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Metal Complexes of Porphine and Azaporphine Compounds as Catalysts of Reactions Involving Oxidation by Molecular Oxygen

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The results of studies of the catalytic action of the metal complexes of porphines and azaporphines in reactions involving oxidation by molecular oxygen are surveyed. Various mechanisms of the action of the metal-porphine catalysts are analysed and a relation between the characteristics of the structures of these compounds and the spectrum of their activity is demonstrated. In terms of the problem of the preparation of new catalysts for the selective oxidation of organic compounds under mild conditions, possible ways of seeking systems in which the metal-porphines function as oxygen transferring agents are outlined.
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I. INTRODUCTION

Porphyrin compounds enter into the composition of many biologically important substances, including a series of oxidative enzymes such as oxidases, peroxidases, and others. The biological activity of porphyrins and their participation in a wide variety of the vital processes of living organisms have aroused much interest in these compounds[1-23]. The characteristic features of the structures of metalloporphines†, which consist of planar cyclic molecules with an extensive π-conjugation system, are responsible for their catalytic activity. In the planar molecules of metalloporphines the fifth and sixth coordination sites of the central metal ion are available for the coordination of the molecules of reactants in the reaction being catalysed and the extensive π-conjugation system facilitates a redistribution of the electron density within the reaction complex, which lowers the activation barrier to the reaction.

We believe that the problem of the modelling of the enzymtic catalytic activity of metalloporphyrins and of the formation on their bases of new catalytic systems for the oxidation of organic substrates under mild conditions, selective with respect to the reaction products, urgently requires solution at the present time. This review deals with the catalysis by metalloporphyrins of reactions involving oxidation by molecular oxygen in terms of the mechanisms of the action of the catalyst.

The studies on these lines were initiated by those of Cook[24-26] and Paquot[27-31] on metallophthalocyanines (M-Pc). Later these catalysts were investigated in other studies[32-68]. The synthesis of metallopolyphthalocyanines (M-Poly-Pc)[69,70] led to an interesting modification of phthalocyanine catalysts with a still more developed π-conjugation system and permitting the introduction of different metal ions into the same catalyst molecule. As a rule M-Poly-Pc exhibits a higher catalytic activity[37,71-80] than the corresponding monomeric analogues. The catalytic activity of metalloporphyrins (M-P) began to be studied comparatively recently[43,81-102], which is apparently due to their lower availability and lower stability compared with M-Pc.

The mechanisms of the catalysis by metalloporphines of oxidations by molecular oxygen have not as yet been finally elucidated. However, the available data show that metalloporphines can act via alternative mechanisms: via a donor mechanism in which an oxygen molecule is activated and via an acceptor mechanism in which the substrate undergoing oxidation is activated. A third mechanism, according to which metalloporphines catalyse the decomposition of the hydroperoxides present in the substrate undergoing oxidation in the form of impurities and thus initiate the free-radical chain auto-oxidation, is also discussed in the literature.

We shall consider each of these mechanisms in greater detail.

II. THE MECHANISM OF THE ACTIVATION OF OXYGEN

In the majority of systems[32-39,44,45,47,51,59-61,67,68,71,74-79,81,83,85,86,88-90,99-102] one is to some extent justified in postulating that molecular oxygen is coordinated to the metal ion of the metalloporphine and that either partial charge transfer from the catalyst to the oxygen,

$$P\text{-}M + O_2 \rightleftharpoons P\text{-}M^{\delta+} \ldots O_2^{\delta-},$$

or the transfer of one electron,

$$P\text{-}M + O_2 \rightleftharpoons P\text{-}M^{+} \ldots O_2^{\cdot-},$$

or two electrons,

$$P\text{-}M + O_2 \rightleftharpoons P\text{-}M^{2+} \ldots O_2^{2-},$$

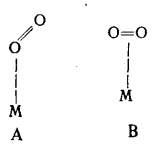
take place with formation of a superoxo- or peroxo-complex respectively.

Although direct evidence for the presence of metalloporphine-oxygen complexes in the catalytic reaction system has not so far been obtained, there are a number of indirect indications in support of the oxygen activation mechanism. One of these is the existence of 1 : 1 oxygen—metalloporphine complexes established by EPR and optical spectroscopy[103-125]. Under the influence of the field of the transition metal ion,

† The metalloporphine compounds include metalloporphyrins and metallophthalocyanines. The molecular skeleton of porphyrins is based on the porphyrin ring; phthalocyanines are derivatives of azaporphine.

the energy levels of the doubly degenerate antibonding π* orbitals of the oxygen molecule are split, the electrons are located at the more stable of the two orbitals, and their spins are paired; this entails the formation of a vacant orbital, which leads to the enhancement of the electron-accepting properties of the oxygen.

Two types of addition in mononuclear complexes of the type M...O_2 are known[126]: inclined terminal addition of oxygen in which the metal atom is linked to only one of the two oxygen atoms and the M–O–O angle is approximately 120° (A) and symmetrical addition of oxygen in which the metal is coordinated to the double bond of the oxygen molecule (B):



A B

In the first case a σ-bond is formed between one of the unshared electron pairs of oxygen and the vacant d_{z^2} orbitals of the metal and in the second it is formed between the occupied bonding π orbital of the oxygen molecule and the unoccupied d_{z^2} orbital of the metal. In both cases reverse donor interaction takes place with transfer of electron density from one of the doubly occupied d_{xz} (or d_{yz}) orbitals of the metal ion to the antibonding vacant π* orbital of the oxygen molecule, the reverse donor interaction predominating over the coordination σ-bonding, since the energy of the π* level of oxygen is lower than the energy of the *d* levels of transition metals.

The electronic configuration and the geometrical structure of the oxygen complexes of metalloporphines apparently depend both on the nature of the central metal ion[127] and on the nature of the porphin ring (Table 1). It is nowadays believed that the structure of the oxygen complexes of Co(II) Co(II)-porphyrins has been established[88,104,107–110,112]. These are octahedral complexes having one unpaired electron located at the coordinated oxygen. According to X-ray diffraction data, inclined terminal addition of the oxygen molecule occurs[115].

Three versions of the electronic structure are considered for the diamagnetic P-Fe...O_2 complexes[110,115,127,128]:

(1) $Fe^{2+}...O_2^*$—the oxygen molecule is present in the singlet state;

(2) $Fe^{2+}...O_2 \leftrightarrow Fe^{4+}...O_2^{2-}$—the quasi-neutral oxygen is involved in a resonance equilibrium with the peroxide ion;

(3) $Fe^{3+}...O_2^-$—a single electron of the iron ion is transferred to the oxygen molecule and the unpaired spins of the iron and oxygen electrons are paired.

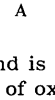
The last two structures make it possible to explain the stabilisation of the oxygen complexes of Fe-P by polar solvents.

The oxygen complexes of Mn-P and Mn-Pc are pentacoordinate compounds. The peroxide structure TPP-$Mn^{4+}...O_2^{2-}$ has been proposed[119,120] for the tetraphenylporphine complex on the basis of the set of available experimental data (EPR and optical spectroscopy) and theoretical considerations, and symmetrical addition of oxygen was postulated by analogy with the peroxide complex of titanium-octaethylporphyrin[129]. The superoxide structure Pc-$Mn^{3+}...O_2^-$ has been proposed for the manganese-phthalocyanine complex[121–123].

In the case of Cr(II)-TPP(Py) irreversible addition of oxygen takes place. Infrared spectroscopic data indicate the superoxide structure of the complex $Cr^{3+}...O_2^-$,[130] while theoretical considerations indicate the peroxide structure $Cr^{4+}...O_2^{2-}$.[127]

The oxygen complex formed in the catalytic reaction system interacts with the substrate undergoing oxidation and as a rule initiates the free radical chain oxidation, but in certain cases the oxidation proceeds via a non-chain mechanism.

Table 1. The structure of the oxygen complexes of metalloporphines.

M-P	Structure	*S*	Geometry	References
Co(II)-TPP(Py)	$Co^{3+}...O_2^-$	1/2		[88, 104, 107—110, 112, 115, 127]
Fe(II)-P	$Fe^{2+}...O_2^*$ $Fe^{2+}...O_2 \leftrightarrow Fe^{4+}...O_2^{2-}$ $Fe^{3+}...O_2^-$	0		[110, 115, 127, 128]
Mn(II)-TPP	$Mn^{4+}...O_2^{2-}$	3/2		[119, 120, 127]
Mn(II)-Pc	$Mn^{3+}...O_2^-$	—	—	[121—123]
Cr(II)-TPP(Py)	$Cr^{3+}...O^-$ $Cr^{4+}...O_2^{2-}$	1		[130, 127]

Notation: *S* = overall spin quantum number; TPP = α, α′, α″, α‴-tetraphenylporphine; Py = pyridine.

$$[M\text{-}P]^{1/2},$$

Table 2. The composition (%) of the cyclohexene autoxidation products.

Catalyst	*t*, °C	Cyclohex-1-en-3-one	Cyclohex-1-en-3-ol	Epoxycyclohexane	References
Ni-Pc	65	69	24	7	[27]
Fe-TPP	25	73	24	3	[82]
Mn-TPP	25	80	18	2	[86]

1. Initiation of the Free-Radical Chain Oxidation

The set of facts such as the inhibition of the process by radical inhibitors[39,82,86,88], products characteristic of chain autoxidation (Table 2), and kinetic data indicate the initiation by metalloporphines of the free-radical chain autoxidation in the majority of systems.

Comparison of the experimental equations for the rates of oxidation of acetaldehyde, benzaldehyde, cyclohexene, and 2,5-dihydrofuran[75,77–79,85,88],

$$-d[O_2]/dt = k[RH]^{3/2}[O_2]^{1/2}.$$

where RH is the substrate undergoing oxidation, with the theoretical equation

$$-d[O_2]/dt = k_p/(2k_t)^{1/2} \quad (1)$$

obtained on the basis of the generally accepted mechanism of

chain autoxidation,

$$RH \xrightarrow{k_i} R^{\cdot},$$
$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot},$$
$$RO_2^{\cdot} + RH \xrightarrow{k_p} ROOH + R^{\cdot},$$
$$2RO_2^{\cdot} \xrightarrow{k_t} \text{non-radical products},$$

assuming a fairly long kinetic chain and a fairly high partial oxygen pressure, leads to an expression for the rate of initiation

$$v_i = k_i[RH][O_2][M\text{-}P],$$

which makes it possible to represent the initiation stage in the following manner:

$$P\text{-}M + O_2 \overset{K_{O_2}}{\rightleftharpoons} P\text{-}M^+ \ldots O_2^-,$$
$$P\text{-}M^+ \ldots O_2^- + RH \xrightarrow{k_i'} P\text{-}M^+ \ldots O_2H^- + R^{\cdot},$$

where K_{O_2} is the equilibrium constant of the reaction involving the formation of the oxygen complex (for brevity we shall refer to it as the oxygenation constant).

Table 3. The rate constants for the overall reaction and for the autoxidation chain initiation in systems catalysed by metalloporphines.

Substrate	Catalyst	t, °C	$10^3 k_p$, litre$^{3/2}$ × mol$^{-3/2}$ × s^{-1}	$10^3 k_i$, litre^2 × mol^{-2} × s^{-1}	Refs.
DHF	Co-T(p-CH_3-P)P	30	2.22—2.50	—	[85]
1-Methyl-CH	Co-T(p-CH_3-P)P	30	1.4 *	140	[85]
4-Methyl-CH	Co-T(p-CH_3-P)P	30	0.24 *	3.97	[85]
CH	Co-T(p-CH_3-P)P	30	0.158—0.184	7.67	[85]
1,3-CH-diene	CopT(p-CH_3-P)P	30	$6.4 \cdot 10^{-3}$ *	0.0414	[85]
Acetaldehyde	Co-T(p-CH_3-P)P	10	28	6	[88]
Benzaldehyde**	Co-T(p-CH_3-P)P	10	470—620	—	[79]
Acetaldehyde	Fe, Cu-poly-Pc	10	210 *	72	[78]
Acetaldehyde	Fe, Mo-poly-Pc	10	120 *	20	[78]
Acetaldehyde	Fe-poly-Pc	10	82*	11	[78]
Acetaldehyde	Fe, Co-poly-Pc	10	81 *	11	[78]
Acetaldehyde	Cu, Co-poly-Pc	10	11 *	0.017	[78]
Isobutyraldehyde	Fe, Cu-poly-Pc	10	450—670	—	[79]
Acroleine***	Fe, Cu-poly-Pc	40	—	66±2	[75, 77]

* Estimated by us from the data of Ohkatsu and Tsuruta[85] and Ohkatsu et al.[78] respectively.

** Solvent—ethyl isobutyrate.

*** Benzene, in the remaining cases—ethyl acetate.

Remarks: DHF = 2,5-dihydrofuran; CH = cyclohexane; CH-diene = cyclohexadiene; Co-T(p-CH_3-P)P = cobalt-tetra(p-tolyl)porphine; the equation for the rate of oxidation of acroleine is more complex than Eqn.(1), since in this case the rate-limiting stage is the reaction of the acyl radical with oxygen (this is associated with the stabilisation of the acyl radical of acroleine as a result of conjugation with the double bond); $k_i = k_i' K_{O_2}$.

The superoxide complex initiates the autoxidation chain, abstracting the mobile oxygen from the molecule of the substrate being oxidised. It is assumed[85] that the complex $P\text{-}M^+\ldots O_3^-$ can rupture C–H bonds whose energy does not exceed 79 kcal mole^{-1}. In the oxidation of unsaturated hydrocarbons there is also the possibility of the initiation of autoxidation by the addition of the superoxide complex to the double bond:

$$P\text{-}M^+\ldots O_2^- + \rangle C{=}C\langle \rightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{O-O-M^+-P}{C}}-$$

The oxidation chain propagation and termination and the regeneration of the catalyst can be represented as follows:

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \quad \text{(chain propagation)},$$
$$RO_2^{\cdot} + RH \rightarrow R^{\cdot} + ROOH$$
$$RO_2^{\cdot} + \rangle C{=}C\langle \rightarrow -\overset{|}{\underset{OOR}{C}}-\overset{|}{C}-$$
$$2RO_2^{\cdot} \quad \text{—non-radical products (chain termination)},$$
$$P\text{-}M^+\ldots O_2H^- \rightarrow M\text{-}P + HO_2^{\cdot} \quad \text{(catalyst regeneration)}.$$

The radical nature of the superoxide complex is manifested to a large extent in the chain oxidation reaction, which is indicated by the attack by the complex $P\text{-}M^+\ldots O_2^-$ on the hydrocarbon undergoing oxidation at the sites with maximum electron density[85].

The constants for the overall reactions and chain initiation have been estimated for a number of systems (Table 3).

2. Catalysis of Non-Chain Oxidation

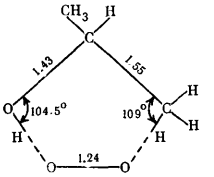
Data on the catalysis of non-chain oxidation by metalloporphines are of special interest for the solution of the problem of the selective oxidation of organic substrates by molecular oxygen.

The reverse donor interaction observed in the formation of an oxygen-metalloporhine complex, consisting in the transfer of electron density from one of the occupied d orbitals of the central metal ion to the antibonding vacant π^* orbital of the oxygen molecule, weakens the O–O bond, which is indicated by the increase of the distance between the oxygen atoms in the complex to 1.24–1.26 Å compared with the corresponding distance of 1.2074 Å in the free O_2 molecule[126]. The interaction with the substrate being oxidised can entail the complete rupture of the weakened O–O bond and the oxidation of the substrate either as a result of the insertion of an oxygen atom in the substrate molecule or as a result of the abstraction of hydrogen atoms from the latter[131,132].

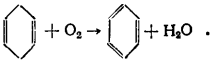
The second mechanism has been put forward for the gas-phase oxidation of propan-2-ol and propane-2-thiol, catalysed by M-Pc (M = Cr, Mn, Fe, Ni, or Cu) at 200–400 °C:[51,59,60]

$$CH_3{-}CHOH{-}CH_3 + {}^1/_2O_2 \rightarrow CH_3{-}CO{-}CH_3 + H_2O,$$
$$2CH_3{-}CHSH{-}CH_3 + {}^1/_2O_2 \rightarrow (CH_3)_2{-}CHSSCH{-}(CH_3)_2 + H_2O.$$

The following geometrical structure of the transition complex in the reaction has been suggested for the oxidation of propanol[59] (the bond lengths are given in ångstroms):



The oxidative dehydrogenation of cyclohexadiene by atmospheric oxygen, catalysed by M-Pc (M = Fe, Co, Ni, Cu, or Zn) at 250 °C, takes place analogously[19]:



The complex salts of certain porphyrins enter into the composition of oxidative enzymes as coenzymes. The attempts to model enzymic catalytic activity were unsuccessful for a long time—only radical chain autoxidation was observed. However, reports have now appeared that in certain homogeneous liquid-phase systems metalloporphines can function as agents transferring oxygen to the substrate being oxidised.

Data have been presented concerning the modelling of the functions of the monoxygenating enzyme cytochrome P.450 [81, 86,92,98] capable of catalysing the hydroxylation of saturated and aromatic hydrocarbons and the epoxidation of unsaturated hydrocarbons in the cells of living organisms. The coenzyme of cytochrome P-450, namely haemin, contains cysteine as an axial ligand. The maintenance of the enzyme in the reduced state is achieved as a result of the functioning of the microsomal respiratory chain[133].

The following modelling systems have been proposed:

(1) Iron-protoporphyrin (haemin) and an excess of thiosalicylic acid for the oxidation of cyclohexane by atmospheric oxygen in an aqueous acetone medium (the reaction products are cyclohexanol and cyclohexanone in proportions of 2 : 1); [81]

(2) TPP-MnCl and an excess of sodium tetrahydroborate for the oxidation of cyclohexane by atmospheric oxygen in a benzene-ethanol mixture (the reaction products are cyclohexanol and cyclohex-2-en-1-ol in proportions of 4 : 1); [86]

(3) TPP-MnCl–H_2–colloidal platinum in benzene with added imidazole or its derivatives for the oxidation of cyclohexene to epoxycyclohexane and cyclohex-2-en-1-one in proportions of 15 : 1 and of adamantane to adamantan-1-ol, adamantan-2-ol, and adamantan-2-one in proportions of 14.7 : 1.7 : 1; [98]

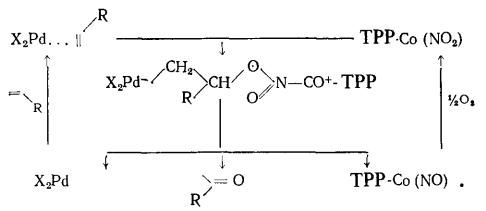
(4) haem-NAD (or NADP) for the hydroxylation of aniline in an alkaline medium (pH > 11) with formation of *p*-aminophenol[92] (NAD = nicotinamide-adenine dinucleotide; NADP = nicotinamide-adenine dinucleotide phosphate).

These systems contain an excess of the reducing agent, have products whose composition is characteristic of autoxidation, and are insensitive to the action of radical inhibitors.

It has been suggested[81,86] that one of the atoms of the oxygen molecule activated by the metalloporphyrin is capable of being inserted in the C–H bond on interaction with an unsaturated hydrocarbon, forming an alcohol, while in the reaction with an olefin it adds to the double bond, forming an epoxy-compound. It has been assumed[98] that the complex TPP-MnO, analogous to that observed in the M–P–iodosobenzene oxidising systems[134–141], is the hydroxylating and epoxidising species. When sodium tetrahydroborate is used as the reductant, the primary oxidation product is epoxycyclohexane, which is reduced by the excess $NaBH_4$ is cyclohexanol.

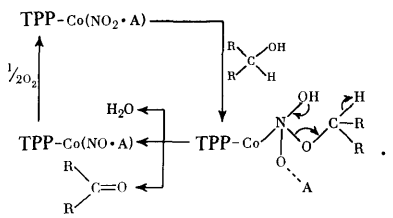
The TPP-MnCl–$(NBu_4)BH_4$ system in solution in methylene chloride catalyses the selective oxidation of olefins (cyclooctene, styrene, oct-1-ene, and phenylprop-1-ene) to the corresponding ketones, which are partly reduced by the excess $(NBu_4)BH_4$ to alcohols[98]. The products of the oxidation of cyclohexene are cyclohexanol and cyclohex-2-en-1-ol in proportions of 2 : 1.

Nitro- and nitroso-complexes of Co-TPP, namely (Py)Co-TPP(NO_2) and Co-TPP(NO), were used as oxygen transferring agents in a new catalytic system proposed for the selective oxidation of olefins: ethylene and propene were oxidised to acetaldehyde and acetone respectively[87]. The nitro-complex can be formally regarded as a species containing the monoanionic ligand $Co^+...NO_2^-$, capable of functioning as a weak nucleophile. In order to activate the olefin undergoing oxidation with respect to nucleophilic attack, it was coordinated to bivalent palladium. One of the oxygen atoms in the NO_2 ligand is then apparently transferred to the olefin and the resulting nitroso-ligand is oxidised by the oxygen supplied to the system in accordance with the scheme

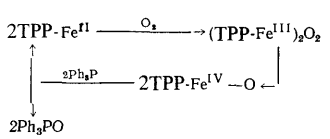


where X is the palladium counterion.

In the presence of Lewis acids [$BF_3.(C_2H_5)_2O$; $LiPF_6$], the complexes (Py)Co-TPP(NO_2) and Co-TPP(NO) also catalyse the selective oxidation of primary and secondary alcohols: benzyl alcohol and cycloheptanol are oxidised to an aldehyde and a ketone respectively[97]. It has been suggested that the Lewis acid (A) is coordinated to the oxygen of the nitro-group, increasing its electrophilicity. The oxidation can proceed via the formation of an ether-like intermediate which decomposes via a non-radical mechanism into a carbonyl product, water, and a nitroso-complex of Co-TPP:



Yet another pathway leading to the activation of oxygen is observed in the oxidation of triphenylphosphine catalysed by Fe-TPP in solution in toluene at 25 °C.[91] In the presence of molecular oxygen Fe-TPP is oxidised to the bridged peroxo-dimer $(TPP\text{-}Fe)_2O_2$, the first stage of the spontaneous decomposition of which involves the formation of the oxo-complex $TPP\text{-}Fe^{II}\text{–}O$. This complex is in fact the agent transferring oxygen to the Ph_3P molecule:



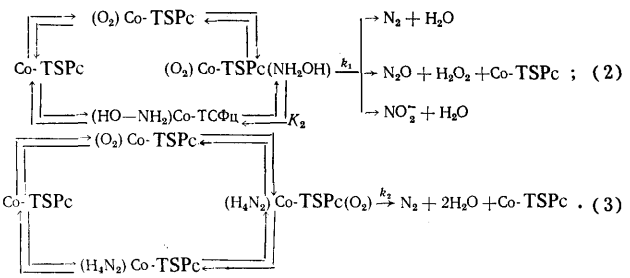
However, the oxo-complex also reacts with $(TPP\text{-}Fe)_2)_2$ and $TPP\text{-}Fe...O_2$:

$$TPP\text{-}Fe^{IV}\text{—}O + (TPP\text{-}Fe)_2O_2 \rightarrow (TPP\text{-}Fe)_2O + TPP\text{-}Fe...O_2 ,$$
$$TPP\text{-}Fe^{IV}\text{—}O + TPP\text{-}Fe...O_2 \rightarrow (TPP\text{-}Fe)_2O + O_2 ,$$

which leads to the deactivation of the catalyst and the cessation of the reaction; in the inactive reaction system the porphyrin compound is present only in the form of the bridged oxo-dimer. A conclusion concerning the mechanism of the oxidation of Ph_3P was reached on the basis of the analysis of the kinetics of the spontaneous decomposition of $(TPP\text{-}Fe)_2O_2$ and its reduction by Ph_3P.

The oxidation of hydroxylamine and hydrazine, catalysed by cobalt-tetrasulphophthalocyanine (Co-TSPc) in an alkaline medium, proceeds, according to Wagnerova et al.[67,68], within the coordination sphere of the ternary complex of Co-TSPc with O_2 in the substrate formed in the first stage of the

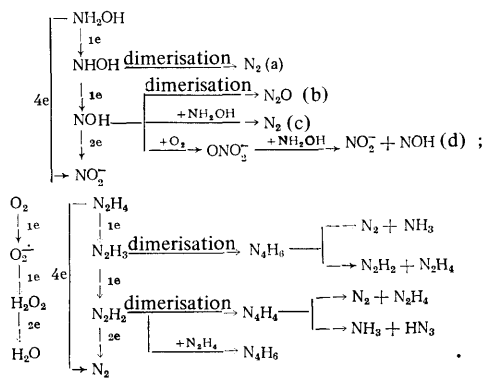
reaction:



This is supported by a series of facts. In an alkaline medium Co-TSPc forms a 1:1 complex with N_2H_4. The addition of hydrazine to the oxygen complex of Co-TSPc, which has two absorption bands at 626 and 670 nm, leads to their disappearance and the appearance of new bands at 450 and 680 nm. Subsequent passage of oxygen restores the initial spectrum.

The change of the reaction order with respect to N_2H_4, NH_2OH, and O_2 from 1 to 0 with increase of the reactant concentration also shows that N_2H_4, NH_2OH, and O_2 react in the coordinated state and the theoretical rate equations, derived for mechanisms (2) and (3), agree with the experimental equations. The constants $k_1 = 25\ s^{-1}$ and $k_2 = 2.0 \times 10^3$ have been estimated for hydroxylamine.

Analysis of the products of the oxidation of NH_2OH and N_2H_4 shows that the process takes place within the coordination sphere of the complex without the release of free radicals into space. The states in the successive oxidation of substrates and the reduction of oxygen are presented below together with their possible subsequent reactions, regardless of whether they are free radicals or enter into the composition of the complex:



If after the transfer of one or two electrons the radicals formed pass into space, then the NH_2OH oxidation products should contain more of the radical dimerisation products, in particular N_2O, and, as a result of the competing reaction (c), the relative NO_2^- content should increase or remain unchanged with increase of the initial NH_2OH concentration. In reality, the main NH_2OH oxidation product is NO_2^- (60%) and the amount of N_2O formed is very small. Furthermore, an increase of the initial NH_2OH concentration leads to a decrease of the relative content of NO_2^- in the products. All these findings support electron transfer within the complex. Molecular nitrogen is formed[68] when the complex Co-TSPc.(NOH) interacts with NH_2OH:

$$\text{Co-TSPc(NOH)} + NH_2OH \rightarrow N_2 + 2H_2O + \text{Co-TSPc} \quad .$$

Similarly the presence of only traces of ammonia, the radical recombination product, in the hydrazine oxidation products also indicates an intracoordination mechanism of electron transfer.

The electron transfer from the substrate to oxygen probably proceeds via the central cobalt ion with participation of the π-electron system of the phthalocyanine ring and the process can proceed in more than one stage.

Despite the fundamental similarity of the mechanisms of the oxidation of NH_2OH and N_2H_4 in the presence of Co-TSPc, the detailed electron transfer mechanisms are apparently different. Thus the amount of hydrogen peroxide formed in the oxidation of hydrazine increases in the course of the reaction, which can be explained by assuming that the oxidation proceeds in two stages, i.e. that oxygen displaces H_2O_2 from the intermediate ternary complex:

$$\text{(O}_2\text{) Co-TSPc(}N_2H_4\text{)} \rightarrow \text{(}H_2O_2\text{) Co-TSPc(}N_2H_2\text{)} \rightarrow$$
$$\xrightarrow{O_2} \text{(O}_2\text{) Co-TSPc(}N_2H_2\text{)} \rightarrow H_2O_2 + N_2 + \text{Co-TSPc} \quad .$$

According to our data[99-101], the oxidation catalysed by metalloporphyrins in an aqueous medium involves the generation of a free superoxide radical-anion. One can put forward two possible mechanisms:

(1) dissociation of the oxygen complex of the metalloporphyrin with formation of O_2^-:

$$\text{P-M}^+ \ldots O_2^- \rightleftarrows \text{P-M}^+ + O_2^- \ ;$$

(2) electron transfer from the substrate S undergoing oxidation to oxygen within the coordination sphere of the ternary complex of M-P with O_2 and S:

$$\text{S}\ldots\text{M-P}\ldots O_2 \rightarrow \text{M-P} + S^+ + O_2^- \quad .$$

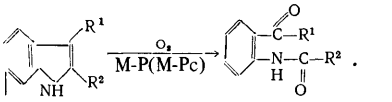
The first reaction involves the formation of the oxidised form of the catalyst and the completion of the catalytic cycle requires a catalyst regeneration stage via the interaction with the substrate or with one of the intermediate products of the reaction.

A typical example of the process with a "superoxide" mechanism is the oxidation of adrenalin in an aqueous medium, catalysed by porphyrin complexes of cobalt: Co-α, α', α'', α'''-tetra(*p*-sulphophenyl)porphine and Co-mesoporphyrin[99,100]. The oxidation process is inhibited by superoxide dismutase and is not catalysed by metal-free porphyrins. The kinetic data indicate the operation of the first mechanism in this system and the catalyst is regenerated via the reaction with the peroxide ion O_2^{2-}:

$$\text{Co}^+\text{-P} + O_2^{2-} \rightarrow \text{Co-P} + O_2^- \quad .$$

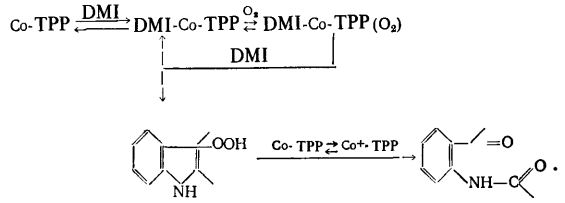
The coordination of the substrate to the metalloporphyrin is not essential in all cases. This is indicated by the catalysis of the oxidation of the Fe^{2+} ion (a substrate which cannot behave as an axial ligand) by cobalt-porphyrin to Fe^{3+}.[102]

The dimethyl ether of metalloprotoporphyrin TPP-M (M = Co, Cu, or Ni) in solution in methylene chloride[83,95] and Mn-Pc in solution in dimethylformamide (DMF)[142] catalyse the dioxygenation of alkyl derivatives of indole with formation of the corresponding ketoamides:



The formation of a ternary complex of the catalyst with O_2 and indole is indicated by the results of ultraviolet spectroscopic and EPR studies. In the case of Mn-Pc, it has been suggested[142] that one such complex of an indole derivative interacts with the oxygen of another complex—the reaction is of second order with respect to Mn-Pc. In the case of

Co-TPP it is believed[95] that the interaction of the ternary complex with a dimethyl indole (DMI) molecule results in the formation of 2,3-dimethylindolyl hydroperoxide—its presence in the reaction system has been demonstrated by NMR. The next reaction stage involves the decomposition of the hydroperoxide, which is also catalysed by Co-TPP:



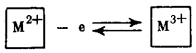
It must be emphasised that the study of the non-chain oxidation processes in the presence of metalloporphines is of great interest from the standpoint of the understanding of the mechanisms of the operation in biological systems of oxidative enzymes containing porphyrin structures. Another important aspect of these investigations is the creation of new catalytic systems for the selective non-chain oxidation of organic compounds by molecular oxygen under mild conditions. We believe that investigations where the reaction is carried out in the presence of a suitable reductant capable of regenerating the catalyst in the course of the reaction and which involve, together with the activation of molecular oxygen on the metalloporphine, the additional activation of the substrate being oxidised with respect to nucleophilic attack by its coordination to a suitable complex-forming agent are the most promising. Bimetallic porphine systems containing electron-donating and electron-accepting active centres may prove to be effective for the simultaneous activation of oxygen and the substrate being oxidised.

3. The Influence of Various Factors on the Catalytic Activity of Metalloporphines

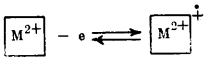
It is of interest to compare the influences of various factors—the nature of the metal, the porphine ring, and the trans-ligand —on the catalytic activities of metalloporphine compounds and on their oxygen affinity (K_{O_2}) in systems involving the oxygen activation mechanism. When oxygen complexes are formed by metalloporphines, electron density is transferred to the oxygen molecule and the oxidation potential of the latter can be conveniently selected as the parameter characterising the influence of the above factors on the properties of M-P.

(a) *The nature of the metal.* Table 4 shows that the lower the oxidation potential of the metalloporphine M-P, the higher its oxygenation constant K_{O_2}. Mn-TPP, for which K_{O_2} is smaller by several orders of magnitude than might have been expected on the basis of the potential, is an exception. This may be associated either with the fact that the oxygen complex of Mn-TPP has a peroxide structure, in contrast to the superoxide complexes of other metalloporphyrins M-P or with the fact that the complex Mn-TPP(O_2) is tetrahedral, while the complexes of other metalloporphyrins M-P are octahedral (it has been shown for Co-porphyrins that the electron-donating *trans*-ligands greatly accelerate the oxygenation[109]).

We shall follow the influence of the nature of the metal on the catalytic activity of metalloporphines in various systems. In the oxidative dehydrogenation of cyclohexadiene by atmospheric oxygen at 250 °C, a clear-cut correlation can be traced between the oxidation potentials of the metallophthalocyanines M-Pc and their activity (Fig. 1). For the series of metals Fe, Co, Ni, Cu, and Zn, the oxidation potentials of Mn-Pc as well as M-TPP (Table 5) have a maximum at the point corresponding to Ni, which is associated with the change in the oxidation mechanism. The iron and cobalt complexes are oxidised via the central metal ion:



and the copper and zinc complexes are oxidised via the porphyrin or phthalocyanine ligand:



(The rectangle denotes a π-electron porphine system).

Table 4. The oxidation potentials $E_{1/2}$ of the metalloporphyrin complexes[143] and their oxygenation constants at −78 °C.[115]

Complex		$\lg K_{O_2}$	$E_{1/2}$, V
Co-TPP(Py)	(in toluene)	−1.7	+0.13
Co-T(p-OCH_3-P)P(N-CH_3-Im	(in toluene)	−0.8	+0.11
Fe-T(piv-P)P(N-CH_3-Im)	(solid)	6.4	−0.11
Mn-TPP	(in toluene)	~2.1	−0.27
Cr-TPP(Py)	(solid)	*	−0.86

* Cr-TPP(Py) combines irreversibly with O_2.

Remarks: K_{O_2} is expressed in mm^{-1}; $E_{1/2}$ is the potential measured in DMSO relative to the saturated calomel electrode; T(piv-P)P = meso-tetra(α, α′, α″, α‴-*O*-pivalimidophenyl)porphine; N-CH_3-Im = *N*-methylimidazole.

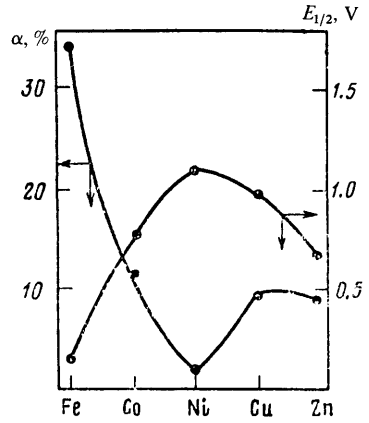


Figure 1. Dependence of the catalytic activity (α is the degree of conversion) in the oxidative dehydrogenation of cyclohexadiene by air and of the oxidation potentials $E_{1/2}$ of M-Pc on the nature of the central metal ion[19].

In the case of nickel both processes take place at the same potential.

The catalytic activity of metalloporphines varies in opposition to the oxidation potentials and is a minimum for Ni-Pc; Cu-Pc exhibits a higher catalytic activity than might have been expected on the basis of its oxidation potential. A similar anomaly has been also observed in other systems. This is apparently associated with the specific features of the interaction of copper complexes with molecular oxygen. The nature of this interaction in terms of the electronic structure can only be postulated, but it is striking that the most important metalloenzymes, catalysing the reduction of oxygen in biological systems, contain iron and copper.

Table 5. The first oxidation potentials of metalloporphines (OEP = octaethylporphyrin) relative to the saturated calomel electrode (in volts).

M	Electronic configuration of M	TPP (Ref.143)	TPP* (Ref. 144, 145)	OEP (Ref.143)	Pc** (Ref. 144, 145)
Cr^{2+}	d^4	−1.06 ***	—	−1.14 ****	—
Mn^{2+}	d^5	−0.23 *****	—	−0.42 ****	−0.11
Fe^{2+}	d^6	−0.19 ****	−0.32	−0.24****	+0.16
Co^{2+}	d^7	+0.32	+0,52	—	+ 0.77
Ni^{2+}	d^8	+1.04	+1.01	+0.73	+1.10
—	—	+0.95	+1.00	+0.81	—
Cu^{2+}	d^9	+0.90	+0.99	+0.79	+1.00
Zn^{2+}	d^{10}	+0.71	+0.78	+0.63	+0.68

* In benzonitrile.

** In 1-chloronaphthalene.

*** In methylene chloride.

**** In DMSO.

***** In acetonitrile. In the remaining cases the solvent was butyronitrile.

Table 6. Data on the oxidation of indole derivatives in solution in methylene chloride[83,95].

Catalyst	$E_{1/2}$, V	3-Methylindole		2,3-Dimethylindole	
		τ, h	α, %	τ, h	α, %
Co-TPP	+0.32	5	70	1	50
Ni-TPP	+1.04	20	traces	20	traces
Cu-TPP	+0.90	20	50	3	40

Remarks: The values of $E_{1/2}$ in butyronitrile[143] are quoted relative to the saturated calomel electrode; τ = reaction time; α = conversion of substrate.

The activity of M-TPP in the liquid-phase oxidation reactions of indole derivatives is also correlated with the oxidation potential of the catalyst and is a minimum for Ni-TPP (Table 6). In the oxidation of adrenalin in an alkaline medium, Co-T(*p*-sulpho-P)P is also more active than Ni-T(*p*-sulpho-P)P.[99]

Co-TPP deviates (is less active) from the correlation between the catalytic activity of M-TPP in the acetaldehyde oxidation reaction (Table 7) and their oxidation potentials.

In the gas-phase oxidation of propane-2-thiol and propan-2-ol at 250–350 °C, manganese-phthalocyanine exhibits a lower activity (Table 8) than suggested by its oxidation potential. This can be associated with the oxidation of the Mn^{2+} ion at high temperatures[146]. The copper complex shows, as usual, an anomalously high activity. Ni-Pc is more active in the oxidation of propanol than might have been expected. In order to account for the activity series obtained for metallophthalocyanines, the authors resorted to the molecular orbital and ligand field theories[51,61].

(b) *The nature of the porphine ring.* It follows from Table 9 that the greater the basicity (the quantity bearing an inverse relation to pK_a) of the free porphyrin base, the lower the oxidation potential of the corresponding metalloporphyrin and the higher its oxygen affinity. Octaethylporphyrin (OEP) is an exception.

Table 7. Kinetic data for the autoxidation of acetaldehyde (0.5 M) in solution in ethyl acetate catalysed by M-TPP (5×10^{-3} M at 10 °C).[89]

Catalyst	$E_{1/2}$, V	$-10^6\, d[O_2]/dt$, mol litre^{-1} s^{-1}	$10^6\, k_i$, litre^2 × mol^{-2} s^{-1}
Mn-TPP	−0.23	3.5	11.2
Co-TPP	+0.32	2.6	6.2
Ni-TPP	+1.04	3.1	8.8
Cu-TPP	+0.90	3.4	10.6

Remarks: The potentials $E_{1/2}$ in butyronitrile[143] (in acetonitrile for Mn-TPP) are quoted relative to the saturated calomel electrode; the k_i were estimated from the data of Ohkatsu and Osa[89].

Table 8. The activation energies (kcal mole^{-1}) for the gas-phase oxidation reactions of propanol and propanethiol catalysed by M-Pc.[51,59–61]

M	Mn	Fe	Co	Ni	Cu	Zn
$E_{1/2}$, V	−0.11	+0.16	+0.77	+1.10	+1.00	+0.68
Propane-2-thiol	15—18	12—14	16—20	30	14—17	23—28
Propan-2-ol	15	10	23	14	9	—

Remarks: The potentials $E_{1/2}$ in 1-chloronaphthalene[144,145] are quoted relative to the saturated calomel electrode.

An analogous relation is observed also between the catalytic activity of metalloporphines and the basicity of the corresponding porphine bases. Thus the cobalt complex of the more basic dimethyl ether of protoporphyrin (Co-DME-proto-P) is a more active catalyst of the oxidation of indole derivatives [3-methylindole (I), 3-methoxypropionylindole (II), and 3-methoxybutyrylindole (III)] than the corresponding complex of the less basic TPP (Table 10). The catalytic activity of tetrasubstituted copper-phthalocyanines in the cumene oxidation reaction at a temperature below 100 °C increases with enhancement of the π-donor properties of the substituents: $NO_2 < C_5H_5N < H < Br < Cl$.[36]

(c) *The nature of the substituents in the phenyl groups of tetraphenylporphine.* The electron-donating and electron-accepting properties of *para*-substituents in the phenyl groups of Co-TPP have a weak influence on its oxidation potential[143] and oxygenation constant[148] (Table 11), which is apparently associated with the fact that the benzene rings

are arranged at right angles to the plane of the porphyrin nucleus and do not therefore contribute significantly to its π-conjugation system.

Table 9. The influence of the basicity of the free porphyrin base on the oxidation potential of Mn-P [146] and the oxygenation constant of Co-porphyrins (−45 °C). [147]

Porphyrin ligand	pK_a	$E_{1/2}$, V	Im	Py	Pip	N-CH_3-Im
OEP	6	—	24.5	1.41	1.78	23.4
DME-meso-P	5.8	−0.19	32.4	—	—	—
DME-deutero-P	5.5	−0.14	—	—	—	—
DME-proto-P	4.8	−0.11	14.4	14.4	4.47	20.0
T(*p*-OCH_3-P)P	>3	—	—	0.76	1.4	6.5
TPP	~3	+0.01	1.58	—	—	—

Remarks: K_a = dissociation constant of the protonated free porphyrin base: $H_3\text{-}P \rightleftarrows H^+ + H_2\text{-}P$; the potentials $E_{1/2}$ in acetonitrile are quoted relative to the standard hydrogen electrode; the values of 10^3 K_{O_2} (mm^{-1}) are quoted in the remaining columns for different axial ligands in solution in toluene; Pip = piperidine.

Table 10. Data on the oxidation of indole derivatives in solution in methylene chloride[83,95].

Substrate oxidised	Catalyst	τ, h	α, %
(I)	Co-DME-proto-P	3	80
(I)	Co-TPP	5	70
(II)	Co-DME-proto-P	20	40
(II)	Co-TPP	30	50
(III)	Co-DME-proto-P	18	40
(III)	Co-TPP	24	60

Table 11. The influence of the substitutents X in Co-T(*p*-X-P)P on $E_{1/2}$, [143] K_{O_2} at −38 °C, [148] and the catalytic activity in the acetaldehyde (0.5 M) oxidation reaction in solution in ethyl acetate at 10 °C. [89]

X	$E_{1/2}$, V	$\lg K_{O_2}$	$-10^6\, d[O_2]/dt$, mol litre^{-1} s^{-1}
OCH_3	0.33	1.65	4.2
CH_3	0.35	1.61	81.0
H	0.39	1.48	2.8
Cl	0.40	1.45	1.2

Remarks: The values of $E_{1/2}$ in butyronitrile are quoted relative to the saturated calomel electrode; K_{O_2} (for Py)Co-T(*p*-X-P)P (mm^{-1}) refers to a solution in toluene; catalyst concentration 5×10^{-3} M; $P_{O_2} = 1$ atm.

The only reaction for which the influence of the nature of the substituents in the phenyl groups of the catalyst has been studied is the oxidation of acetaldehyde in the presence of Co-T(*p*-X-P)P. [89] The tetramethyl-substituted catalyst exhibits an anomalously high activity in this system (Table 11).

At the present time the above finding cannot be explained and the lack of data for other reactions would make premature any conclusions concerning the influence of the nature of the substitutent X in M-T(*p*-X-P)P on the catalytic activity.

(d) *The nature of the trans-ligand.* A general correlation between the basicity of the axial ligand L in the complex (L)Co-P and the oxygenation constant of the latter has not been observed[105,106,109,115,147] (Fig. 2). However, for a series of structurally similar axial bases [substituted pyridines (Fig. 2) and substituted phosphines[149]], a linear relation can be traced between K_{O_2} and pK_a. The lack of a general correlation is associated with the fact that the parameter pK_a characterises only the σ-donor properties of the ligand but does not take into account its π-donor properties. However, π-donor *trans*-ligands should enhance the reverse donor interaction of (L)M-P with O_2 and hence should increase its oxygen affinity. Indeed, Fig. 2 shows that powerful π-donors such as imidazole and DMF increase the oxygenation constant.

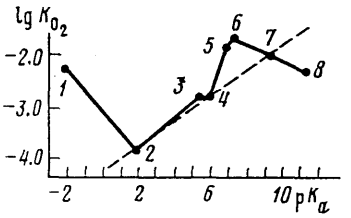


Figure 2. Relation between $\lg K_{O_2}$ (toluene, −45 °C) for (L)Co-DME-proto-P and the pK_a of the axial ligand L: [115] *1*) dimethylformamide; *2*) 4-cyanopyridine; *3*) pyridine; *4*) 4-butylpyridine; *5*) imidazole; *6*) 1-methylimidazole; *7*) 4-aminopyridine; *8*) piperidine.

Table 12. The values of K_{O_2} and the oxidation potentials of the complexes (L)Co-T(*p*-OCH_3-P)P. [147]

L	$-\lg K_{O_2}$	$E_{1/2}$, V
N-Methylimidazole	1.72	−0.48
4-Picoline	2.20	−0.23
5-Chloro-*N*-methylimidazole	2.26	−0.24
Piperidine	2.28	−0.31
3,4-Lutidine	2.35	−0.22
Pyridine	2.46	−0.20

Remarks: The values of K_{O_2} are expressed in mm^{-1} (obtained at −65 °C in toluene); the potentials $E_{1/2}$ were obtained in DMF; L = axial ligand.

In connection with the foregoing, it would apparently be more useful to compare the K_{O_2} with the oxidation potentials of the metalloporphyrins M-P having an axial ligand (Table 12). Despite the existing deviations, a general trend can be seen, namely an increase of the oxygenation constant with decrease of the oxidation potential of (L)Co-T(*p*-OCH_3-P)P.

The influence of electron-donating additives on the rate of the catalytic oxidation has been studied in a series of systems. The rate of oxidation of acetaldehyde catalysed

by Co-T(p-CH_3-P)P passes through a maximum as a function of the relative content of the additive (pyridine or DMF) corresponding to the ratio [additive]/[catalyst] = 1 (Fig. 3). It has been shown by EPR that, depending on the amount of added pyridine, a 1 : 1 or 1 : 2 Co-TPP-pyridine complex is formed. Consequently the axial base occupying the fifth coordination site in the catalyst molecule increases its catalytic activity. However, in the presence of large amounts of the additive, the latter occupies both coordination sites of the catalyst and prevents the coordination of oxygen, which lowers the rate of reaction.

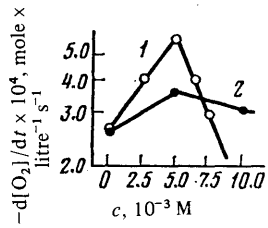


Figure 3. The influence of added pyridine (line *1*) and dimethylformamide (line *2*) on the rate of oxidation of acetaldehyde catalysed by Co-TPP in solution in ethyl acetate at 10 °C. [89]

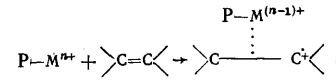
An analogous accelerating effect of basic additives (acetone, benzamide, urea, pyridine, acridine, aniline, and piperidine) has been demonstrated in the oxidation of benzaldehyde in the presence of Co-T(p-CH_3-P)P [89] and it has been shown that the higher the basicity of the additive the smaller its amount required to increase the rate of reaction.

It has been stated that catalytic amounts of pyridine have an accelerating effect in the oxidation of cumene in the presence of metallopolyphthalocyanines[74,75].

Thus analysis of data concerning the influence of various factors on the catalytic activity of metalloporphines reveals the following tendency: factors increasing the oxygenation constants of metalloporphyrins as a rule increase also their catalytic activity in oxidation reactions proceeding via an oxygen activation mechanism.

III. THE MECHANISM OF THE ACTIVATION OF THE SUBSTRATE UNDERGOING OXIDATION

In the systems examined above, metalloporphines function in accordance with a donor mechanism, transmitting electron density to the oxidant molecule. The presence of an extensive π-conjugation system in the metalloporphines, capable of stabilising different valence states of the central metal, gives rise to the possibility of the operation (under certain conditions) of an alternative mechanism of the catalysis—an acceptor mechanism characterised by partial or complete transfer of an electron from the oxidised substrate to the catalyst:



A similar mechanism has been postulated in the oxidation reactions of cyclohexene in solutions in nitrobenzene and benzene[84,93] and of squalene in solution in benzene[94] in the presence of Co(III)-OEP on the basis of the following data: firstly, the diamagnetic Co(III)-OEP cannot activate oxygen, since it does not form complexes with it, and, secondly, an EPR signal ($g = 2.0060$, $A_N = 14.33$, $a_H = 8.5$) has been detected in the Co(III)-OEP-cyclohexene system by the "spin trapping" method using nitrosodurene, which the authors[84] attributed to the cyclohexene radical-cation. We may add that there are indications in the literature of the formation of complexes by metalloporphines with unsaturated hydrocarbons[19,38,50] and, as shown in relation to the cyclohexa-1,4-diene-Co-Pc system, the complex formation equilibrium constant ($K_{cyclohexadiene}$) increases after the introduction of electron-accepting substituents into the phthalocyanine ring[19] (Table 13).

Table 13. The catalytic activity of substituted Co-Pc in the cyclohexa-1,4-diene-nitrobenzene system at 240 °C and the equilibrium constants (litre mol^{-1}) for the complex formation reactions between the catalyst and reactants[151].

Catalyst	α, %	K_{TNB}	$K_{CH\text{-}diene}$
Co-Pc	14	586	2.1
Co-Pc(F)$_4$	5	36	8.5
Co-Pc(F)$_{16}$	71	0.295	45

Notation: α = yield of benzene; K_{TNB} and $K_{CH\text{-}diene}$ are the equilibrium constants for the complex formation reactions of the catalyst with trinitrobenzene and cyclohexadiene respectively.

An acceptor mechanism of the catalysis has also been demonstrated for the oxidation reactions of thiols in an alkaline medium[52-58,62-66]. The catalysis of these reactions[54,57,58] consists of the coordination of the RS^- anion to M–Pc, the alternate reduction of M(II)-Pc by the thiol and the oxidation of the resulting M(I)-Pc by oxygen:

$$RSH + OH^- \rightarrow RS^- + H_2O ,$$
$$M(II)\text{-}Pc + RS^- \rightarrow M(I)\text{-}Pc + RS^{\cdot} ,$$
$$4M(I)\text{-}Pc + O_2 + 4H^+ \rightarrow 4M(II)\text{-}Pc + 2H_2O ,$$
$$2RS^{\cdot} \rightarrow RSSR .$$

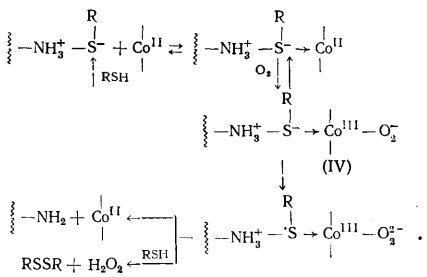
It has been shown by spectroscopy in the visible region[54] that in a phosphate buffer (pH 8.5–10.0) cysteine reduces the tetrasodium salt of cobalt(II)-4,4,4,4-tetrasulphophthalocyanine [Co(II)-Pc(SO_3Na)$_4$] to Co(I)-Pc(SO_3Na)$_4$. Subsequent introduction of oxygen into the system leads to a spectrum similar to that of Co(II)-Pc(SO_3Na)$_4$ when the reaction product is cysteine. Apparently Co(II)-Pc(SO_3Na)$_4$ forms a complex with cysteine.

The rate of oxidation of thiols usually depends on the M-Pc and O_2 concentrations but is independent of the thiol concentration[58], which shows that the thiolate anion reacts in the coordinated state. However, according to Kundo et al.[53], the rate of oxidation of cysteine is proportional to the cysteine and catalyst concentrations. Such conflicting data may be due to the difference between the ratios of the concentrations of the reactants used in different studies.

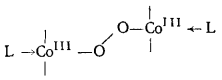
The coordination of the RS^- anion to the M-Pc during the reaction is also indicated by the decrease of the rate (up to the cessation of the reaction) caused by the addition of a strong complex-forming agent (the cyanide ion) in the oxidation of cysteine[57] and ethanethiol[58].

Effective catalysts have been proposed recently for the oxidation of thiols, the catalysts containing oxidation centres and basic groups involved in a cooperative interaction[62-66]. Such bifunctional catalysts consist of Co(II)-Pc(SO_3Na)$_4$ and a polymeric base (for example polyvinylamine or polyacrylamide modified by amino-groups) and exhibit a higher activity in the oxidation of 2-mercaptoethanol than the NaOH/Co(II)-Pc(SO_3Na)$_4$ low-molecular-weight system.

It has been suggested that RSH forms a complex with the polymeric base. The thiolate ion in this complex, which is a powerful π-donor, forms a complex with Co(II)-Pc(SO_3Na)$_4$, which coordinates an oxygen molecule, whereupon an electron is transferred within the coordination sphere from RS^- to O_2:[63]



The higher catalytic activity of polymeric catalytic systems compared with low-molecular-weight systems is associated with the fact that in the former case the very reactive mononuclear superoxo-complex (IV) is the effective species, while in the latter case dimerisation results in the formation of the less reactive dimericperoxo-complex (V):



(V)

Thus metalloporhines can catalyse oxidation-reduction reactions via two alternative mechanisms. The alteration of the electron-donating and electron-accepting properties of metalloporphines by the introduction of the appropriate substituents in the porphine ring can lead to the inversion of the mechanism of the catalysis in the same system. A similar phenomenon has been observed in the gas-phase oxidative dehydrogenation of cyclohexa-1,4-diene by nitrobenzene[151]. The metallophthalocyanines M-Pc catalyse this reaction by activating the oxidant, which is indicated by a series of facts—in particular by the increase of catalytic activity with decrease of the oxidation potentials of M-Pc (M = Mn, Fe, Co, Ni, Cu, or Zn) and with increase of the constants for their complex-formation reaction with trinitrobenzene. The enhancement of the electron-accepting properties of Co-Pc by the introduction of 16 fluorine atoms into its molecule changes the mechanism of the catalysis (Table 13). Depending on the number of fluorine atoms (from 0 to 16) in the phthalocyanine ring, the catalytic activity passes through a minimum; the oxidative dehydrogenation of cyclohexadiene in the presence of Co-Pc(F)$_{16}$ takes place also in the absence of nitrobenzene; with increase of the number of fluorine atoms in the catalyst molecule, the constant for its complex formation reaction with trinitrobenzene diminishes and that for the reaction with cyclohexadiene increases.

IV. CATALYSIS OF THE DECOMPOSITION OF HYDROPEROXIDES

The presence of a variable-valence metal ion in metalloporphines gives rise to the possibility of yet another mechanism of the catalysis. They can initiate the autoxidation chain, catalysing via the Haber–Weiss mechanism[152] the decomposition of the hydroperoxides present in the substrate as impurities:

$$ROOH + M^{n+} \rightarrow RO^{\cdot} + OH^- + M^{(n+1)+} ,$$
$$ROOH + M^{(n+1)+} \rightarrow RO_2^{\cdot} + H^+ + M^{n+} . \qquad (4)$$

This mechanism usually operates at elevated temperatures. According to a number of studies[32-36], it predominates in the liquid-phase oxidation of cumene and a number of other hydrocarbons in the presence of M-Pc at temperatures above 105 °C; below 100 °C, the M-Pc activate oxygen. A change in the mechanism of the catalysis in the range 100–105 °C is indicated by the break in the temperature variation of the rate constant represented by a plot of $\lg k$ against $1/T$ as well as the lack of constancy of the ratio of the hydroperoxide formed to the oxygen which has reacted, observed above 105 °C. According to the results of other investigators the M-Pc catalyse the decompostion of cumenyl hydroperoxide also at 60–100 °C.[41,42,153].

In systems involving the oxygen activation mechanism, there is a possibility of the parallel catalysis of the decomposition of the hydroperoxides formed in the course of the reaction.

The composition of the cumene oxidation products in the presence of M-Pc at 80 °C and the catalytic activity of M-Pc depend on the nature of the metal (Table 14). In the case of Mn-, Fe-, and Co-Pc, the main reaction products result from the decomposition of cumenyl hydroperoxide: carbinol and acetophenone; in the case of Cu-, Zn-, and Mg-Pc, cumenyl hydroperoxide is virtually the only product; in the presence of Ni-Pc, the main product is cumenyl hydroperoxide but a certain amount of carbinol and acetophenone is also formed.

Table 14. The compositions (%) of the products of the oxidation of cumene catalysed by M-Pc at 80 °C over a period of 10 h.[154]

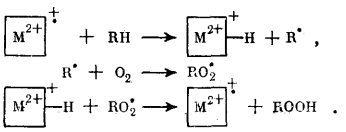
M	Mn	Fe	Co	Ni	Cu	Zn	Mg
Conversion of cumene	63.1	70.3	77.1	42.2	12.9	14.2	10.3
Hydroperoxide	17.9	12.4	5.8	31.7	12.9	14.2	10.3
Carbinol	31.8	40.8	50.0	9.0	0	0	0
Acetophenone	13.4	17.1	21.3	1.5	0	0	0
Selectivity with respect to hydroperoxide*	28.4	17.6	7.5	7.5	>98	>98	>98

* The content (%) of cumenyl hydroperoxide in the oxidation products.

The Mn-, Fe-, and Co-Pc catalysts are extremely active, since, together with the activation of oxygen, they also catalyse the decomposition of hydroperoxides; Cu-, Zn-, and Mg-Pc are capable of activating oxygen but do not catalyse the decomposition of hydroperoxides; Ni-Pc occupies an intermediate position—it is involved to some extent in reaction (4). These data can be interpreted from the

standpoint of the influence of the central metal on the mechanism of the oxidation of M-Pc (see Section II). The variable-valence metal ion necessary for the catalysis of the decomposition of hydroperoxides is present only in Mn-, Fe-, and Co-Pc, whose oxidation-reduction cycle proceeds via the central metal ion, and in Ni-Pc, whose oxidation-reduction takes place partly by the same mechanism; Cu- and Zn-Pc cannot catalyse the decomposition of hydroperoxides because their oxidation-reduction cycle proceeds only via the phthalocyanine ligand.

According to Manassen[155], the M-Pc whose oxidation involves a change in the valence of the metal ion catalyse the oxidation of cumene at elevated temperatures via the decomposition of the hydroperoxide, while the M-Pc whose oxidation proceeds via the ligand act as chain carriers:



Both mechanisms are possible for Ni-Pc.

V. CONCLUSION

The presence of an extensive π-conjugation system and of the central variable-valence metal ion in metalloporphine molecules gives rise to the possibility that they catalyse oxidation-reduction reactions via two alternative mechanisms: the donor mechanism, in which an electron is transferred in the course of the reaction from the catalyst to the oxidant, and the acceptor mechanism characterised by electron transfer from the substrate being oxidised to the catalyst molecule. The ratio of the oxidation-reduction potentials of the metalloporphine and the reactants of the reaction catalysed determines the mechanism of the catalysis in each specific system.

The presence of a variable-valence metal ion in the metalloporphine molecules also permits the initiation of the chain in the free-radical autoxidation by catalysing the decomposition of hydroperoxides via the Haber–Weiss mechanism.

Although porphyrin structures enter into the composition of oxidative enzymes and are active oxygen transferring agents in biological systems, synthetic metalloporphines catalyse under laboratory conditions as a rule the free-radical chain autoxidation. However, in certain systems the functioning of metalloporphines as agents transferring oxygen to the molecules of the substrate being oxidised is postulated. The search for such systems is of interest both from the standpoint of the elucidation of the mechanisms of enzyme catalysis and from the standpoint of the creation of new catalysts for the oxidation reaction which are selective as regards products.

We believe that studies in which the reaction is carried out in the presence of a suitable reductant, maintaining the catalyst in the reduced state, and the substrate being oxidised is activated with respect to nucleophilic attack by being coordinated to a suitable complex-forming agent merit attention. The employment of bimetallic porphyrin systems of the type obtained in a number of studies[156–161], one of the metallic centres of which (the donor) activates oxygen and the other (the acceptor) activates the substrate being oxidised, may also prove promising.

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