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Applied Aspects of the Chemistry of the Porphyrins

O.A.Golubchikov and B.D.Berezin

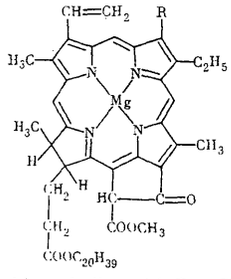
The review deals with the prospects for the practical application of porphyrins as catalysts and reactants in various chemical, electrochemical, and photochemical processes.
The bibliography includes 347 references.

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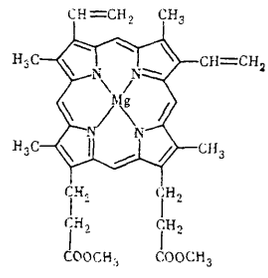
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I. INTRODUCTION

Porphyrin complexes play an important role in nature. It is sufficient to quote the example of chlorophyll [MgChl (I)], which, forming part of the composition of chloroplasts, effects photosynthesis, and haem [FePP (II)], which, as a component of haemoglobin, transports oxygen to animal tissues, as a component of myoglobin, it ensures its storage, and, as a component of cytochromes, it catalyses biochemical oxidation–reduction reactions. There is no doubt that the primary stimulus which led to the investigation of porphyrins and their metal complexes was provided precisely by the biocatalytic properties of metalloporphyrins. This stimulus still remains important.



chlorophyll *a*, with R = CH_3;
chlorophyll *b*, with R = CHO
(I)

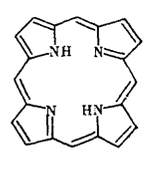


protohaem (II)

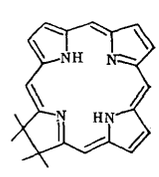
During the last 20–25 years, there has been a sharp growth of interest in porphyrins. Together with fundamental theoretical investigations, numerous applied studies have been made. Porphyrins proved to be universal catalysts of many chemical, electrochemical, and photochemical reactions.

The high catalytic activity of porphyrins is due to the aromatic character of the conjugated π-system of the macroring, the conjugation of the coordinated metal atom to the π-system of the ligand, and the ease with which the oxidation state of the central metal atoms, for example, those of Co, Fe, Mn, and others, changes. It is also important that the extensive π-electron systems of porphyrins have a distinct electron-buffer character. Depending on the other reactant, porphyrins can exhibit both electron-donating and electron-accepting properties. It is significant that porphyrins are chemically stable in the ground and photoexcited states and also in the form of radical-cations and radical-anions. The unique properties of the porphyrins can serve as a basis for the solution of many problems of practical importance.

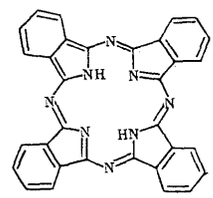
In this review the term porphyrin is used in a wide sense. Porphyrins (H_2P) are assumed to include porphin (H_2Po) (III), chlorin (H_2Ch) (IV), phthalocyanine (H_2Phc) (V), and their derivatives and metal complexes (MP). Tetraphenylporphins (H_2TPhPo) (X_4) (VI) and tetrabenzoporphins H_2TBPo (X_4) (VII) are important among the H_2Po derivatives.



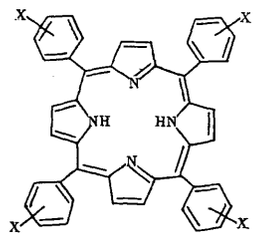
porphin (III)



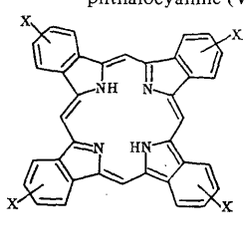
chlorin (IV)



phthalocyanine (V)



tetraphenylporphin (VI, X = H) and its derivatives



tetrabenzoporphin (VII, X = H) and its derivatives

The principle applications of the porphyrin are listed in Table 1.

II. CATALYSIS OF ELECTROCHEMICAL PROCESSES

Metalloporphyrins are widely investigated and used as catalysts of electrochemical oxidation-reduction reactions. Most studies in this field concern the catalysis of the reduction of molecular oxygen in low-temperature fuel cells. The catalytic activity of metal complexes of porphyrins in the cathodic reduction of oxygen was first observed by Jasinski:[1-3]

$$O_2+4H^++4e^-\rightarrow 2H_2O\ . \qquad (1)$$

A large number of publications on this topic soon appeared.[4-59] There are two reviews on the cathodic reduction of oxygen.[10,11]

Table 1. Practical applications of porphyrins

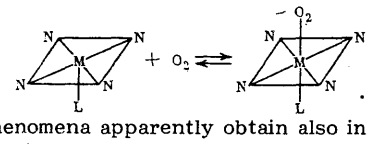
Application	References
Catalysis of cathodic reduction of oxygen	[1-59]
Catalysis of anodic oxidation of sulphur dioxide	[60-65]
Catalysis of cathodic reduction of hydrogen peroxide	[11, 66]
Catalysis of cathodic reduction of carbon dioxide	[67, 68]
Catalysis of cathodic reduction of nitrous oxide	[69]
Catalysis of electrochemical synthesis of organic compounds	[70, 71]
Catalysis of oxidation of hydrogen sulphide, mercaptans, and other sulphur derivatives	[72-90]
Catalysis of decomposition of hydrogen peroxide	[42, 91-105]
Catalysis of decomposition of organic peroxides	[106-113]
Catalysis of oxidation of hydrocarbons	[114-138]
Catalysis of oxidation of alcohols and phenols	[98, 99, 135, 137, 139-151]
Catalysis of oxidation of aledhydes and carboxylic acids	[99, 129, 137, 148, 149, 152-157]
Catalysis of oxidation of carbon monoxide	[158, 159]
Catalysis of reduction of organic compounds	[160-163]
Catalysis of oxidation and reduction reactions of nitrogen-containing compounds	[142, 160, 164-169]
Catalysis of polymerisation and regulation of degree of polymerisation	[170-180]
Catalysis of isomerisation of unsaturated compounds	[181-188]
Three-dimensional phase holography	[189-190]
Catalysis of photochemical decomposition of water	[191-215]
Catalysis of photoelectrochemical reactions	[216-239]
Semiconductors and photosemiconductors	[222-224, 236, 240-293]
Electrochromic materials	[294-299]
Pigments, dyes, and food dyes	[300, 301]
Enrichment of radioisotopes	[99, 302-315]
Analytical chemistry	[316-347]
Other applications	

Oxygen is usually reduced in fuel cells in a highly acidic or highly alkaline medium under the conditions of an appreciable polarisation of the cathode. For this reason, one of the central problems in the development of catalysts for the electrochemical reduction of oxygen is the problem of corrosion resistance.

The investigations have shown[1-59] that, apart from noble metals, whose applicability is limited, metalloporphyrins can serve as active and stable catalysts of reaction (1). The catalytic activity of MP depends on a number of factors, among which the nature of the coordinated metal atom proved to be the most important. Among tens of MP investigated, iron,[10,11,30,35,37] cobalt,[11,25,55] and ruthenium and iridium[45] complexes exhibit the greatest activity. The nature of the porphyrin ligand has a smaller effect on the catalytic activity. However, the increase of the activity of the catalyst with increase of the size of the conjugated π-bond system of the porphyrin has been demonstrated. Polymeric phthalocyanines $(MPhc)_i$ are less active than the monomeric compounds.[11,15-17,25,33,35,36,43] There exist contradictory views about the electronic effect of the substituents in porphyrins. It was concluded[10,11,25,59] that electron-donating substituents activate the catalyst, while Been et al.[45] claimed that they deactivate it.

In the practical application of reaction (1) in fuel cells, the MP, whose electrical conductivity is low, are deposited on various conducting carriers. Metals and carbonaceous materials (graphite, carbon black, activated charcoal) have been investigated as carriers. Metalloporphyrins deposited on carbonaceous materials show the highest activity.

The catalytic activity of MP in reaction (1) is closely related to their ability to bind oxygen reversibly. The extracoordination of O_2 to MP entails partial transfer of electron density from the central metal atom to the antibonding π orbital of oxygen. Thus the extracoordination constitutes the initial stage in the reduction of O_2. The stability of oxygen extracomplexes of MP is determined by the nature of the second, *trans*-extraligand L:



(2)

Analogous phenomena apparently obtain also in the electrochemical reduction of O_2. The functional groups on the surface of the carrier fulfill the role of the extraligand. Chemical modification of the surfaces of carbonaceous carriers therefore constitutes one of the most promising ways of increasing the activity of porphyrin catalysts of the cathodic reduction of molecular oxygen.

One of the most important applications of porphyrins is catalysis of the anodic oxidation of sulphur dioxide. Studies in this field have begun to develop during the last 5–7 years in connection with the research into the problems of atomic-hydrogen power engineering.[60-65]

There exist various projects for the manufacture of hydrogen from water. The thermoelectrochemical sulphuric acid method, in which hydrogen is obtained in two stages, is closest to practical realisation. In the first stage, sulphuric acid is subjected to catalytic thermal dissociation by the heat of a nuclear reactor:

$$2H_2SO_4\rightarrow O_2+2H_2O+2SO_2\ , \qquad (3)$$

In the second stage sulphur dioxide is electrochemically oxidised after its separation from oxygen and water. Hydrogen is evolved at the cathode and is used as the fuel:

$$SO_2+2H_2O-2e^-\rightarrow H_2SO_4+2H^+\ ; \qquad (4)$$

$$2H^++2e^-\rightarrow H_2\ . \qquad (5)$$

The normal electrode potential of reaction (4) is 0.17 V, which makes it possible, in principle, to obtain fairly cheap hydrogen. However, under real conditions, the sulphur dioxide oxidation reaction is accompanied by intense anodic polarisation. For example, the oxidation of SO_2 on carbonaceous materials proceeds at an appreciable rate only at potentials in excess of 0.8 V.[64] Reaction (4) takes place under very severe conditions: in concentrated sulphuric acid at an elevated temperature and under the conditions of appreciable anodic polarisation. Thus fuel hydrogen can be obtained in the thermoelectrochemical sulphuric acid cycle subject to the condition that highly active catalysts of the anodic oxidation of sulphur dioxide, which at the same time possess a high chemical stability, are found. Until recently, only one catalyst meeting the above requirements was known: metallic platinum in a pure state or deposited on carbonaceous carriers.[60] Investigations[61-65] have shown that metalloporphyrins deposited on carbonaceous carriers are effective catalysts of the anodic oxidation of SO_2. Fig. 1 presents the polarisation curves for the oxidation of sulphur

dioxide. Evidently, the activity of CoTPhPo(p-OCH_3)$_4$ is comparable to that of the platinum catalyst. It is significant that the activity and stability of MP-based catalysts increase sharply as a result of heat treatment at 900–1000 K.

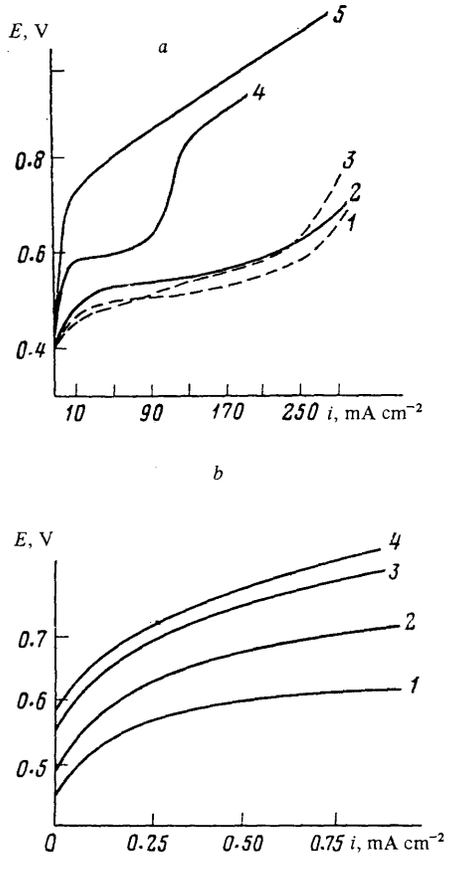


Figure 1. Polarisation curves for the oxidation of SO_2 in sulphuric acid electrolytes: *a*) on porous PG-50 graphite anodes heat-treated at 1020 K and activated by different substances [*1*) CoTPhPo(p-OCH_3)$_4$; *2*) Pt; *3*) NiTPhPo.(p-OCH_3); *4*) FeTPhPo(p-OCH_3); *5*) without catalyst[64]]; *b*) pyrographite anodes activated by different substances [*1*) CoTPhPo; *2*) CoTPhPo(p-OCH_3)$_4$; *3*) CoPhc; *4*) without catalyst[65]].

The catalytic activity of MP in the anodic oxidation of sulphur dioxide is determined by the nature of the porphyrin ligand and the metal atom. Metal-free porphyrins are inactive in the oxidation of SO_2. The copper complexes and other metalloporphyrins are almost inactive. The catalytic activity of the heat-treated CoTPhPo(p-OCH_3)$_4$ is higher than that of CoTPhPo.

It is noteworthy that the catalysis of the electrochemical oxidation of SO_2 has been investigated for heat-treated specimens. The nature of the chemical transformations of H_2P and MP in the high-temperature treatment is insufficiently clear. It is therefore impossible to formulate at present unambiguous conclusions about the effect of the structure of the porphyrin ligands on the catalytic activity of the MP in the anodic oxidation of sulphur dioxide.

Among other electrocatalytic processes occurring with participation of MP, mention may be made of the cathodic reduction of hydrogen peroxide,[11,66] carbon dioxide,[67,68] nitrous oxide,[69] and organohalogen derivatives.[70,71] The study of the cathodic reduction of hydrogen peroxide is important in connection with the development of oxygen and air electrodes, since hydrogen peroxide is an intermediate in the reduction of oxygen. It has been established that in alkaline electrolytes iron- and cobalt-phthalocyanines exhibits a high activity, which increase in the sequence CoPhc < FePhc < $(CoPhc)_i$.[11] Protohaem is an effective catalyst of the cathodic reduction of H_2O_2.[66]

Metalloporphyrins catalyse the electrochemical reduction of carbon dioxide.[67,68] Methanol, formic and oxalic acids, and other valuable compounds have been found among the reduction products. The practical application of this reaction is a matter for the remote future, since the reduction process requires a large energy expenditure.

The catalytic activities of several cyclophan dimers of cobalt-porphyrins in the cathodic reduction of nitrous oxide have been investigated.[69] The reduction proceeds with formation of molecular nitrogen. The dimers investigated are much more active than the monomeric complexes. The authors[69] suggest that the reduction proceeds via a two-electron concerted mechanism.

The catalysis of the electrochemical synthesis of organic compounds may be a promising application of MP.

Methods have been developed[70,71] for the chemical modification of the surfaces of electrodes made of carbonaceous materials by the covalent binding of MP based on H_2TPhPo.(p-NH_2)$_4$. It has been shown that the cathodic reduction potentials of a series of halogeno-derivatives of organic compounds on the modified electrodes are lower by approximately 1 V than on the unmodified electrodes.

III. CATALYSIS OF OXIDATION-REDUCTION REACTIONS

A very important practical application of porphyrins is the catalysis of the oxidation of hydrogen sulphide and mercaptans (RSH) by atmospheric oxygen. This process is used to purify the waste water from petroleum distilleries and non-ferrous metallurgical undertakings and for the removal of sulphur from petroleum products and natural gas. Mercaptans and similar compounds are oxidised to dialkyl disulphides:

$$4RSH + O_2 \rightarrow 2RSSR + 2H_2O \quad . \qquad (6)$$

At the end of the 1950s and the beginning of the 1960s it was observed[72] that the porphyrin complexes of cobalt and vanadium as well as their sulphonate and carboxylate derivatives catalyse the oxidation of mercaptan sulphur by atmospheric oxygen in aqueous alkaline solutions. This process has been used to purify petroleum distillates. Mercaptans are oxidised under the conditions of homogeneous catalysis. In the homogeneous-catalytic oxidation, the hydrocarbon distillate is treated with an aqueous solution of alkali (2–50% NaOH) containing ~0.5% of the catalyst, usually the CoPhc sulphonate. After the extraction of the mercaptans and separation of the aqueous and organic phases, the mercaptides are oxidised by blowing atmospheric oxygen into the aqueous solution. The dialkyl disulphides rising to the surface are separated and the regenerated solution of the alkali and the catalyst is again directed to the extraction of mercaptans. The heterogeneous version of the purification

process differs from that described above by the use of a catalyst adsorbed on an appropriate carrier, usually on activated charcoal.

The catalysis of the oxidation of hydrogen sulphide, mercaptans, and similar compounds has been investigated mainly on metallophthalocyanines. Metalloporphyrins have been investigated in this reaction to a lesser extent, although it is known[72,76] that derivatives of CoTPhPo are catalytically active. The catalytic activity of MPhc depends in many respects on the nature of the central atom. For example, the effectiveness of the catalysis in the oxidation of hydrogen sulphide by atmospheric oxygen increases in the following sequence:[73]

$$\underset{0.30}{\text{ZnPhcTS}} < \underset{0.46}{\text{CuPhcTS}} < \underset{2.9}{\text{V(O)PhcTS}} < \underset{17.3}{\text{NiPhcTs}} < \underset{140}{\text{FePhcTS}} < \underset{5600}{\text{CoPhcTS}}.$$

Here MPhcTS is the tetrasulphonic acid of the metallophthalocyanine. The catalytic activities, measured in moles of absorbed O_2 per mole of the catalyst per minute, are indicated under the formulae. A series close to that quoted above has been obtained[77] in the homogeneous oxidation of propanethiol:

$$\text{Cr(Cl)PhcDS} < \text{ZnPhcDS} < \text{Al(Cl)PhcDS} < \text{Sb(Cl)PhcDS} < \text{NiPhcDS} < \\ < \text{FePhcDS} < \text{CuPhcDS} < \text{CoPhcDS}.$$

Here MPhcDS is the disulphonic acid of the metallophthalocyanine. The cobalt complexes show the highest activity in aqueous solutions of alkalis.

The structure of the ligand also has a significant effect on the rate of oxidation of mercaptans and hydrogen sulphide. The following catalytic activity series has been obtained for CoPhc derivatives:[74]

$$\underset{1.67\ (2.74)}{\text{CoPhc}(SO_3Na)_4Cl_4} > \underset{1\ (1)}{\text{CoPhc}(SO_3Na)_4} > \underset{0.2\ (0.5)}{\text{CoPhc}(SO_3Na)} > \underset{0.07\ (0.23)}{\text{CoPhc}(SO_3Na)_8} > \\ > \underset{0.02\ (0.062)}{\text{CoPhc}(SO_3Na)_4(COOH)_4}.$$

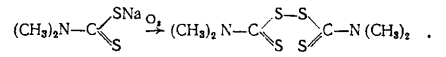
The relative rate constants for the oxidation of cysteine and hydrogen sulphide are indicated under the formulae, the values in brackets referring to the latter; the rate constants for the reactions on $CoPhc(SO_3Na)_4$ were assumed to be unity. It has been established in recent years[77–80] that the catalytic activity of the cobalt-phthalocyanine-sulphonic acids increases greatly when strongly electron-donating (OH, NH_2) and electron-accepting (NO_2) substituents are introduced into the catalyst molecule. For example, the following series has been quoted.[77]

$$\text{CoPhc}(SO_3Na)_2 < \text{CoPhc}(SO_3Na)_2(NO_2)_4 < (\text{CoPhc})_i < [\text{CoPhc}(SO_3Na)_2]_i < \\ < \text{CoPhc}(SO_3Na)_2(OH)_4 < \text{CoPhc}(SO_3Na)_2(NH_2)_4.$$

Further progress in this field is expected in three directions. Firstly, studies on the structural modification of porphyrin ligands in order to increase the catalytic activity of their metal complexes are promising. Secondly, the development of methods for the activation of heterogeneous catalysts for the oxidation of mercaptans constitutes an urgent problem. In this connection interesting patents have been taken out.[81–85] These describe procedures in which the activation of the MPhc adsorbed on activated charcoal is attained by modifying the carrier with the aid of tetraalkylammonium salts $(R_4N)^+X^-$ containing bulky organic groups R. Methods have also been developed for the immobilisation of complexes of H_2TPhPo and its derivatives[76] and MPhc[90] on the surfaces of polymeric carriers. The catalytic activity of the modified polymers[76,90] in the oxidation of alkanethiols has been demonstrated. Thirdly, the replacement of aqueous solutions by non-aqueous solutions may prove to be promising in the field of the elimination of sulphur. Thus, when dimethylformamide (DMF) was used as the solvent, it was possible to achieve the selective oxidation of hydrogen sulphide to elemental sulphur.[88] In aqueous solutions the most active catalysts of the oxidation of mercaptans and hydrogen sulphide are the cobalt complexes, whereas in organic solvents the porphyrin complexes of iron are more effective. The following catalytic activity series has been established for phthalocyaninetetrasulphonic acid derivatives:[88] Fe > Co > Zn > Cu > Al > Cr.

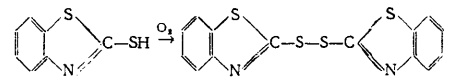
In toluene solution Fe(Cl)TPhPo catalyses the oxidation of alkanethiols by atmospheric oxygen, the addition of pyridine having an appreciable activating effect on the catalyst.[89]

The sulphonic acids of CoPhc and their derivatives with substituents in the benzene ring can be used in the synthesis of certain sulphur-containing accelerators of the vulcanisation of raw rubber. The catalytic activity of CoPhc derivatives in the oxidation of *NN*-dimethyldithiocarbamate has been demonstrated:[78,80]



(7)

The catalytic oxidation of 2-mercaptobenzothiazole has been investigated:[79]



(8)

It has been shown[78,79] that the tetrahydroxy-, tetra-amino-, and tetranitro-derivatives exhibit a high catalytic activity among phthalocyaninedisulphonic acids.

In conclusion one should note that the oxidation of hydrogen sulphide and mercaptans by atmospheric oxygen can take place in the gas phase at temperatures in the range 470–620 K.[86,87] The metal complexes of phthalocyanine catalyse this process. In the oxidation of hydrogen sulphide the catalytic activity of polymeric phthalocyanines varies in the following sequence as a function of the nature of the metal: Fe > Co > Cu > Mn.[86] The activity series of the monomeric complexes has been obtained in the oxidation reaction of isopropanethiol: Fe > Cu > Mn > Co > Zn > Ni.[87]

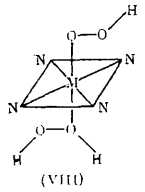
Numerous studies[91–103] have been devoted to the catalytic activity of MP in the disproportionation of hydrogen peroxide:

$$2H_2O_2 \rightarrow 2H_2O + O_2 . \qquad (9)$$

These investigations are important for the protection of plants and animals against the H_2O_2 formed as a result of their vital activity. In living organisms hydrogen peroxide is decomposed with the aid of haem-containing enzymes—catalases. The structure, properties, and the mechanism of the activity of catalases have been discussed in detail in a monograph.[104] The catalase activity of MP has also been investigated in connection with the development of oxygen cells in which H_2O_2 is formed as an intermediate in the cathodic reduction of molecular oxygen.[11]

MP exhibits a catalase activity under both homogeneous and heterogeneous conditions. The catalytic activity is determined mainly by the nature of the metal atom. It has been established[92] that, under the conditions of heterogeneous catalysis, the highest activity is shown by the osmium, ruthenium, and iron complexes of H_2Phc. The catalytic activity of MPhc with other metals is lower by at least two orders of magnitude. The catalysis of reaction (9) by metal complexes of phthalocyanine deposited on carbonaceous carriers has been investigated[100] and it has been shown that the catalytic activity depends significantly on

the nature of the carbonaceous carrier. Depending on the nature of the central metal atom in the monomeric phthalocyanines adsorbed on the carbonaceous carriers, the activity falls in the sequence: Os ≫ Fe > Ru > Pt > Rh > Pd, Ir whereas for polymeric phthalocyanines under the same conditions we have: Fe > Os > Pt, Ru > Ir, Rh, Pd; Fe > Co ≫ Ni > Cu.[100] It is important to note that, when individual heterogeneous phthalocyanine catalysts are used, the polymeric complexes have no advantages over the monomeric complexes.[94,105] On the other hand, the metallophthalocyanine polymers adsorbed on carriers are significantly more active than the monomers.[100] The fact that the activities of both homogeneous and heterogeneous catalysts change on formation of extracomplexes of metallophthalocyanines is important for the development of ideas about the mechanism of the catalytic decomposition of hydrogen peroxide. Small amounts of added extraligands such as pyridine, imidazole, and triphenylphosphine activate the catalyst[11] evidently as a result of the formation of pentacoordinated complexes. An appreciable excess of the extraligand suppresses the catalytic activity,[92] apparently as a consequence of the formation of hexacoordinated extracomplexes. The facts listed above are inconsistent with the mechanism of the catalytic decomposition of hydrogen peroxide based on the hypothesis that hexacoordinated extracomplexes of metalloporphyrin (VIII) with two hydrogen peroxide molecules are formed.[101,103]



(VIII)

Metalloporphyrins catalyse the decomposition of organic hydroperoxides ROOH.[106–113] This reaction constitutes an important link in the catalytic oxidation of hydrocarbons on MP and is therefore considered to some extent in all studies devoted to this question. In contrast to the hydrogen peroxide disproportionation reaction, which apparently takes place without the formation of free radicals, organic hydroperoxides are decomposed via a radical mechanism. The porphyrin and phthalocyanine complexes of metals such as cobalt, iron, nickel, and manganese are effective catalysts of the decomposition of the peroxides. In discussing the reaction mechanism, the authors[108–111] assume that the central metal atom is the active centre of the catalyst. On the other hand, in other studies[106,112] it has been suggested that the hydroperoxide decomposition reaction can take place on the periphery of the MPhc molecule, for example, via the formation of a hydrogen bond between the molecule and one of the peripheral nitrogen atoms. The second reaction pathway appears less likely, since it is known that the complexes of porphyrins themselves, which have no peripheral nitrogen atoms, exhibit a high catalytic activity in the reaction considered. It has been established[113] that organic peroxides form fairly stable extracomplexes with CoTPhPo. The authors[113] noted a significant role of the extracoordination in the decomposition of ROOH.

Extensive studies have been made on the utilisation of MP as the catalysts of the oxidation of hydrocarbons by atmospheric oxygen. The catalytic activities of MP and MPhc in the oxidation reactions of cumene, ethylbenzene, propene, cyclohexane, tetralin, indoles, and other compounds have been studied. A review has been published on this subject.[114] Hydrocarbons are oxidised via a radical chain mechanism and the reaction involves the intermediate formation of hydroperoxides which serve as autocatalysts of the oxidation process. Systematic investigations of the autocatalytic oxidation of cumene and certain other hydrocarbons have been described.[115–120] It has been established that below 370 K the main cumene oxidation product on the phthalocyanine complexes of copper, nickel, magnesium, and tin is the hydroperoxide, whose yield exceeds 90% under these conditions. Hydrocarbon hydroperoxides decompose catalytically on iron and cobalt complexes at the usual temperatures and on virtually all the MPhc investigated at high temperatures (420 K and above) with formation of the final oxidation products.

The catalytic activity of MPhc has been explained[115–120] by the activation of molecular oxygen as a result of extracoordination. The extracoordination of oxygen is accompanied by the transfer of electron and spin density from the central metal atom of the catalyst to oxygen:

$$\mathrm{MPhc} + \mathrm{O_2} \rightarrow \mathrm{MPhc^{\delta+} \ldots O^{\delta-}_2} \quad . \qquad (10)$$

The coordinated oxygen has radical properties and is therefore capable of abstracting a hydrogen atom from the hydrocarbon molecule:

$$\mathrm{RH} + \mathrm{MPhc^{\delta+} \ldots O^{\delta-}_2} \rightarrow \mathrm{R^{\cdot}} + \mathrm{HO^{\cdot}_2} + \mathrm{MPhc}; \qquad (11)$$

$$\mathrm{R^{\cdot}} + \mathrm{O_2} \rightarrow \mathrm{ROO^{\cdot}} \quad ; \qquad (12)$$

$$\mathrm{ROO^{\cdot}} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R^{\cdot}} \; ; \qquad (13)$$

$$\mathrm{ROO^{\cdot}} \rightarrow \text{other oxidation products.} \qquad (14)$$

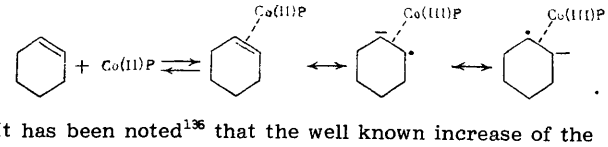
At high temperatures the oxidation of hydrocarbons proceeds autocatalytically. The catalytic decomposition products of the hydroperoxides serve as the source of free radicals:

$$\mathrm{MPhc} + \mathrm{ROOH} \rightarrow \mathrm{MPhc^{+}} + \mathrm{RO^{\cdot}} + \mathrm{OH^{-}}; \qquad (15)$$

$$\mathrm{MPhc^{+}} + \mathrm{ROOH} \rightarrow \mathrm{MPhc} + \mathrm{ROO^{\cdot}} + \mathrm{H^{+}}; \qquad (16)$$

$$\mathrm{RO^{\cdot}} + \mathrm{RH} \rightarrow \mathrm{ROH} + \mathrm{R^{\cdot}} \; . \qquad (17)$$

Next the oxidation reaction proceeds in accordance with Eqns.(12)–(14). It is noteworthy that a careful study of the kinetics of the oxidation of cumene containing minimal amounts of hydroperoxides has led to the conclusion[134] that the Cu, Zn, Ni, V, and Mg complexes of tetra-t-butylphthalocyanine at 330–350 K catalyse the oxidation of cumene via the decomposition of cumenyl hydroperoxide and not via the activation of oxygen. The activation of oxygen has also been ruled out in studies[122,124,125] of the catalytic oxidation of cyclohexene and squalene on iron(II), cobalt(II), and cobalt(III) complexes of protoporphyrin and octaethylporphin. It has been suggested[122,123,125] that the catalytic activity of the MP is due to the activation of the double bond via the transfer of spin density from the central metal atom to the double bond of the extracoordinated alkene, for example:

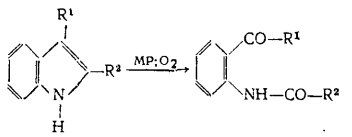


(18)

It has been noted[136] that the well known increase of the selectivity of the oxidation of alkenes in the presence of MPhc with a simultaneous increase of the induction period

of the reaction indicates unambiguously that the mechanism of the catalytic activity consists in the catalysis of the interaction of hydroperoxides or hydroperoxy-radicals with the olefin.

As a consequence of the radical mechanism, the autoxidation reactions of hydrocarbons have a low selectivity. For example, the liquid-phase oxidation of propene on the phthalocyanine complexes of Mo, V, Sn, and Ru (individual and adsorbed on various carriers) involves the formation, together with the target product (epoxypropane), also of acetaldehyde, isopropyl alcohol, acetone, methyl formate, and other products.[136] The yield of epoxypropane does not exceed 45%. In the oxidation of cyclohexene, the main products are the corresponding epoxy-derivative, cyclohexenol, and cyclohexenone. In some cases the oxidation proceeds with a fairly high selectivity. Thus the oxidation of substituted indoles on the cobalt(II), cobalt(III), and manganese(III) complexes of H_2TPhPo and deuterioporphyrin (H_2DPo) affords a satisfactory yield of the corresponding ketoamides:[126,127]

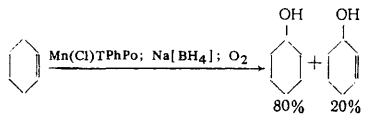


(19)

The catalytic activity series has been established in the oxidation reaction of skatole: CoDPo > CoTPhPo ≫ CuTPhPo ≫ NiTPhPo ≅ 0.[126]

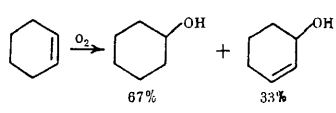
The practical employment of MP for the oxidation of hydrocarbons is complicated by the rapid poisoning of the catalyst as a result of the irreversible oxidation of the MP by alkylperoxy-radicals. Studies where a significant stabilisation of porphyrin catalysts after approximately equimolar amounts (relative to the MP) of copper acetylacetonate had been added are of interest in this respect.[122,124]

An interesting reaction involving the selective oxidation of alkenes to alcohols on treatment with molecular oxygen, tetrahydroborate, and the Mn(Cl)TPhPo catalyst has been discovered recently.[128,130,131,133] The oxidation of cyclohexene has been studied:[133]

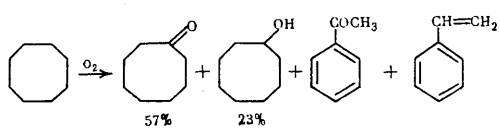


(20)

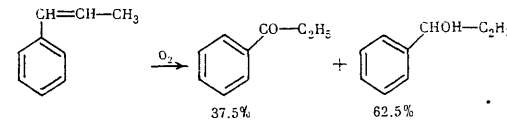
The mechanism of this reaction differs from the usual radical autoxidation, since the reaction has no induction period and is not inhibited by 2,6-di-t-butylphenol. It is noteworthy that the oxidation process proceeds under very mild conditions: at room temperature and normal pressure, and is much faster than radical autoxidation. It has been concluded[133] that the main reaction pathway involves the formation of epoxycyclohexane, which is then reduced by the excess tetrahydroborate to cyclohexanol. The study of the oxidation of alkenes in the Mn(Cl)TPhPo–$[Bu_4N]^+[BH_4]^-$–O_2 ternary system[130] yielded the following results:



(21)



(22)



(23)

It was concluded that under these conditions the alkenes are oxidised selectively with formation of ketones and the latter are reduced by the excess tetrahydroborate to alcohols. In their study of the oxidation of alkenes of different structure by atmospheric oxygen in the presence of Mn(Cl)TPhPo and $NaBH_4$, Enikolopov and co-workers[128,131] established that the rate of reaction increases as the alkyl substituents at the double bond accumulate. The oxidation proceeds selectively with respect to the most substituted hydrogen atom. The data obtained for the oxidation of steroids demonstrate unambiguously that neither ketones nor epoxides can be intermediates in the oxidation reaction. The authors[128,131] suggest that the oxidation intermediate is a complex of the olefin, the activated oxygen, and Mn(II).TPhPo. Depending on the nature of the olefin, the complex can disproportionate to a ketone or can be reduced by the tetrahydroborate to the alcohol.

The metal complexes catalyse the autoxidation of alcohols with phenols,[98,99,135,139–151] aldehydes, and carboxylic acids.[99,129,137,148,149,153–157] The reaction has a radical chain mechanism. The aldehyde oxidation products are peracids or carboxylic acids. Phenols are oxidised to the corresponding quinones and other products. Carboxylic acids undergo oxidative decarboxylation. Studies in this field have been surveyed in monographs.[11,112]

The method of synthesis of aromatic aldehydes RCHO from a wide variety of compounds of the type RCH_2X (X = OH, OR, NH_2, etc.), described by Tabushi and Koga,[145] is of great interest to organic chemists concerned with synthesis. Manganese(IV) complexes of haematoporphyrin (H_2HaePo) or H_2TPhPo, obtained directly in the reaction system by the oxidation of manganese(III) complexes with sodium hypochlorite, are used as the oxidants. The reaction can be carried out also in a catalytic version. With the aid of Mn(IV)P, the oxidative cleavage of the ether linkage, for example in benzyl methyl ether, goes to completion at room temperature in 1 min, after which the oxidation proceeds selectively to give benzaldehyde.

A method of synthesis of MPhc, dispersed unimolecularly in zeolite matrices, has been developed.[151] With the aid of catalysts of this type based on CuPhc, CoPhc, and NiPhc, it is possible to carry out a very interesting reaction involving the oxidation of carbon monoxide by atmospheric oxygen. It is significant that the oxidation proceeds very rapidly even at 195 K.[158] The importance of this process for the protection of the environment is evident. However, the proposed catalysts[158] are very rapidly poisoned, apparently by carbon dioxide or carbonate ions.

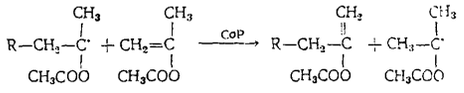
The catalysis of the electrochemical oxidation of carbon monoxide on metal complexes of octaethylporphin (H_2OEPo), H_2TPhPo, H_2TBPo, and H_2Phc has been studied[159] and it has been established that IrTPhPo and RhTPhPo are active in acid and alkaline media. The iron and cobalt complexes exhibit an appreciable activity in alkaline solutions. It has been noted[159] that the catalytic activities of the iron complexes increase in the sequence FeTBPo < FeOEPo < FeTPhPo.

MP exhibit a catalytic activity not only in oxidation reactions but also in the reduction and photochemical reduction of organic compounds. The catalytic activity of CoTPhPo.$(p\text{-}SO_3H)_4$ in the hydrogenation of acetylene[160] and of the MPhc radical anions in the hydrogenation of alkenes[161–163] has been demonstrated. The high-temperature (373–573 K) hydrogenation–dehydrogenation reactions of alcohols and aldehydes in the presence of MPhc have been investigated.[141]

A number of studies of the catalytic oxidation–reduction reactions of nitrogen-containing compounds have been described in the literature. The report[160] of the catalytic activity of $CoTPhPo(SO_3H)_4$ in the reduction of molecular nitrogen by sodium tetrahydroborate is the most interesting in this field. The catalytic activity of MP in the oxidation of hydrazine and hydroxylamine by atmospheric oxygen,[164,165] in the reduction of nitric oxide by hydrogen,[142,166] and in the photochemical reduction of nitro-compounds[167] has been demonstrated. The catalytic activity of MPhc in the electrochemical oxidation of hydrazine has also been established.[168,169] Depending on the nature of the metal, the catalytic activity increases in the sequence NiPhc ≅ CuPhc < CoPhc < FePhc.

IV. CATALYSTS OF ISOMERISATION AND POLYMERISATION REACTIONS

Studies have shown[170–180] that cobalt-porphyrins are unique regulators of the degree of polymerisation of acrylates and it has been established that CoP catalyses the reaction involving chain transfer to the monomer:

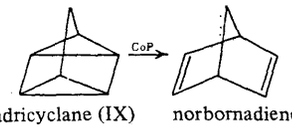


(24)

The degree of polymerisation is regulated by the simple alteration of the concentration of the CoP introduced into the initial monomer. The efficiency of the catalyst in the reaction involving chain transfer to the monomer can be inferred from the following example:[176] the polymerisation of methyl methacrylate in bulk at 233 K and at an initiator (azobisisobutyronitrile) concentration of 2×10^{-2} M without added regulator yielded a polymer with an average degree of polymerisation of 4×10^3. Under the same conditions but with addition of 6×10^{-4} M CoHaeP to the initial mixture, the average degree of polymerisation fell to 8.1.

The catalytic activity in the chain transfer to the monomer is shown only by the cobalt complexes of the porphyrins proper. The Ni, Cu, Zn, Cr, Mn, Pd, and TiO complexes as well as MPhc inhibit the polymerisation of methyl methacrylate.[177] The nature of the side groups in the porphyrins is relatively insignificant. The phenomenon described is observed in the polymerisation of acrylates and styrene. Catalytic chain transfer to the monomer with the aid of MP has not been observed for other monomers. It has been established[180] that the mechanism of the chain transfer to the monomer involves the transfer of a hydrogen atom from the methyl group of the growing chain to the cobalt atom of the catalyst with its subsequent transfer to the monomer. Catalysts grafted to a heterogeneous carrier have been synthesised and investigated in order to achieve the practical realisation of the method described above for the regulation of the degree of polymerisation of acrylates.[178]

Certain MP are able to catalyse the dark and photochemical isomerisation of unsaturated compounds. For example, the catalytic activity of CoP in the isomerisation of quadricyclane to norbornadiene has been established:[181–183]



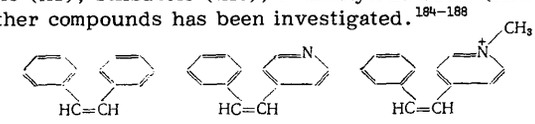
quadricyclane (IX) norbornadiene (X)

(25)

In conformity with the Woodward–Hoffman rules, this reaction is symmetry-prohibited and therefore proceeds at a very low rate. The complexes of H_2TPhPo with Co(II) and Co(III) increase sharply the rate of isomerisation probably via the extracoordination of quadricyclane. The catalytic activity of Co(III)TPhPo is greater by two orders of magnitude than that of Co(II)TPhPo. The reaction rate depends strongly on the nature of the organic solvent.

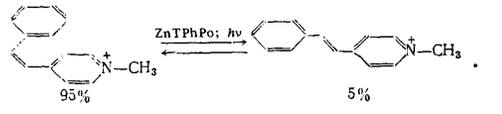
V. CATALYSIS OF PHOTOCHEMICAL AND PHOTOELECTROCHEMICAL REACTIONS

The metalloporphyrin-sensitised photoisomerisation of stilbene (XI), stilbazole (XII), *N*-methylstilbazole (XIII), and other compounds has been investigated.[184–188]



cis-stilbene (X) *cis*-stilbazole (XII) *cis*-*N*-methyl-4(β-styryl)-pyridinium (XIII)

It has been shown that under photostationary conditions the N-methyl-4-(β-styryl)pyridinium salt forms an equilibrium mixture of *cis*- and *trans*-isomers enriched in the *cis*-isomer:



95% 5%

(26)

It must be emphasised that, in the absence of metalloporphyrins [ZnTPhPo or Sn(Cl)TPhPo], the *cis*- and *trans*-isomers of *N*-methyl-4-(β-styryl)-pyridinium are completely stable in the dark. The authors[188] concluded that the isomerisation proceeds via electron transfer from the photoexcited MTPhPo molecule to the substrate.

The photoisomerisation of stilbene, stilbazole, and related compounds is observed in the presence of zinc and magnesium[185,187] as well as platinum and palladium[184] complexes of the porphyrins. Under photostationary conditions, the *trans*-isomers of the compounds accumulate. Thus, in the isomerisation of stilbene the content of the *trans*-isomer can reach 85%; stilbazole is converted under photostationary conditions into the *trans*-isomer in 95–99% yield. It was of interest that, in the presence of the zinc complex of aetioporphyrin (ZnAePo), stilbene undergoes *cis–trans* isomerisation with a quantum yield of 0.01, while the analogous reactions of stilbazole and its derivatives have a quantum yield up to 6.6. This means that the absorption of one quantum of light by the ZnAePo molecule leads to the conversion on average of 6.6 *cis*-stilbazole molecules into *trans*-stilbazole. In the discussion of the reaction mechanism, the authors[185] suggested the formation of an extracomplex of stilbazole with MP in an excited triplet state.

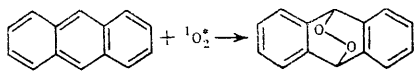
The unique photophysical and photochemical properties of porphyrins have been used in the development of new light-sensitive materials for three-dimensional phase holography. The proposed[189,190] light-sensitive materials consist of a polymer matrix in which substituted anthracene and a porphyrin sensitiser, for example, mesoporphyrin (H_2MPo) are dispersed. Before recording the hologram, the polymer matrix is saturated with oxygen at a pressure of 80–140 atm. Next, the holographic image is recorded in the usual way. On irradiation with light, porphyrin passes to an excited state, initially singlet and then triplet. The porphyrin in the excited triplet state undergoes a bimolecular reaction with molecular oxygen and leads to the transition of the latter from the ground triplet state to the excited singlet state:

$$H_2P + h\nu \rightarrow {}^1H_2P^* \; ; \qquad (27)$$

$$^1H_2P^* \rightarrow {}^3H_2P^* \; ; \qquad (28)$$

$$^3H_2P^* + {}^3O_2 \rightarrow H_2P + {}^1O_2^* . \quad (29)$$

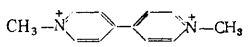
Singlet oxygen is a powerful oxidant which oxidises anthracene, the reaction being controlled by the rate of diffusion:



(30)

The endoperoxide formed has a refractive index which differs from the initial anthracene. Thus, when a hologram is recorded, regions with different refractive indices are generated in the polymer matrix. The image is then fixed. For this purpose, the hologram is kept in the dark at normal pressure in order to remove the oxygen dissolved in the matrix. In order to reproduce the holographic image, visible light is passed through the hologram. The interference pattern, giving rise to the effect of a three-dimensional image, arises as a result of the different phase shifts in the electromagnetic vibrations of the visible light which has passed through regions with different refractive indices.

One of the possible practical applications of porphyrins in the future may be catalysis of the photochemical decomposition of water in order to utilise solar energy. Comparatively recently, Shilov[191] showed that irradiation of a system comprising ethylenediaminetetra-acetic acid, methylviologen (MV^{2+}) (XIV) (an acridine dye), and a colloidal solution of platinum results in the evolution of hydrogen:



methylviologen (XIV) .

The acridine dyes used in the first studies in order to sensitise the photochemical reduction of water utilise only a limited proportion of the sun's rays. Porphyrins, whose absorption spectra cover an appreciable proportion of the spectrum of the sunlight reaching the surface of the Earth, are of great interest in this respect. For example, H_2TPhPo can absorb 46% of the energy of the sun's rays, while ZnTPhPo and PdTPhPo can absorb 40 and 25% respectively.[192] One must bear in mind that many H_2P and MP exhibit a very high photochemical stability.

Studies have shown that the metal complexes of phthalocyanine and its derivatives are relatively ineffective sensitisers of the photochemical decomposition of water.[193–195] This can be accounted for by the low energy level of the triplet excited states of MPhc. The porphyrin complexes, particularly those which have positively charged functional groups, for example, the complexes of tetra(*N*-methylpyridyl)-porphin ($MTMePyPo^{4+}$) are more promising. The quantum yield in the evolution of hydrogen on reduction of water in the $ZnTMePyPo^{4+}$/EDTA/MV^{2+}/Pt system reaches 0.3.[196–200]

The sequence of reactions in the photochemical reduction of water can be represented as follows:

$$MP \xrightarrow{h\nu} MP^* ; \quad (31)$$

$$MP^* + MV^{2+} \rightarrow MP^+ + MV^+ ; \quad (32)$$

$$MV^+ + H_2O \xrightarrow{Pt} MV^{2+} + {}^1/_2H_2 + OH^- ; \quad (33)$$

$$MP^+ + EDTA \rightarrow MP + EDTA^+ . \quad (34)$$

The first stage involves the photoexcitation of the metalloporphyrin, which then reduces methylviologen. When colloidal platinum is used as the cocatalyst, the accumulation in solution of the reduced form of methylviologen is a sufficient condition for the evolution of hydrogen from water. Without methylviologen, the quantum yield in the photochemical reduction of water on a MP is 10^{-4}–10^{-3}.[198,200,201]

Methylviologen is an effective quenching agent for the singlet and triplet states of porphyrins. However, one must bear in mind that MV^+ can recombine with the oxidised form of the sensitiser:

$$MV^+ + MP^+ \rightarrow MV^{2+} + MP . \quad (35)$$

Thus the yield of hydrogen in the reduction of water depends on the ratio of the rates of the competing reactions (33) and (35).

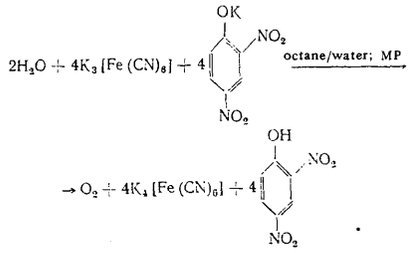
The rate of recombination can be diminished, firstly, by employing a sensitiser in the triplet excited state as the reductant in reaction (32). The recombination reaction is then spin-prohibited, since the reverse electron transfer from MV^+ to MP^+ requires a change in the spin state of the system:

$$^3(MP^+ \ldots MV^+) \rightarrow {}^1MP + {}^1MV^{2+} .$$

Secondly, in order to suppress the recombination process, it is useful to employ positively charged sensitisers, for example, complexes of tetra-(*N*-methylpyridyl)porphin. In this case the electrostatic repulsion of the reactants $MTMePyPo^{5+}$ and MV^+ prevents their recombination. The rate of reduction of methylviologen [reaction (32)] diminishes at the same time. However, experiment has shown that the introduction of positively charged functional groups into the molecule of the porphyrin sensitiser sharply increases the yield of hydrogen.[196–200] When negatively charged sensitisers are used, for example, the complexes $H_2TPhPo(SO_3^-)_4$, the quantum yield in the photogeneration of hydrogen does not exceed several tenths per cent.[199] Thirdly, in order to eliminate reaction (35) and the regeneration of the initial form of the sensitiser, the so-called sacrificial donors (EDTA, cysteine, amines) are used. The role of these compounds is to reduce the oxidised sensitiser [reaction (34)]. The oxidised donor, for example $EDTA^+$, does not react with MV^+ and is irreversibly consumed in the reduction of water. Hydroquinone, which can be, in principle, regenerated in the photochemical oxidation of water to molecular oxygen, has been proposed as a reductant of this kind.[202]

Mainly zinc complexes have been used in the study of the porphyrin sensitisers of the photochemical reduction of water. However, it is known that magnesium,[202,203] tin,[204] ruthenium,[205] and metal-free haematoporphyrin[337] exhibit a high activity in this process. It has been shown[202,203,206–209] that, together with water-soluble sensitisers, complexes of neutral porphyrins dispersed in micelles can be used in the reduction of water. A review of studies on the photodissociation of water sensitised by porphyrins has been published.[192]

The systems described can be used, in principle, to obtain hydrogen subject to the obligatory condition that the process can be combined with the photochemical oxidation of water, i.e. the reaction involving the irreversible consumption of the sacrificial donor is eliminated. Studies[213,214] where it has been shown that metalloporphyrins, for example, chlorophyll, can sensitise the photochemical oxidation of water to oxygen in two-phase systems of the type of water–octane, are interesting in this respect. For the reaction to be carried out, it is essential that oxidants [potassium hexacyanoferrate(III), etc.] and weak proton acceptors, for example, potassium 2,4-dinitrophenoxide, are present:



(36)

The oxidation of water in these systems involves the photoexcitation of the MP with its subsequent oxidation by a weak oxidant:

$$MP^{*}+[Fe(CN)_6]^{3-}\rightarrow MP^{+}+[Fe(CN)_6]^{4-}. \quad (37)$$

The products of reaction (37) do not recombine, because the reactants are in different phases: MP is in octane while the reduced form of the oxidant is in water. Next, water is oxidised by the metalloporphyrin radical-cation. Together with chlorophyll, the iron complex of coproporphyrin exhibits a fairly high photocatalytic activity in this reaction. This is extremely remarkable, because FeP do not have long-lived triplet states.

The photocatalytic systems described above suffer from two significant disadvantages. Firstly, they are complex and, secondly, the water photochemical oxidation and reduction reactions cannot as yet be combined in a single process. The comparatively simple photoelectrochemical method for the decomposition of water into hydrogen and oxygen is attractive in this respect.[216,221]

It has been established[216,218-221] that, when the electrochemical cell $Pt|(MgChl\alpha.2H_2O)_n|H_2O|Pt$ is irradiated with red light, a photocurrent flows through it and water is cleaved into hydrogen and oxygen. The electrophotodissociation of water can be described as follows:

$$Pt|(MgChl\alpha.2H_2O)_n(\text{photocathode}):\ 2H_2O + 2e^- \rightarrow H_2 + 2OH^-; \quad (38)$$

$$Pt(\text{photoanode}):\ 2H_2O \rightarrow 4H^+ + O_2\ 4e^-. \quad (39)$$

The photoelectrochemical reduction of water apparently takes place on chlorophyll *a* dihydrate dimers $[MgChl\alpha.2H_2O]_2$. The quantum yield of hydrogen on irradiation of the above cell with light at a wavelength of 735 nm is 0.88%.[221] A photoelectrolytic apparatus based on a platinised polycrystalline chlorophyll *a* dihydrate deposited on a platinised metallic support has been described in a patent.[219] This apparatus makes it possible to photodissociate water with a quantum yield up to 0.2. It has been shown[217] that polycrystalline chlorophyll *a* dihydrate can be used as the photoanode in the electrochemical cell. However, the activity of such anodes is greatly inferior to that of the platinum anode.

The photoelectrochemical oxidation-reduction reactions catalysed by H_2P and MP have been widely investigated in order to devise converters of solar energy into electrical energy.[222-236] The pigmented electrode serves as the photocathode in almost all photoelectrochemical cells of the type electrode |MP (or H_2P)|electrolyte|electrode. The charge carriers are generated in most cases at the MP|electrolyte interface and in some cases at the electrode|MP interface. The mechanism of the generation of the photocurrent as a rule involves the formation of an excited triplet state of the sensitiser, the migration of the triplet exciton state to the MP|electrolyte interface, the generation of charges on this interface as a result of electron transfer from the photoexcited sensitiser to H^+, O_2, or to an oxidant specially introduced into the electrolyte, and finally the migration of the charges to the current measuring devices. In agreement with this mechanism, the photocurrent flowing through photoelectrochemical cells increases sharply when oxidants such as methylviologen,[224,233] potassium hexacyanoferrate-(III),[222] etc. are introduced into the electrolyte. An appreciable increase of the photocurrent quantum yield is observed when the thickness of the pigment layer is decreased to approximately 3 nm.[222,223,233] Ilatovskii[223] states that, for a greater thickness of the porphyrin sensitiser layer, the exciton states formed in the bulk of the film cannot reach the MP|electrolyte interface. Furthermore, with increase of the thickness of the pigmented film, its ohmic resistance and the probability of the recombination of the charge carriers also increase.

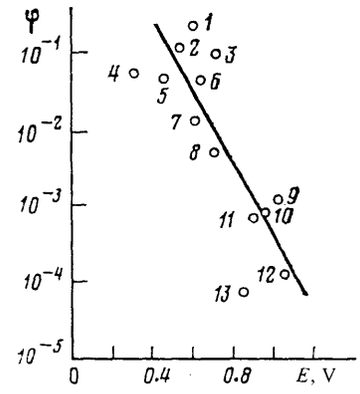


Figure 2. Dependence of the photocurrent quantum yields ϕ of the cells $Al|MP|[Fe(CN)_6]^{3-}, [Fe(CN)_6]^{4-}|Pt$ on the first oxidation potentials of the porphyrins:[236] *1*) MgPo; *2*) MgTPhPo; *3*) ZnPo; *4*) ZnTPhIBCh; *5*) CdTPhPo; *6*) CdTPhPo; *7*) ZnTPhCh; *8*) ZnTPhPo; *9*) CdTPhPo; *10*) H_2TPhPo; *11*) CuTPhPo; *12*) CoTPhPo; *13*) PtTPhPo (H_2TPhIBCh = tetraphenylisobacteriochlorin; H_2TPhCh = tetraphenylchlorin).

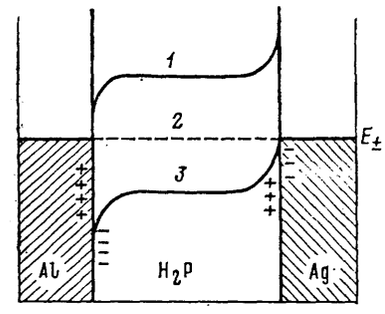


Figure 3. Schematic illustration of the energy levels in the cell $Al|H_2P|Ag$:[266] *1*) conductivity level; *2*) Fermi level; *3*) valence level.

The photocurrent quantum yield depends significantly on the nature of the porphyrin sensitiser and in the first place on its reducing properties. The photoelectrochemical

properties of 30 porphyrins and metalloporphyrins have been investigated[236] with the aid of the cell Al|porphyrin|[(Fe.$(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$|Pt and it has been established (Fig.2) that the photocurrent quantum yield increases with decrease of the oxidation potential of the porphyrin sensitiser. The most active sensitisers MgPo, ZnTPhPo, and ZnPo ensure a photocurrent quantum yield up to 0.2. Certain MPhc exhibit a high electrochemical activity. Thin-film converters of solar energy, ensuring a photocurrent quantum yield up to 0.15 and an energy efficiency up to 2% have been developed on their basis.[222,223] The photoelectrochemical activity of complexes of tetra(*N*-methylpyridyl)porphin,[225] tetra(*N*-stearylpyridyl)porphin,[226,227] chlorophyll,[216–221,232] and other porphyrins[236] has also been demonstrated.

VI. SEMICONDUCTORS AND PHOTOCONDUCTORS

Porphyrins possess semiconducting properties and their electrical and photoelectrical properties have been investigated vigorously.[222–224,236,240–292] They are known to possess intrinsic hole conductivity.[212,225,256,279,283] Sandwich cells with two different electrodes, for example Al|H_2P(MP)|Ag, have voltage-current characteristics typical for barrier diodes. The blocking layer in the cells is formed as a consequence of the flow of electrons from an aluminium or another electrode with a low electron work function to the porphyrin. This results in the formation of a zone depleted in charge carriers. Its size is 1.5–3 nm depending on the nature of the H_2P. At the H_2P|Ag interface, electrons pass from the porphyrin cell to the electrode (Fig.3). The resulting distortion in the valence and conductivity levels ensures the migration of the charge carriers photogenerated in the porphyrin film to the electrodes: positive ones to the silver electrode and negative ones to the aluminium electrode.

Porphyrins have a molecular crystal lattice and a low intermolecular interaction energy. The absorption of light results in their intramolecular excitation. The high-lying conductivity band is not then populated. The generation of charge carriers is achieved in the interaction of excited H_2P molecules with acceptor centres, which may consist of molecules of oxygen,[222,223,243,283] iodine,[283] or other doping additives. In the sandwich cells Al|H_2P|M (M = Ag, Pt, etc) charges are generated in the acceptor traps on the Al|H_2P interface, or more precisely on Al|Al_2O_3|H_2P.[225,256,285] In agreement with the hole character of the conductivity of H_2P and MP, the efficiency of the operation of the photocells is related directly to the ability of the porphyrins to be converted into radical-cations. Indeed, the photocurrent quantum yield increases with decrease of the oxidation potentials of the porphyrins.[225–283]

An evident way of increasing the concentration of charge carriers in semiconductors, namely by the introduction of doping admixtures, has only limited applicability to H_2P and MP. If the amount of admixture exceeds a specific level (~1%), the quality of the pigment films and hence the quality of the operation of the photocells are sharply impaired. A possible solution of this problem consists in the employment of MP with highly charged cations which contain donor or acceptor groups as the extraligands. For example, it has been established[241] that Al(Cl)Phc and In(Cl)Phc have specific conductances higher by 3–5 orders of magnitude than MgPhc and CuPhc, while their photosensitivity is higher by 2 orders of magnitude.

The specific conductances of H_2P and MP are usually in the range from 10^{-15} to 10^{-3} S m^{-1}. Studies[288–292] where it has been shown that, on application of a high pressure (h.p.) and on shear deformation (s.d.), the specific conductances of certain H_2P increase by 5–6 orders of magnitude are therefore of great interest. For example, the specific conductance of H_2TPhCo increases from 10^{-5} to 10–100 S m^{-1} following the application of a pressure of 2–4 GPa and of s.d., while the activation energy for electrical conduction diminishes by a factor of ten.[288] The increase of electrical conductivity and the joint influence of high pressure and shear deformation depend on the nature of the side substituents in porphyrins,[289] on the nature of the central metal atom,[289,290] and on the size and structure of the conjugated system of π-bonds in polymeric phthalocyanines.[292] The increase of electrical conductivity following the application of high pressure and shear deformation has been explained[288–292] by the decrease of the potential barrier to the intermolecular jump of the charge carriers as a result of the mutual approach in space of neighbouring molecules in porphyrin crystals and the increase of the intermolecular overlap of their π orbitals.

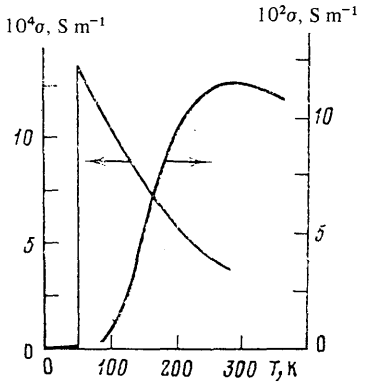


Figure 4. Temperature variation of the specific conductances of organic metals based on different porphyrin derivatives: *1*) NiOMTBPo$(I_3^-)_{0.35}$;[272] *2*) NiPhc$(I_3^-)_{0.33}$.[273]

Metal complexes of phthalocyanine and octamethyltetrabenzoporphin (MOMTBP) have been used[268–274,293] to synthesise organic metals of a new type. Compared with the initial MP, the organic metals obtained on their basis have specific conductances higher by 11–13 orders of magnitude. The increase of conductivity is achieved by treating crystalline MP with iodine vapour or solutions. Iodine plays the role of the oxidant and is converted into the anions I_3^-, which are arranged in chains within long narrow channels in the crystal lattice formed via stacks of parallel MP molecules. A fundamental feature of such crystals is the fractional positive charge per MP molecule. As a result, neutral and positively charged MP species alternate in the stack. There is also a possibility of structures with alternation of porphyrin mono- and di-cations. It is of interest that the electrical properties of $MP_n^{m+}(I_3^-)_m$ crystals depend very little on the average fractional positive charge per MP species. The organic metals based on MPhc exhibit metallic electrical conductivity, i.e. their conductivity diminishes with increase of temperature. The temperature dependence of the electrical conductivity of partly oxidised NiOMTBP is represented by a curve with a maximum at 260–330 K (Fig.4).

In conclusion, one should note that materials with a high electrical conductivity can apparently be obtained not only from partly oxidised but also from partly reduced MP.[294]

VII. ELECTROCHROMIC MATERIALS

By splitting off or combining with one or several electrons, H_2P readily form radical-ion species.[295] The porphyrin radical-ions are very stable and can be generated by chemical or electrochemical methods. It is significant that different radical-ion species have different spectroscopic characteristics. The electrochemical method for the generation of porphyrin radical-ions deposited on optically transparent electrodes, for example, SnO_2 or In_2O_3 electrodes, is of special interest from the practical point of view. The colour of such electrodes is determined by the applied electrical potential and this can be used in a wide variety of electrochromic devices. The phthalocyanine complexes of Co, Mo, Fe, Mn, Zn, and the lanthanides possess electrochromic properties.[296–299]

Compared with liquid crystals, which are used widely as electrochromic materials, MP have the advantage that they can repeatedly change their colour depending on the sign and magnitude of the polarising potential. The diphthalocyanine complexes of the lanthanides are of particular interest in this respect. For example, as the electrical potential varies, the diphthalocyanine complex of lutetium changes colour five times;[299] its colour can be red, green, blue, and violet. The electrochromic materials based on MP are very durable in use, permitting not less than 100000 colour change cycles.[298]

VIII. PIGMENTS, DYES, AND FOOD DYES

Tens of thousands of tonnes of MPhc are produced annually as pigments and dyes in industrially developed countries.[268] The interest in these dyes is due to their high photostability, chemical and migrational stability, and the purity of colour tones. Hundreds of publications, mainly patents, have been devoted to phthalocyanine pigments and dyes. Porphyrins proper can also be used as technical dyes. They have all the advantages of the phthalocyanine dyes and have a very wide colour range. However, the practical use of porphyrin pigments and dyes is possible only when their cost is sharply reduced.

Certain readily available porphyrins have found applications as food dyes.[300,301] Thus chlorophylls (a + b), their copper analogues, and the copper complexes of phaeophorbide (a + b) are permitted food colourants in almost all the major foreign countries. As early as 1926, about 20 tonnes of chlorophyll were processed in the U.S.A. for the colouring of food products.[301]

It has been suggested[300] that the cobalt complex of the disodium salt of haematoporphyrin be used to impart a red colour to sausage products. Sodium nitrate is used at present for this purpose. The addition of $(3–5) \times 10^{-3}$ wt.% of the cobalt complex makes it possible to reduce greatly the amount of nitrite introduced into the sausage meat and to eliminate the appearance of residual nitrite and nitrosamines.

IX. ENRICHMENT OF RADIOISOTOPES

Phthalocyanines are used to synthesise and enrich radioisotopes by the Szilard–Chalmers method,[302–325] which consists of bombarding MPhc specimens with thermal neutrons. Isotopes with higher mass numbers are formed as a result of neutron capture by the nuclei of the coordinated metals. The nuclear reaction is terminated by the emission of a γ-quantum. Recoil results in the decomposition of the MPhc and the liberated isotope forms a new chemical compound. For the successful application of the Szilard–Chalmers method, the initial coordination compound must have high chemical, thermal, and radiation stabilities. Metalloporphyrins satisfy these requirements. Phthalocyanine complexes have been used to obtain Cu, Zn,[99] Co,[303,306] Ro,[305] and lanthanide[315] isotopes. The yields of radioisotopes obtained by the Szilard–Chalmers method using MPhc are as a rule high. For example the yields of 13 lanthanide isotopes were between 60 and 90%.[315] The enrichment factors were in the range $10^2–10^3$.[99,315]

Table 2. Porphyrins as analytical reagents

Element to be determined	Analytical reagent	Analytical method	c, M	Refs.
Cu(II)	$H_2TPhPo(SO_3H)_3$	SPPM	$1\cdot10^{-7}–1\cdot10^{-6}$	[317, 318, 342]
	$H_2TPhPo(SO_3H)_4$	F	$10^{-7}–10^{-6}$	[319]
	"	E		[326]
	H_2TPhPo	SPPM	$7\cdot10^{-8}–2,5\cdot10^{-6}$	[323]
	$MTPhPo(COOH)_4$	"	$10^{-7}–10^{-6}$	[328]
	$MTPhPo(SO_3H)_4$ (M = Cd, Hg, Pb*)			
	H_2OAePo	E	$5\cdot10^{-5}$	[341]
	$H_2T(3\text{-MePy})Po$	SPPM	$10^{-7}–10^{-6}$	[336, 347]
	$H_2T(4\text{-MePy})Po$	"	$10^{-7}–10^{-6}$	[318, 321, 324]
	$H_2T(4\text{-MePy})Po$	SPPM-CIER	$10^{-8}–10^{-7}$	[335, 344]
	"	AD-SPPM	10^{-7}	[327]
	"	E	10^{-7}	[326, 346]
	$PbT(4\text{-MePy})Po$	TLS	10^{-6}	[346]
	Haemoglobin	P		[343]
Zn(II)	H_2TPhPo	SPPM	$6\cdot10^{-6}–3\cdot10^{-5}$	[316]
	$H_2T(3\text{-MePy})Po$	"	$1.3\cdot10^{-7}–2.5\cdot10^{-6}$	[332]
	$H_2TPhPo(4\text{-NMe}_3)_4$	P		[339]
Cd(II)	$H_2TPhPo(SO_3H)_4$	SPPM	$10^{-7}–10^{-6}$	[325]
	$H_2TPhPo(COOH)_4$			
	$H_2T(3\text{-MePy})Po$ and	SPPM and	10^{-6}	[330]
	$H_2T(4\text{-MePy})Po$	AD-SPPM	10^{-7}	
	$H_2TPhPo(SO_3H)_4$	C	10^{-9}	[345]
Hg(II)	$H_2TPhPo(SO_3H)_4$	C	$10^{-9}–10^{-8}$	[334]
Mn(II)	$CdTPhPo(COOH)_4$	SPPM	$5\cdot10^{-7}–1\cdot10^{-5}$	[331]
Mg(II)	$H_2T(4\text{-MePy})Po$	F	10^{-6}	[320]
Ce(IV)	$CaPhc(SO_3H)_4$	SPPM	$7\cdot10^{-7}–3.2\cdot10^{-5}$	[340]
	$H_2Phc(SO_3H)_4$	"	$7\cdot10^{-7}–1.3\cdot10^{-5}$	
	$NiPhc(SO_3H)_4$	"	$7\cdot10^{-7}–1.3\cdot10^{-5}$	
As(III)	$H_2Phc(SO_3H)_4$	SPPM-INCE	$2.7\cdot10^{-6}–2.7\cdot10^{-5}$	[340]
	$NiPhc(SO_3H)_4$			
	$CaPhc(SO_3H)_4$			

Notation. SPPM = spectrophotometry; SPPM-CIER = spectrophotometry with preliminary concentration on ion-exchange resins; AD-SPPM = analogue derivative spectrophotometry; TLS = pulsed laser thermal lens spectrophotometry; SPPM-INCE = indirect spectrophotometric determination using Ce(IV); F = fluorimetry; P = polarography; E = extraction–photometric method; C = catalytic method; c = concentration of the element to be determined.

*The metalloporphyrins indicated can be used also to determine Zn, Co, and Mn.

X. ANALYTICAL REAGENTS

Porphyrins have found applications as analytical reagents in the quantitative analysis of trace amounts of many metals (Table 2). Spectrophotometric analytical methods, based on the use of highly intense absorption bands in the electronic absorption spectra of porphyrins and metalloporphyrins, are mainly employed. The MP formation reactions are highly sensitive, which makes it possible to determine Cu, Zn, Cd, and other metals at concentrations in the range 10^{-7}–10^{-6} M with an error of 0.5–2%. Preliminary concentration of the salts on ion-exchange resins of the Chelex or Dowex types makes it possible to increase the sensitivity of the reaction by two orders of magnitude.

Selective highly sensitive methods for the catalytic determination of Cd and Hg, whereby it is possible to determine these metals at concentrations of 10^{-9} M, have been developed. The methods[334,345] are based on the catalytic acceleration of the coordination of H_2P to Mn(II) salts in the presence of Cd(II) or Hg(II). Porphyrin analytical reagents have been employed to determine Cu and Zn in tap water, in high-purity chemical reagents, hair, etc.

XI. OTHER APPLICATIONS

MP and MPhc are being studied vigorously as molecular oxygen transferring agents. The ability of the porphyrin complexes of Co, Fe, Mn, Ti, and Mo to fix oxygen reversibly under certain conditions has been demonstrated. These studies are in the main theoretical although patents on this subject have appeared in recent years.

Porphyrins are used in the therapy and early diagnosis of cancer. The ability of H_2P to accumulate selectively in cancer cells is used in this case. On irradiation with u.v. light, the diseased regions exhibit a red fluorescence.

Porphyrins manifest radioprotecting and radiosensitising properties and, depending on the concentration, they can intensify the radiation damge of a living organism and biological objects or can exhibit the opposite effect. Methods have been developed for the local decomposition of cancer cells based on the radiosensitising activity of H_2P and on their ability to accumulate selectively in cancer tumours.

Among other applications, mention may also be made of applications of porphyrins in fields such as the determination of the quality of meat products and their use as inhibitors of the burning of plastics, as antistatic agents, and even as deodorants and stimulants of hair growth.

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Institute of the Chemistry
of Non-Aqueous Solutions,
USSR Academy of Sciences,
Ivanovo