised at the opposite exocyclic nitrogen atoms but are uniformly distributed throughout the macroring, since their pairing would lead to the breakdown of conjugation. Thus 18 electrons move in the plane of the macroring, giving rise to a ring current of delocalised π electrons. This imparts aromatic§ properties and high stability to the azaporphin ring and determines the specific physical and physicochemical properties of compounds containing such rings.

The introduction of a metal in the "window" of the macroring (IV) entails the filling of the dsp^2-hybrid or other orbitals of the metal ion, which is accompanied by a change in the electron density at the peripheral nitrogen atoms and a consequent difference between the properties of the metal complexes and the metal-free analogues. The

† The abbreviation of tetra-azaporphins.

‡ Henceforth in this review the following abbreviations will be used: PC = metal-free phthalocyanine, PC_M = phthalocyanine complexes of different metals (where M = Cu, Fe, Ni, etc.), PPC = metal-free polyphthalocyanine, PPC_M = polyphthalocyanine complexes of metals, PTCE = metal-free polytetracyanoethylene, $PTCE_M$ = polymeric metal complexes of tetracyanoethylene, and AA_M = metal acetylacetonates.

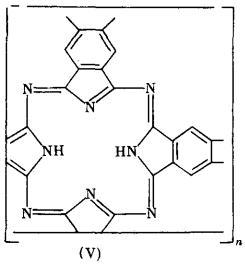
§ The extreme aromatic nature of these compounds is indicated particularly by the finding that the magnetic anisotropy of phthalocyanine is approximately 15 times greater than that of benzene[6].

more covalent the >N–M–N< linkage, the greater the stability of the ring, and the greater the differences between the optical, magnetic, and electrical properties of the metal-free and metal-substituted porphyrazines[7-8].

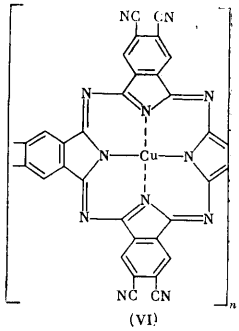
The unusual properties of phthalocyanines[9-12] stimulated the development of research on the synthesis of polymers containing azaporphin macrorings in their structure—polyazaporphins (PA) or polyporphyrazines. One might expect the possibility of the formation on the basis of these polymers of valuable materials combining the specific physicochemical and mechanical properties of high-molecular-weight compounds with the chemical and thermal stability, catalytic activity, and semiconductor properties characteristic of phthalocyanines.

The interest in systems of this kind is because the structure of PA resembles most closely (among the known synthetic polymers) that of natural compounds such as haemoglobin, chlorophyll, and the prosthetic groups of a number of enzymes (for example catalase). This fact is responsible for the exceptional importance of PA also as objects for the modelling of the biological activity of natural products.

All the PA known at the present time can be usefully divided into three groups differing in the nature of the functional groups joining the azaporphin rings in the macromolecule. The first group includes the PA in which the repeating units are joined via aromatic or heteroaromatic rings condensed to the pyrrole ring; these rings are shared by two adjoining units. In the naming of such polymers, it is reasonable to employ the name of the connecting ring¶—for example, polyphthalo-(V) and (VI), polynaphthalo-, polythiopheno-(VII), and polyfurano-cyanines (VIII)[14-16].



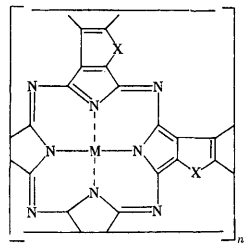
(V)



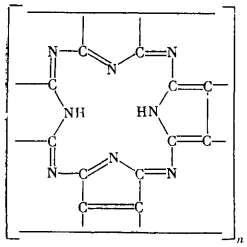
(VI)

The PA whose elementary units are linked directly by the pyrrole rings of the azaporphin in the 3- and 4-positions, for example, the polymers of tetracyano-ethylene[17,18], (IX) and (X), the copolymers of azaporphin with the nitrile of maleic acid, phthalonitrile (XI), etc.[19] should be included in the same group.

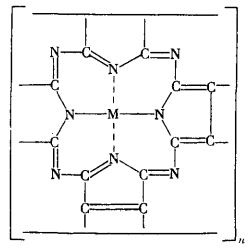
A distinctive feature of the PA of this group is the presence of a continuous conjugation chain throughout the macromolecule regardless of whether these polymers have ribbon [compounds (VI) and (XI)] or planar-network [compounds (V), (VII), and (X)] structures.



(VII) X = S;
(VIII) X = O

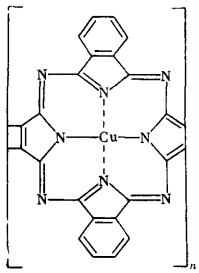


(IX)

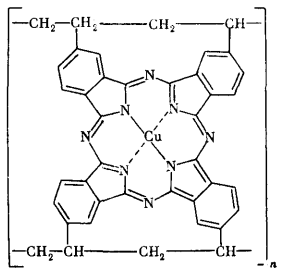


(X)

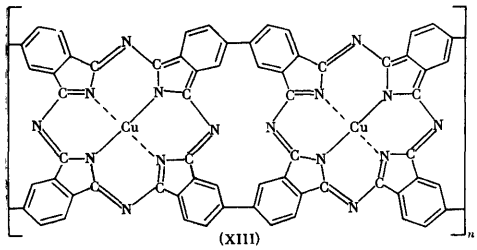
In the macromolecule of a PA belonging to the second group each aromatic (or heteroaromatic) ring linking up the azaporphin is associated with only one unit. In certain cases these rings can be linked in the macromolecule by various bridging groups, such as –O–, –S(O)–, –NH–C(O)–$(CH_2)_{n-2}$–, –C(O)–NH–, etc. The PA of the second group include polymers obtained by the interaction of *N*,*N*′-bis-(3,4-dicyanophenyl)alkylenediamines with metals or their salts[20], of bis-(3,4-dicarboxyphenyl) sulphone with copper[21], of 3,4-dichlorostyrene with copper cyanide [compound (XII)][2], of 3,3′,4,4′-tetracyanobiphenyl with copper [compound (XIII)][2], and of 2,3-dicyanohydroquinone with metal salts or oxides[22], as well as the copolymers of phthalic anhydride and bis(dicarboxyphenyl) ether [compound (XIV)][23], of phthalonitrile and bis(dicarboxyphenyl) sulphone[24], etc.



(XI)

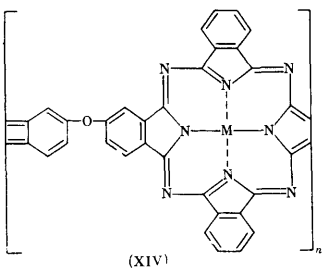


(XII)



(XIII)

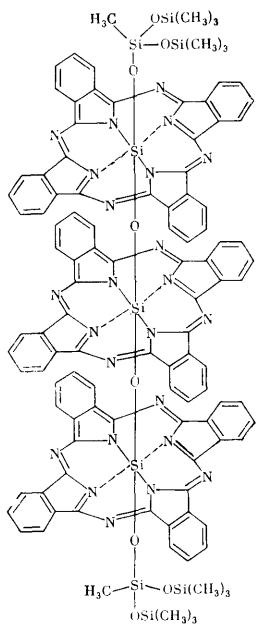
¶For a different nomenclature of the PA, see Smith[13].



(XIV)

The degree of delocalisation of π electrons and the type of conjugation of the PA of this group are various and are determined by the nature of the bridging groups. Together with the PA in which the conjugation between the units is almost unaffected or is only slightly affected, polymers are known with saturated bonds in the macromolecular chain where the azaporphin macrorings are present only at the ends of the chain[25] or exist in the form of individual fragments separated from one another by considerable distances[20,26-29]. However, even when azaporphin rings are only occasionally incorporated in the macromolecular chain, they alter the properties of the latter significantly. Polymers with such rings exhibit an enhanced electrical conductivity and thermal and chemical stabilities, which makes it possible to employ them as special binders, coatings, and adhesives[20,28,29].

Finally, the third group comprises PA whose individual units are joined by oxygen atoms linked directly to the metal atoms of two neighbouring rings[30-32]. These are PPC_{Ge}, PPC_{Si} (XV), etc., obtained by the interaction of the derivatives of the corresponding phthalocyanines. A distinctive feature of these polymers is the fact that the individual units are located in parallel planes and are joined to one another via -O-M-O- bridges, forming in space unusual stacks of rings.



(XV)

The above systematic arrangement is to a large extent arbitrary, requiring further improvement. Nevertheless, it can assist in a better understanding of the large class of PA and facilitates the comparison of the properties and the determination of the specific features of the polymers in each group.

Polymers have been obtained recently whose macrorings constitute a kind of modification of azaporphin: one or several pyrrole rings of the latter have been replaced by pyridine, pyrazine, or other heterocycles[33-35]. Owing to the insufficiency of experimental data, these polymers as well as other structural analogues of PA (polyporphyrins)[36] are not considered in this review; for the same reason, very little space has been devoted to the PA of the second and third groups.

This review presents a survey of the results of studies on the synthesis and certain properties of polymers with a continuous conjugation system whose macromolecules consist of repeating azaporphin macrocycles (PA belonging to the first group), carried out during the last 15–18 years.

II. PRINCIPAL METHODS OF SYNTHESIS

The majority of the PA known hitherto are oligomeric compounds in which the number of units varies from three to six–seven, i.e. having a molecular weight of 1500–5000[39,40]. For certain PA, the degree of polymerisation is 11 and even 14†.[39] According to Berezin and Shlyapova[39], the degree of polymerisation of metal-containing polyphthalocyanines depends on the nature of the metal. In the case of metals with a sterically strained coordination (Ru, Os, and Mo) it is lower than for metals whose coordination does not involve a distortion of the ligand field (for example, Cu, Ga, and Zn).

Metal-containing PA are obtained by the polycyclotetramerisation of tetrafunctional derivatives of aliphatic or aromatic acids having a suitable structure with metals or their oxides and salts. Pyromellitic acid tetranitrile[41] and dianhydride[42], diphthalyl ketone[43], tetracyanoethylene[19], 2,3,4,5-tetracyanothiophen, 2,3,4,5-tetracyanofuran, bis-(3,4-dicarboxyphenyl) ether[44], bis-(3,4-dicyanophenyl) ether[16], etc. are used as the initial compounds in this reaction. In the synthesis of PA having a ribbon structure, the above monomers are sometimes copolymerised with bifunctional compounds such as phthalonitrile, maleic acid dinitrile, etc.

The polycyclotetramerisation process accompanying the formation of the PA is frequently referred to as the "phthalocyanine synthesis" and is carried out similarly to the synthesis of low-molecular-weight porphyrazine complexes. The initial reactants are heated to a temperature from 100° to 300–350°C in solution (in nitrobenzene, ethylene glycol, cyclohexanone, biphenyl, etc.) or in the monomer melt for 10–20 h. The reaction catalysts are ammonia, urea, ammonium molybdate, etc., which in many instances not only accelerate the process but are also involved in the formation of the final products. Low-molecular-weight admixtures are extracted with acetone, alcohol, and benzene, depending on the nature of the starting materials and are also eliminated by vacuum heat

† Although various methods for the determination of the molecular weights of PA have been mentioned in the literature (spectroscopic[39], potentiometric titration of end groups[39,40] etc.), none of them yield exact information about the molecular weight of the polymers. The data obtained with the aid of these methods must be regarded as highly approximate.

treatment at 190–250°C and a residual pressure of 10^{-3}–10^{-5} mmHg. In order to remove traces of inorganic impurities (metals and their salts which failed to react, residues of inorganic catalysts, and their reaction products), the final products are subjected to an acid treatment. The choice of acid and of the conditions of this treatment depend on the type of complex-forming agent. Similarly, using mixtures of various metal salts, one can obtain di-, tri-, and poly-metallic complexes of PA with two and more different metals in the macromolecule[16,45].

The polycyclotetramerisation of the above compounds in the absence of metals leads to metal-free PA.[46,47] The latter are also obtained by the acid treatment of PA_{Na}, PA_{Ca}, etc.[42,48] (see Section IV).

When the "phthalocyanine synthesis" is used, the following factors should be taken into account.

1. The structure of the PA obtained in this way is as a rule inhomogeneous with respect to its chemical composition and contains an appreciable proportion of different defects. These include uncyclised sections of the macromolecule, intermediates attached to the chain, and residual amounts of the solvent and low-molecular-weight compounds firmly linked to the polymer. The higher the chemical reactivity of the monomer, i.e. the greater the tendency of the monomer to undergo various types of reactions in the course of polymerisation, the more defects are to be expected in the structure of its polymers under these conditions. Indeed, comparative study of the polymers obtained from tetracyanoethylene and tetracyanobenzene showed that the structure of the former is much more defective‡.

Copolymerisation of chemically reactive and relatively inactive monomers leads to the formation of copolymers with a more homogeneous chemical composition compared with the corresponding homopolymers (for example, the structures of the tetracyanoethylene–phthalonitrile of tetracyanoethylene–tetracyanobenzene copolymeric copper complexes are much more homogeneous with respect to chemical composition than that of $PTCE_{Cu}$[52]).

2. The use of ammonium molybdate as the reaction catalyst[53–55] leads to the formation of molybdenyl-phthalocyanine together with the main product[56]. Although PPC_{MoO_2} decomposes on prolonged treatment with concentrated H_2SO_4, the use of this catalyst complicates the isolation of the final products and contaminates them.

3. The acid purification of the PA synthesised is accompanied by the hydrolysis of the free groups of the polymer [terminal and surrounding ("framing") groups] and of various intermediates formed in the course of the synthesis, which increases the chemical inhomogeneity of the system to a still greater extent.

The inhomogeneity of the structure of the PA obtained by "phthalocyanine synthesis" is reflected significantly in their properties and hinders a comparative study of the properties of the PA complexes of different metals, particularly those synthesised by different workers. In this connection the series of critical comments by Boston and Bailar[14] concerning the work of Inoue et al.[45] apparently requires additional careful tests.

In order to reduce the defectiveness of the structure and to increase the degree of its homogeneity with respect to chemical composition, polymers are subjected to a prolonged vacuum heat treatment. This involves the splitting off of free functional groups and the removal of the residues of the solvent, monomer, and low-molecular-weight intermediates with simultaneous cross-linking and additional cyclisation, which leads to an increase of the regions of continuous conjugation and of the molecular weight of the specimen.[57–60] The latter is confirmed, in particular, by the change in the nature of the absorption spectrum of the heat-treated polymer relative to the initial specimen. The spectrum of the treated polymer is less steep, apparently owing to the increase of the absorption in the long-wavelength region due to the larger molecules formed on cross-linking[61]. The vacuum heat treatment can be accompanied by a change in the crystal lattice parameters of the PPC or the conversion of their structure into an amorphous form. As a rule, polymers lose their solubility and ability to be pressed after heat treatment.

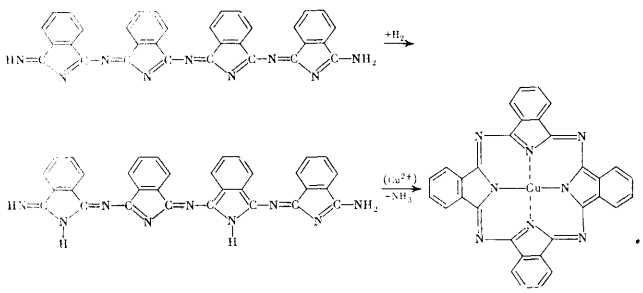
The most effective way of increasing the chemical homogeneity of the structure involves polymerisation in the monomer vapour, developed in 1958–1960 in relation to the synthesis of polymeric tetracyanoethylene complexes[17,19]. Subsequently it was used to obtain also other PA. In order to obtain PA by this method, powders, films, or other types of solid metallic or non-metallic materials are heated in the vapour of the corresponding monomer in the presence of small amounts of moisture, ammonia, or other initiators. The reaction proceeds on the surface with formation of both metal-containing and metal-free PA in the form of films of any size and with any profile, depending on the form of the supports used. This method is free from many of the disadvantages of the usual "phthalocyanine synthesis". It does not require the application of acids, alkalies, or solvents, which promotes the formation of products with a more homogeneous chemical composition. When the reaction is carried out in the monomer vapour, the polymers are obtained in the form of film coatings, which eliminates the necessity for reprocessing, greatly facilitates the investigation, and leads to practical applications of the PA.

Despite the many years which have elapsed since the synthesis of the first porphyrazines§, the mechanism of their formation has been inadequately investigated. It is only known that transition from aromatic dinitriles, *o*-arylenedicarboxylic acids and their anhydrides and imides to phthalocyanines proceeds via 3-aminoiminoisoindolenine, a series of transformations of which leads to the azaporphin[62]. The final reaction stage has come to be

‡ The electron affinity of tetracyanoethylene is much greater than that of tetracyanobenzene [it amounts to 1.6–1.8 (Brieglebe[49]) or 2.8 (Batley and Lyene[50]) compared with 0.4 eV for tetracyanobenzene[51]] and the compound exhibits an exceptionally high chemical reactivity in substitution, Diels–Alder, oxidation-reduction, etc. reactions.

§ Phthalocyanines were discovered accidentally in 1928 and soon (1929–1930) systematic studies on these compounds were begun. The phthalocyanine dimer was obtained in 1949. The first publications on the synthesis of PA appeared in 1958–1959[15,17,18,23,40].

represented by the following scheme:



The replacement of bifunctional acids by tetrafunctional acids greatly complicates the reaction. Polycyclotetramerisation is determined to a greater extent than the formation of phthalocyanines by the nature of the initial reactants, particularly in its first stages. Thus it has been shown that the polycyclotetramerisation of tetracyanoethylene proceeds via the radical-anions of this monomer, the rate of formation of which parallels the rate of formation of the polymer[64,65]. Polyphthalocyanines are apparently synthesised via pyromellitic acid diimidine, which was detected in the interaction of tetracyanobenzene with ammonia and served as the starting material for the synthesis of PPC and PPC_{Cu}.[66] It is quite likely that pyromellitic acid diimidine plays the same role in the polycyclotetramerisation reactions as that of 3-aminoiminoisoindolenine in the synthesis of PC.

The study of the formation of PPC from tetracyanobenzene showed that oligomeric porphyrazines, soluble in organic solvents, are formed in the initial stages and are subsequently converted in the course of the reaction into insoluble planar cross-linked polymers. It is then unimportant whether the reaction takes place in the melt or in a monomer solution. In our view, the reported synthesis[47] of insoluble PPC did not involve polymerisation in solution at all, as stated erroneously by Radyushkina et al.,[67] but was associated with the nature of the solvent (formamide) employed in the reaction, which in this case behaves as a cross-linking agent. It has been shown that the polymerisation of tetracyanobenzene in the presence of specific amounts of the initiator leads to PPC which are believed to have a ribbon structure and are soluble in organic solvents.

The transition to insoluble PPC with a planar cross-linked structure takes place gradually and is faster the higher the reaction temperature and the greater amount of the initiator introduced into the system. An increase of pressure in the reaction mixture apparently has a similar influence on the rate of transition[68].

The formation of metal-substituted PA is accompanied in addition by oxidation-reduction reactions. This is indicated by the presence of the heterovalent Fe^{3+} and Fe^{2+} ions in the PPC_{Fe} molecules obtained by the interaction of tetracyanobenzene with $FeCl_3$.[69] The polycyclotetramerisation of tetracyanoethylene under analogous conditions leads to $PTCE_{Fe}$ with Fe^{3+} in the macroring and with Fe^{2+} in radical-ion salts, which are apparently located at the end of the macromolecule[69,70].

The method of "phthalocyanine synthesis" has been inadequately investigated. Nevertheless, this is the principal, widely used procedure for the synthesis of PA. Only a few types of PA among those investigated hitherto have been obtained by other methods. Germanium- and silicon-polyphthalocyanines having a "loop" structure have been synthesised by the interaction of derivatives of the corresponding phthalocyanines[30-32]. When PC_{Cu} was fused with sulphur, P_4S_{10}, or SCl_2 at 460°C, the products were PPC_{Cu} with sulphide bridges in the macromolecule[71]. New polyamides with azaporphin macrorings have been obtained by the condensation polymerisation of phthalocyanines, containing functional groups, with various diamines[26].

The synthesis of metal-substituted PA by treating the corresponding metal-free polymers with metal salts merits particular attention[19,70]. This method makes it possible to obtain the PA complexes of various metals under comparable conditions. With its aid, it has been possible to obtain for the first time and to separate the univalent complexes of PPC_{Fe} with bivalent and tervalent iron in the macroring[69,70]. The homogeneity of the structure is specified in this case by the initial metal-free polymer and does not undergo any appreciable changes on treatment with metal salts.

A more detailed development of methods specific to polymeric compounds, different from the method of "phthalocyanine synthesis", will lead in the future to new procedures for the formation of PA.

III. THE STUDY OF STRUCTURE

The structure of PA is studied mainly in order to detect azaporphin macrorings in the macromolecules synthesised. For this purpose, one uses as a rule elemental and spectroscopic analyses. However, this is difficult owing to the insolubility and infusibility of the majority of PA; the most reliable results have been obtained only for the soluble fractions of the polymers.

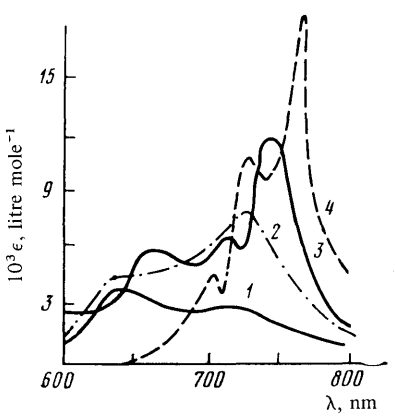


Figure 1. Electronic absorption spectra of PPC; solvents: 1) acetone; 2) dimethylacetamide; 3) concentrated H_2SO_4; 4) PC in concentrated H_2SO_4.

The azaporphin structure of the polymers synthesised has been confirmed by the presence in the spectra of these polymers of bands which are usually attributed to the azaporphin "skeleton". The infrared bands at 745–750, 810–885, 945–950, 1045–1060, 1080–1090, and 1118–1123 cm^{-1} correspond to the vibrations of the "skeleton"[72]; in the electronic absorption spectra there is a long-wavelength band in the range 600–800 nm.

Agreement between the spectra of the polymers and the corresponding low-molecular weight analogues is observed for all types of PA, both metal-free and metal-substituted, regardless of the nature of the metal and the molecular weight of the PA. The nature of the spectra depends significantly on that of the solvent employed (Fig. 1) for both PA and various derivatives of low-molecular-weight porphyrazines[73,74].

Recently published communications[69,75,76] concerning the studies of iron-phthalocyanines by Mössbauer spectroscopy report the development of a new extremely effective method for the investigation and identification of the structures of azaporphin complexes, including insoluble planar cross-linked complexes. The use of this method made it possible for the first time to carry out a comparative investigation of soluble and insoluble PA, to compare data for different types of PA, and to elucidate the influence of the conditions of synthesis and treatment on the structure of the polymers obtained. The study of the Mössbauer spectra of PC_{Fe}, soluble and insoluble PPC_{Fe}, obtained both by "phthalocyanine synthesis" (in solution, in the melt, and in the monomer vapour) and from PPC, as well as $PTCE_{Fe}$ revealed a fairly satisfactory agreement between their isomeric shifts (δI) and quadrupole splittings (ΔE). This indicates the presence in the structures of all the complexes of ligands having the same electronic structure[69,70]. Consequently all the polymers investigated have a structure analogous to that of PC_{Fe}, i.e. they contain azaporphin macrorings.

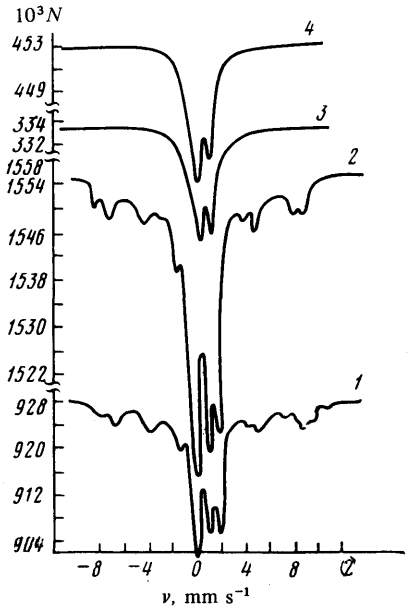


Figure 2. The Mössbauer spectra recorded at different temperatures for PPC_{Fe} obtained by the introduction of iron into PPC; temperature (K): 1) 2; 2) 4.2; 3) 90; 4) 300; v = speed of the source relative to the absorber; N = quantity proportional to the number of pulses.

It is noteworthy that hitherto there has been no unanimous view in the literature concerning the structures of polymeric tetracyanoethylene derivatives, because it is impossible to obtain reliable spectra of these polymers owing to their poor solubility. Their azaporphin structure was confirmed only by the results of elemental and chemical analyses[19,60,77]. However, there have been studies[78] in which a different structure was attributed to polymeric tetracyanoethylene derivatives. The agreement between the values of ΔE and δI for the Mössbauer spectra of $PTCE_{Fe}$, PC_{Fe}, and PPC_{Fe} constituted a convincing confirmation of the azaporphin structure of the given class of polymers.

The application of Mössbauer spectroscopy also made it possible to determine the valence of the metal in the polymeric iron-azaporphins and to elucidate the conditions for the formation of PPC_{Fe} with the metal having a particular valence[69,70].

As for PC_{Fe},[75,76] the values of $E\theta$ and δI for PA_{Fe} depend only slightly on temperature and the metal content or not at all. The study of PPC_{Fe} with different metal contents in the macromolecule[70] at 4.2 and 2 K revealed a hyperfine structure of the Mössbauer spectroscopic lines (Fig. 2), which indicates the operation of a powerful spin–spin mechanism of the relaxation of the electronic spin of Fe^{3+}. This suggests in its turn the occurrence in such systems of an exchange magnetic dipole interaction between the iron ions in the macromolecules.

A wider employment of Mössbauer spectroscopy will throw light in the future on many hitherto obscure problems concerning not only the structure but also the mechanism of the formation of PA.

IV. CERTAIN PHYSICOCHEMICAL, ELECTRICAL, AND CATALYTIC PROPERTIES

1. Physicochemical Properties

Polyazaporphins are infusible thermally stable dark-coloured compounds whose colour ranges from blue-green to black. Depending on the method of synthesis and the conditions in the subsequent treatment, they can be obtained in the amorphous and fully crystalline forms[16,68,79]. The thermal stability of the PA is determined by its chemical structure and the degree of its homogeneity, the nature and number of free functional groups, and the nature of the metal in the macroring. Unfortunately the available literature data do not allow a complete analysis and survey of the characteristics of the thermal stabilities of such systems. One can only reach a conclusion (and even that only very approximately) about the temperature to which PA may be heated without appreciable decomposition. Thus diphthalyl ketone polymers withstand heating to 450°C[43] and certain specimens of polymeric tetracyanoethylene derivatives are stable in air up to 300–350°C and in an inert atmosphere up to 500–550°C.[57]

On the other hand, polymeric tetracyanothiophen and tetracyanofuran derivatives decompose in air below 300°C.[16] The comparatively low stability of the latter is apparently associated with the presence of acetylacetonato-groups in their structure. The presence of such groups together with a variable-valence metal creates favourable conditions for the formation of peroxy-radicals capable of initiating the decomposition of the polymer, which has been demonstrated in the study of the thermal stabilities of $PTCE_{Cu}$, $PTCE_{Fe}$, etc.[57] In those cases where it was

possible to eliminate these groups from the structure, the stability of the polymers increased appreciably. The increase of the chemical homogeneity of PA also promotes an increase of their thermal stability regardless of whether such homogeneity is obtained by the alteration of the conditions of synthesis or in the course of an additional treatment of the specimen[57].

Comparative study of the thermo-oxidative degradation of PC_{Co} and its polymeric analogue, on the one hand, and metal-free and metal-substituted PA, on the other, revealed a lower rate of thermolysis of PPC_{Co}, while the other reaction parameters remained unchanged[80], and a higher stability in air of metal-free polymers relative to PPC_{Cu} and PPC_{Fe}. The reduced stability of complexes of variable-valence metals on heating in air is associated with the fact that copper, iron, and other variable-valence metals are excellent initiators of the formation of peroxy-radicals (this is well known), which promote in their turn the degradation of the polymers. The stability series is based on their resistance to thermo-oxidative degradation, found for polymeric tetracyanoethylene complexes:[19] $PTCE > PTCE_{Mg} > PTCE_{Cu} > PTCE_{Fe}$; this series can apparently be repeated also for other PA.

The solubility of PA depends on the configuration of the chain and the "frame" surrounding the azaporphin macrorings. While planar cross-linked polyphthalocyanines, referred to as poly(tetramethineporphyrazines) by Akopov[13], do not dissolve in organic solvents, ribbon polyphthalocyanines [Akopov calls them poly(dimethinedibenzoporphyrazines)] partly dissolve in dimethylformamide, dimethylacetamide, and pyridine. Their solubility is higher the greater the number of end groups forming the "frame" in the macromolecule. A large number of functional groups in polymer macromolecules as well as bulky substituents in the molecules of low-molecular-weight porphyrazines[81,82] prevent the close packing of such systems, which increases their solubility.

Oligomeric PPC with a large number of surrounding ("framing") nitrile groups, which are soluble in acetone, have been obtained recently; poly(disulphonephthalocyanine), obtained from PA-bis(3,4-dicarboxyphenyl) sulphone, is soluble in water[24].

Despite the fact that the basicity of the azaporphin compounds is greatly reduced owing to the involvement of the free electron pairs of the peripheral nitrogen atoms in the construction of the metal-like molecule, a characteristic feature of these compounds is their solubility in concentrated H_2SO_4, the dissolution being accompanied by the protonation of the macromolecule[23]. The solubility of the PA in the acid is lower than the solubility of their low-molecular-weight analogues and depends on the structure of the polymer and on the nature of the central metal atom. Thus, in contrast to the ribbon PA, which are readily soluble in acid, the planar cross-linked PA dissolve in concentrated H_2SO_4 only after prolonged (up to 5–6 days) treatment. The solubility of metal-containing PA in concentrated H_2SO_4 is higher the more pronounced the electron-donating properties of the metal atom in the "window" of the macroring.

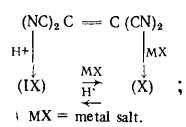
The resistance of PA to acid is determined by the configuration of the polymer chain and the nature of the central metal atom in the ring. As a rule, the PA of the first group (the section I) are less stable in acid than their low-molecular-weight analogues. Thus the stability of PC_{Zn} in acid is approximately 10 times greater than that of PPC_{Zn},[84] and the rate constant for the degradation of PC_{Co} in H_2SO_4 at 25°C is smaller by three orders of magnitude than for PPC_{Co}.[85] The resistance of silicon complexes to acid is also considerably inferior to that of their low-molecular-weight analogues, although the PPC_{Si} of the third group, having a "loop" structure, are much more stable in acid than PC_{Si}.[86,87]

Depending on the nature of the central metal atom, the PA as well as phthalocyanines[88] can apparently be divided into two groups in terms of their resistance to the action of concentrated H_2SO_4: stable PA which do not undergo an appreciable change when treated with the acid and labile complexes which lose the metal after the acid treatment and are converted into the metal-free polymers. In terms of the degree of elimination of the metal from the macroring, which is inversely proportional to the strength of the M–N interaction, metals can be arranged in the following sequence[26]:

$$Zn^{2+} > Fe^{3+} > Ni^{2+} > Co^{2+} \gg Cu^{2+} .$$

The ability of the PA complexes of sodium, magnesium, calcium, etc. to lose the metal in the course of the acid treatment has found an application, as already stated, in the synthesis of metal-free PA. The ability of metal-free porphyrazines to interact with metals or their salts on heating is used to synthesise metal-substituted azaporphin complexes[89]. The reaction is carried out both in solutions[19,70] and in suspensions, the polymer powder being treated with a solution of the salt[90,91].

Thus PA as well as their low-molecular-weight analogues are a kind of molecular sieve which absorb and, under appropriate conditions, give up metal ions. In other words, they are capable of undergoing the polymer complex–metal-free polymer transition, illustrated schematically below for polymeric tetracyanoethylene derivatives[48]:



This property of polyazaporphins may lead in the future to their utilisation as complex-forming ion exchangers and organic molecular sieves operating at elevated temperatures.

2. Electrical Properties

The electrical properties of PA, whose study was begun in 1959–1960,[41,92] have been frequently discussed in connection with the consideration of the properties of organic semiconductors[93–95]. We shall therefore deal below only with questions which have not been adequately dealt with in the above monographs.

The specific conductances σ of polyazaporphins are higher by several orders of magnitude than for their low-molecular-weight analogues and the activation energies for electrical conduction E in the polymers are much lower (see Table). The dependence of E on the medium in which the measurements are made has been observed for a whole series of complexes (it is more pronounced in nitrogen and less so in ammonia than in air[16]) and E has been found to vary in parallel with the optical excitation energy (see Table).

The conductivity of $PTCE_{Cu}$ films obtained in monomer vapour has been found to be anisotropic: σ is greater by 3–7 orders of magnitude parallel to the film surface than in the perpendicular direction. The dielectric constants and σ of PA vary exponentially not only with temperature

but also with pressure. The linear decrease of the resistivities ρ with increase in pressure has been attributed to the increase of the intermolecular overlap, which facilitates charge transfer in the case of closer-packed polymer chains and layers [99].

One of the important problems in the study of the electrical properties of porphyrazines is that of the influence of the nature of the central metal atom and of the ligand on the electrophysical parameters. Many investigators have explained the slight decrease of E after the introduction of the metal into the PC by the fact that the conductivity of such systems is determined exclusively by the π electrons of the conjugated system of the macroring. Furthermore, the mobility of the current carriers μ depends on the degree of overlap of the metal and macroring orbitals. The greater the overlap, the higher the value of μ [thus $\mu(PC_{Ag}) > \mu(PC_{Cu})$], [100] so that the conductivity of the system should also be higher ($\sigma = en\mu$, where n is the concentration of current carriers). Indeed σ and E for polymeric tetracyanoethylene complexes of a number of metals are different and also differ from the analogous parameters of the metal-free polymer. For example E = 0.53, 0.32, and 0.18 eV have been obtained for PTCE, $PTCE_{Cu}$, and $PTCE_{Ag}$ respectively [101]¶.

The dependence of the electrophysical parameters on the nature of the central metal atom is manifested also in the study of bimetallic PA [16,102] (see Table). An attempt has been made [16] to compare the experimental values of σ for the polymeric tetracyanothiophen complexes of various metals with the ionic radii and ionisation potentials (Fig. 3) of their cations.

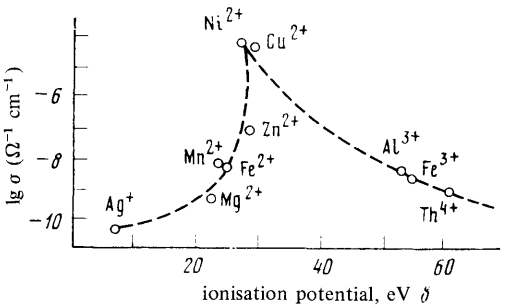


Figure 3. Dependence of the electrical conductivity of the polythiophenocyanine complexes of a number of metals on the ionisation potentials of the cations.

The electrophysical parameters and the positions of the longest-wavelength absorption maximum for certain azaporphin compounds.

No.	Specimen*	σ_{300}, Ω^{-1} cm^{-1}	σ_0, Ω^{-1} cm^{-1}	E, eV	λ_{max}, nm	Refs.
1	β-PC_{Cu}	$1.9\cdot10^{-14}$	$1.2\cdot10^{3}$	1.95	—	71
2	PC_{Cu} dimer	—	—	1.0–0.7	—	12
3	PPC_{Cu}	$5.9\cdot10^{-6}$	$1.6\cdot10^{-2}$	0.41	750	71
4	PPC_{Cu}**, ***	$2.3\cdot10^{-2}$	—	0.15	—	97
5	$PTTPC_{Cu}$**	$3\cdot10^{-7}$	$2\cdot10^{-3}$	0.45	—	96
6	$PThiC_{Cu}$**, ***	$5.5\cdot10^{-5}$	$1.0\cdot10^{-1}$	0.36	—	96
7	$PThiC_{Cu}$**	$3.3\cdot10^{-12}$	$5.8\cdot10^{-7}$	0.62	—	16
8	$PThiC_{Cu}$**-Ni	$8\cdot10^{-6}$	$1.3\cdot10^{-2}$	0.37	—	16
9	$PThiC_{Cu}$**-Mg	$6.8\cdot10^{-7}$	$5.6\cdot10^{-4}$	0.36	—	16
10	$PTCE_{Cu}$**, ***	$18\cdot10^{-7}$	—	0.50	—	97
11	$PTCE_{Cu}$	10^{-5}	$10^{-0.4}$	0.32	—	19
12	$PTCE_{Cu}$***	10^{-2}	10	0.18–0.1	—	19
13	Chloro-PC_{Zr}	$2.0\cdot10^{-10}$	$2\cdot10^{2}$	1.43	693	98
14	PPC_{Zr}	$2.2\cdot10^{-7}$	$8.8\cdot10^{-2}$	0.54	746	98
15	PPC_{Sc}	$4.3\cdot10^{-8}$	$1.42\cdot10^{-3}$	0.53	750	98
16	PPC_{Co}	$3.2\cdot10^{-9}$	$6.22\cdot10^{-4}$	0.62	726	98

*All the specimens except Nos. 7, 11, and 12 were synthesised in melts of the initial reactants. Specimen No. 7 was obtained in solution in cyclohexanol and specimens Nos. 11 and 12 were synthesised in tetracyanoethylene vapour.

**The polymers were obtained by the interaction of the corresponding tetranitriles with metal acetylacetonates.

***The specimens were subjected to a preliminary heat treatment at 200–300°C.

¶For polymers obtained in the monomer vapour.

The fact that the maximum values of σ have been observed for PA containing metals whose cationic radius is approximately 0.75 Å is striking. If account is taken of the fact that the cations having such a radius can be accommodated most favourably in the "window" of the azaporphin macroring [103], the influence of the degree of overlap of the electronic orbitals of the metal and the ring on the conductivity of such systems becomes evident: the most complete overlap of the electronic orbitals of the metal and the ring leads to an increase of μ and hence also σ.

Analogous relations have been obtained also for polytetrathiafulvalenocyanines (PTTFC) [96]. The observed relations give rise to the following sequence of metal cations arranged in terms of decreasing electrical conductivities of their polyporphyrazine complexes:

$$Ni^{2+} > Co^{2+},\ Cu^{2+} > VO^{2+},\ Mn^{2+},\ Zn^{2+} > VO_2^{2+},\ Cr^{3+},\ Fe^{3+} > Mg^{2+}$$

Comparison of the electrophysical properties of various PA_{Cu} also revealed the influence of the nature of the ligand on σ and E. It was observed that E decreases in parallel with the decrease of the aromaticity of the rings connecting the azaporphin macrorings into a polymer chain—from benzene, via thiophen, to furan, i.e. in the sequence $PPC_{Cu} > PThiC_{Cu} > PFuC_{Cu}$, where $PFuC_{Cu}$ is the polymeric copper complex of tetracyanofuran and $PThiC_{Cu}$ is the polymeric copper complex of tetracyanothiophen [16].

We do not believe it is possible to arrive at more far-reaching conclusions about the influence of the nature of the ligand and the metal on the electrophysical properties of PA, because, despite the extensive experimental data available, there are no literature data on the purities and homogeneities of the structures of the given polymers. Frequently there is no description of the nature of the preliminary treatment of the specimens. At the same time, the Table shows that the change in the conditions of the synthesis (cf. specimens Nos. 6 and 7 and Nos. 10 and 11)

and additional heat treatment of (Nos. 11 and 12) have a significant influence on the electrophysical parameters of PA.

Numerous experiments have shown that an increase of the duration of the synthesis, additional vacuum heat treatment of the polymers, polymerisation in the monomer vapour, as well as copolymerisation with chemically inactive monomers promote the formation of more homogeneous and sometimes more ordered structures with an enhanced electrical conductivity (see Table). In this connection we may mention that the method of synthesis of metal-substituted PA with the aid of metal acetylacetonates, previously proposed by the present authors [79], does not appear to us to be altogether successful at the present time. Indeed, the polymers obtained by this method contain acetylacetonato-end groups (which frequently also make up the "frame") and these as a rule impair many of the properties of PA (see Section IV). Furthermore, and this is the most important factor, in the course of the above reaction appreciable numbers of insoluble side products are formed and are difficult to separate from the main bulk of the polymer, remaining in the specimen as impurities.

This makes the reaction of acid tetranitriles with metal acetylacetonates unsuitable for the synthesis of PA on a preparative scale, particularly when the aim is to discover the relation between the chemical structure and the properties of the polymers.

In order to investigate the mechanism of conduction in semiconductors, one usually determines the temperature variation of n, μ, thermo-e.m.f. (α), etc. Measurements of thermo-electromotive forces showed that the PA known at the present time exhibit different types of conductivity. Copper- and zinc-polytetrathiafulvalenocyanines exhibit p-type conductivity [96], while heat-treated films of the polymeric tetracyanoethylene complexes of various metals show n-type conductivity [104]. Electronic conductivity has been observed for scandium-, zirconium-, and cobalt-polyphthalocyanines. Over the entire experimental temperature range, the sign of the current carriers remains unchanged [98]. Sulphur-containing PPC_{Cu} specimens, synthesised from PC_{Cu}, exhibited p-type conductivity, whereas polymers obtained from tetracyanobenzene and subjected to a special treatment with sulphur showed n-type conductivity [71].

A change in the sign of the majority current carriers has been observed for the $PTCE_{Fe}$–metallic iron and $PTCE_{Ag}$–metallic silver compositions as a function of the conditions of the preparation of the system. The compositions obtained were converted in the course of 10–14 h into systems with hole conductivity, the sign of the current carriers changing with increase of the reaction time to 15–20 h [105]. The values of α for a number of PA are 50–70 $\mu V\ K^{-1}$. [96,104]

The mechanism of conduction has been studied in greatest detail for PPC_{Cu}. [106] In the study of the conductivity of this polymer, both positive and negative current carriers were detected, their concentration being almost independent of temperature, while α varied exponentially with temperature. This enabled the authors [106] to conclude that the migration of the current carriers in PPC_{Cu} is an activated process. Although the signs of the majority carriers in PPC_{Cu} and PC_{Cu} were the same, μ for the polymer proved to be smaller than for its low-molecular-weight analogue†. Extrapolation of the measured mobility to an "infinite" temperature, at which there is no hindrance to the migration of current carriers at the breaks in conjugation, leads to $\mu_\infty = 1.4\ cm^2\ V^{-1}\ s^{-1}$.

The results suggest that the comparatively high value of σ in such substances is associated with the high concentration of current carriers whose mobility is low and varies exponentially with temperature. On the basis of an estimate of the concentration of current carriers (10^{18}–10^{19} cm^{-3}), the authors of this investigation believe that the required concentrations of the impurities in polymers resembling those investigated must be reduced at least by 5–6 orders of magnitude compared with inorganic semiconductors.

The Hall effect was measured after frequent unsuccessful attempts only in one study [41]. The authors [41] observed two states for PPC_{Cu}: one state has $E = 0.26$ eV and $n = 10^{16}\ cm^{-3}$, n being independent of temperature, and the other (heat-treated polymer with p-type conductivity) has $n = 10^{18}\ cm^{-3}$, which remains constant within the limits of the measured temperatures. However, these results were not subsequently confirmed‡. Having estimated the sensitivity of the apparatus in which the Hall effect was measured for PPC_{Cu}, the authors [106] concluded that the mobility of the current carriers in the test specimens is not greater than 0.3 $cm^2\ V^{-1}\ s^{-1}$ at 18–250°C. This implies in its turn that the comparatively high electrical conductivity of the specimens (for example, $\sigma_{300} = 10^4\ \Omega^{-1}\ mm^{-1}$) must be due to a high concentration of current carriers, exceeding $2 \times 10^{17}\ cm^{-3}$. [106]

It is now well known that measurements carried out using a direct current cannot yield a unique picture of the conduction mechanism, which apparently involves two processes: the transport of carriers from one continuous conjugation region to another and the conduction within these regions themselves. In order to elucidate the conduction mechanism, measurements must be made of the frequency dependence of the electrical parameters; some of these parameters for polymeric tetracyanoethylene derivatives have been published [93].

The study of the frequency dependence of the dielectric constants and σ as a function of the electric field strength for PPC showed that these polymers are one-dimensional semiconductors in which the conductivity regions extend over 100–1000 Å. [99]

3. Catalytic Properties

The study of the catalytic properties of PA showed that, as in many other organic semiconductors, these compounds exhibit an enhanced activity in relation to oxidation-reduction reactions such as the oxidation of aromatic alkyl-substituted hydrocarbons [109,110] and certain aromatic and saturated aliphatic aldehydes [111], the decomposition of formic acid and hydrogen peroxide [112], etc.

In terms of their reactivity, the polymeric complexes are as a rule superior to their low-molecular-weight analogues. An exception is $PPC_{Os(SO_4)_2}$, whose catalase activity is five times smaller than that of $PC_{Os(SO_4)_2}$ and PPC_{RuHSO_4}, the latter having the same activity as

† According to Heilmeir et al., [107] μ for PC_{Cu} is 0.1–0.4 $cm^2\ V^{-1}\ s^{-1}$.

‡ It is quite likely that the Hall effect cannot be measured at all for PA as well as a whole series of semiconductors with a jump conductivity mechanism [108].

PC_{RuHSO_4}.[113] A characteristic feature of the polymeric complexes as oxidation-reduction catalysts is their appreciably greater selectivity than that of the corresponding low-molecular-weight analogues, reaching 100% in many instances, for example in the dehydrogenation of formic acid, the oxidation of cumene[110], etc.

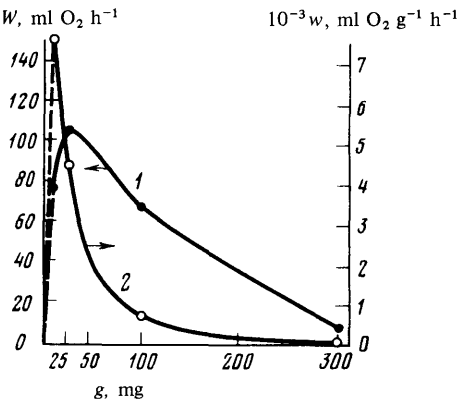


Figure 4. The influence of the amount of PPC_{Fe} on the rate of oxidation of cumene: 1) overall rate of reaction (W) relative to the catalyst sample (g); 2) specific rate of reaction (w) per gramme of catalyst.

Like certain other catalysts, PA exhibits a dual function in reactions. Depending on the amount of PA introduced into the reaction, the complexes behave as both process initiators and inhibitors. This property is illustrated in Fig. 4 in relation to the effect of PPC_{Fe} in the oxidation of cumene.

The problem of the centres which determine the catalytic activity of porphyrazines has not at first sight been solved unambiguously. On the one hand, there is evidence for the decisive influence of the nature of the metal on the catalytic activity of phthalocyanines and, on the other hand, there is evidence showing that the peripheral nitrogen atoms of the macroring play the main role without any participation of the metal. Indeed, while the activity of PPC and PTCE in the oxidation of cumene is insignificant, the complexes of these polymers with iron and copper show a fairly high activity, which depends on the amount of metal in the macromolecule and increases with the latter[110]. However, the introduction of a second metal does not cause an appreciable enhancement of the catalytic properties of PPC_{Cu} in this reaction[110], in contrast to the effect observed by Inoue et al.[102]

The dependence of the catalytic activity on the nature of the metal has been investigated much more extensively for phthalocyanines than for PA and has been demonstrated in relation to various reactions. Thus it has been shown[110] that in the oxidation of cumene the phthalocyanine complexes of variable-valence metals (copper, nickel, and cobalt) exhibit a much higher activity than the phthalocyanine complexes of zinc, mercury, and silver. In formic acid decomposition reactions the specific activity of PC_{Cu} is smaller by more than an order of magnitude than that of PC_{Fe}; in the decomposition of hydrazine the differences between the specific activities of these phthalocyanines exceeded two orders of magnitude, while the addition of PC had almost no influence on this process[114].

It is of interest that even the selectivity of phthalocyanines (but not PA) is related to the nature of the metal. For example, in the oxidation of cumene to its hydroperoxide the phthalocyanine complexes of manganese, iron, cobalt, and nickel are much inferior in their selectivity to the copper and zinc complexes[115].

The finding that PPC_{Fe} obtained without a catalyst is more active in the decomposition of hydrogen peroxide than "the same" complex synthesised in the presence of ammonium molybdate[54] can serve as additional confirmation of the dependence of the catalytic properties of PA on the nature of the metal. The presence in the specimen of admixtures of PPC_{MoO_2}, formed in the catalytic synthesis of PPC_{Fe}, reduced the activity of the latter in the above reaction. This finding shows yet again that catalytic properties as well as electrophysical characteristics must be studied only on carefully purified and chemically homogeneous compounds free from impurities which are not susceptible to analytical determination.

Theoretical calculations, confirmed by experimental data obtained in the study of the electrochemical reduction of oxygen[116,117], showed that the phthalocyanine complexes of metals can be arranged in the following sequence in terms of their decreasing catalytic activities: $PC_{Fe} > PC_{Co} > PC_{Ni} > PC_{Cu}$. Analogous relations have been observed for polymeric complexes. The influence of the nature of the metal on the catalytic activity of phthalocyanines has been observed also in the electrochemical reduction of oxygen on carbon electrodes saturated by the above complexes[67]. The activity series for the phthalocyanine complexes in relation to this reaction, based on the nature of the metal, did not agree with similar series for other reactions[118,119].

However, under certain conditions, there are no differences between the catalytic activities of the phthalocyanine complexes of a number of metals. It has been shown[121] that the catalytic activity of phthalocyanines is determined by the crystal form of the given substances to a greater extent than by the nature of the metal. The observed decrease of the activity of PC_{Cu} in the oxidation of cumene has been explained[122] by the conversion of the catalyst from the α-form into the β-form and the authors concluded that the π-conjugated phthalocyanine system is important.

It has been shown by spectroscopic methods[123,124] that the active centres for the adsorption of organic and inorganic acids can be the nitrogen atoms of the phthalocyanine ring and that the metal atom is not essential for the formation of the phthalocyanine–acid molecule complex. Investigators of polymeric compounds arrived at similar conclusions. Thus it has been shown[125] by kinetic and EPR methods that the active centres for deuterium exchange in PPC_{Cu}, which are active at temperatures above 100°C, arise as a result of the dissociation of double bonds and do not include copper atoms. The authors[125] carried out a thermodynamic estimate, which showed that the chemisorption of hydrogen and hence the catalytic processes involving it are possible on non-metallic centres on organic semiconductors for a width of the forbidden gap below a certain limiting value.

The study of the adsorption of formic acid on PPC_{Cu} by spectroscopic methods at temperatures close to that of the onset of the catalytic reaction demonstrated a decrease of the intensity of the stretching vibration bands of the C–N groups in the infrared spectrum (1090–1310 cm^{-1}) and of the bands in the PPC_{Cu} spectrum in the visible region

(630 and 725 nm) corresponding to the presence of a conjugated system in the polymer. Together with results obtained previously[126,127], these data show that the active centres for the adsorption and dehydrogenation of formic acid in polyphthalocyanines may be the peripheral nitrogen atoms of the azaporphin macrorings of the polymer. The same conclusion follows also from studies of the *para–ortho* transformation of H_2 and deuterium exchange on PPC_{Cu}.[128]

The phthalocyanine activity series in the oxidation of cumene $PC_{RuHSO_4} > PC_{Os(SO_4)_2} > PC_{Co} > PC_{Ni} > PC_{Cu}$ shows, according to Berezin and Shlyapova[129], that the initiation of the reaction is not associated with the interaction of oxygen or the hydroperoxide with the metal in the phthalocyanine complex, since this possibility is altogether lacking in the case of the very active $PC_{Os(SO_4)_2}$.

The above data concerning the nature of the active centres of azaporphin show that the π electrons of the macroring and the *dsp* electrons of the metal constitute a single conjugated system, whose properties depend significantly on the nature of both the ligand and the metal in the "window" of the macroring.

It is of interest that an enhanced activity in oxidation-reduction reactions is manifested only by semiconducting compounds and that polymers (for example, polyphenylene, polyphenylacetylene, etc.) exhibit no such activity whatever in the above reactions, behaving as insulators at the experimental temperatures. This is usually attributed to a correlation between the catalytic and semiconducting properties of compounds of this kind. Indeed, as for many organic semiconductors, it has been noted for PA that the higher the value of σ, the higher the activity of the compound in model reactions[109,110,129,130].

This is manifested particularly clearly when the catalytic activities of PA and their low-molecular-weight analogues are compared. As already mentioned, the electrophysical parameters of the latter are greatly inferior to those of the corresponding polymeric complexes (see Table). This was also observed when the catalytic properties were compared. For example, PPC_{Fe} and PPC_{Cu} exhibit a much higher specific activity in the oxidation of cumene than PC_{Fe} and PC_{Cu} respectively[110]. A similar behaviour has been observed also for the cobalt complexes in the electrochemical reduction of oxygen in the presence of PC_{Co} and its polymeric analogue[67]. In the hydrogen peroxide decomposition reaction the specific activity of PPC_{Cu} is only five times smaller than that of one of the best catalysts for this reaction—manganese dioxide, whereas PC_{Cu} is altogether inactive in this reaction[112]. The specific activities of the phthalocyanine complexes of copper and iron are inferior to those of their polymeric analogues also in the hydrazine decomposition reactions[131].

A correlation between the semiconducting and catalytic properties is also indicated by the parallel variation of the catalytic activity and the concentration of paramagnetic centres, which has been established for certain organic semiconductors[131]. A whole series of chemical reactions involving organic semiconductor catalysts can be accounted for solely in terms of the semiconducting properties of the latter. However, a clear-cut correlation between the electrical and catalytic properties of semiconductors, which might have been expected on the basis of the electronic theory of catalysis on semiconductors[132], is not observed in practice. This led some workers to the conclusion that such a correlation is altogether lacking[133]. For example, the catalytic properties of polychelates have been attributed[134,135] to the electronic state of the metal in the chelate unit and not to the semiconducting properties of these systems. The absence of a correlation between the catalytic and semiconducting properties has also been reported in other studies.

The available literature data do not permit at present any unambiguous conclusions concerning the relation between the semiconducting and catalytic properties. A more detailed investigation of the mechanism of the catalytic action of organic semiconductors together with the study of the mechanism of their conduction and comparison of these data will apparently provide in the future an answer to the question of the fundamental factors influencing the catalytic activity of semiconducting systems. Here one should take into account also other no less significant factors which determine the catalytic activity of semiconductors, namely the local chemical properties of their surfaces, their collective electronic properties, etc.

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In conclusion, one should note that during the last 15–18 years extensive experimental data have been accumulated on the synthesis and properties of polymeric azaporphins, which undoubtedly constitute one of the most striking examples of polymers with a conjugation system. However, the lack of reliable methods for the synthesis and purification of PA has led to a very limited and extremely one-sided study of their properties and only a qualitative interpretation of the experimental data obtained.

Nevertheless, the unusual physical and physicochemical properties observed for these polymers make them valuable objects not only for a wide variety of scientific investigations but also for the creation on their basis of chemically and thermally stable specific catalytic systems as well as special semiconducting materials with a wide range of electrophysical parameters.

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