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# Catalysis by Metalloporphyrins of Reactions Involving Oxidation by Molecular Oxygen and Oxygen-containing Compounds

N.S.Enikolopyan, K.A.Bogdanova, L.V.Karmilova, and K.A.Askarov

Data on the catalysis by metalloporphyrins of reactions involving the oxidation of organic compounds by molecular oxygen, iodosobenzene, sodium hypochlorite, hydroperoxides, and peracids are surveyed and analysed. The possible mechanisms of the catalytic action of metalloporphyrins in these systems are proposed. The promising trends in the research designed to create, on the basis of metalloporphyrins, new catalytic systems for the selective oxidation of organic compounds under mild conditions are outlined.
The bibliography includes 188 references.

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## I. INTRODUCTION

Metalloporphyrin compounds[1-26] constitute the prosthetic groups in many enzymes—oxygenases, peroxidases, and others.[27-34] In particular, haemin forms part of the composition of cytochromes P-450, which are responsible for the detoxication of living organisms and which effect the hydroxylation of saturated and aromatic hydrocarbons and the epoxidation of olefins by molecular oxygen in their cells. The unique structure of metalloporphyrins, which contain the planar porphyrin ring with an extensive $\pi$-conjugation system and a central variable-valence metal ion,[7,8,35,36] determines their high catalytic activity. Oxygen-containing compounds such as hydroperoxides[37-43] and iodosobenzene[44-47] can successfully replace oxygen as the corresponding electron donor [acceptor] in selective oxidation reactions catalysed by cytochromes P-450.

The problem of modelling the catalytic functions of cytochromes P-450 by synthetic metalloporphyrins is of crucial importance at the present time. Its solution will make it possible to create new catalytic systems for the selective oxidation of organic compounds by molecular oxygen under mild conditions. The development of highly selective industrial methods of synthesis of epoxides and alcohols is an important task in present day chemistry.

One of the central aspects of the relevant research involves the study of the mechanisms of the catalytic action of metalloporphyrins in reactions involving the oxidation of organic substrates by molecular oxygen and oxygen-containing compounds. The understanding of these mechanisms will assist

in the further development of studies designed to create new effective catalytic systems, based on metalloporphyrins, for selective oxidation. Furthermore, investigation of the mechanisms of the catalytic action of synthetic metalloporphyrins should help in understanding the mechanisms of the action of porphyrin-containing enzymes which have not so far been elucidated. This is very important not only for the development of biochemistry but also for chemotherapy.

The possible mechanisms of the catalytic action of metalloporphyrins in the oxidation of organic compounds by molecular oxygen, iodosobenzene, sodium hypochlorite, hydroperoxides, and peracids are proposed in this review on the basis of current ideas and the analysis of experimental data for such systems.

## II. REACTIONS INVOLVING MOLECULAR OXYGEN

The results of studies of the catalysis by metalloporphyrin complexes of reactions involving oxidation by molecular oxygen have already been surveyed.[25] Here we shall not consider these data again and the bibliography of the previous review will be merely supplemented by a number of publications[24,48-89] and the possible mechanisms of these reactions will be discussed.

As a rule, metalloporphyrins initiate the radical chain autoxidation of organic substrates (alkanes, olefins, and aldehydes) via the following mechanism. Molecular oxygen is coordinated to the metal ion of the metalloporphyrin (P–M), forming a charge-transfer complex whose electronic structure depends on the nature of the metal. This can be both a superoxide complex, for example (Py)TPhP-$Co^{3+}...O_2^-$ [90-98] (where Py = pyridine and TPhP = tetraphenylporphin ligand) and a peroxide complex, whose formation has been suggested for TPhP-$Mn^{4+}...O_2^{2-}$.[98-101] These complexes initiate the chain in the autoxidation of organic substrates, abstracting the mobile hydrogen from the latter:

$$P\text{-}M^+ \ldots O_2^- + RH \rightarrow P\text{-}M^+ \ldots O_2H^- + R^\cdot ,$$

where RH is the oxidisable substrate. In the case of olefins, the initiation of the autoxidation is also possible as a result of the addition of the superoxide (or peroxide) complex to the double bond:

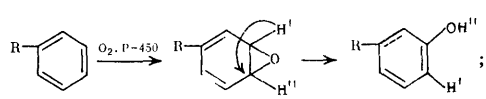
$$P\text{-}M^+ \ldots O_2^- + \rangle C{=}C\langle \rightarrow -\overset{|}{C}-\overset{|}{C}\cdot- \quad (-O-O-M^+\text{-}P)$$

Fe(III)-protoporphyrin (IX) (haemin) is known to occur as the prosthetic group in the composition of mono-oxygenating enzymes–cytochromes P-450 (the complexes of their reduced forms with carbon monoxide have a characteristic Soret absorption band at 450 nm). The nature of the axial ligand linked to haemin cannot be regarded as firmly established. It has been suggested that the iron ion in cytochrome P-450 is linked to cysteine and histidine residues.[27]

Cytochromes P-450 catalyse the following reactions involving oxidation by molecular oxygen:[102]

(1) hydroxylation of aliphatic hydrocarbons;

(2) hydroxylation of aromatic hydrocarbons with formation of an intermediate epoxidation product and the migration of hydrogen atoms:[103,104]



; (1)

(3) epoxidation of olefins;

(4) mono-oxygenation of sulphur- and nitrogen-containing organic compounds.

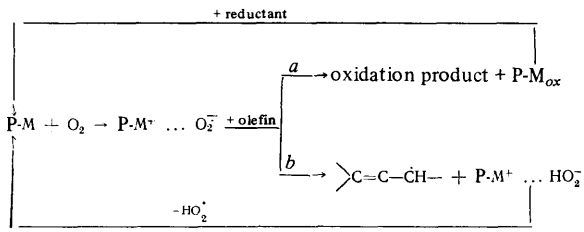
It is noteworthy that both in the cells of living organisms and under laboratory conditions cytochromes P-450 act as mono-oxygenating enzymes only in the presence of a reductant, which is necessary to reduce the second atom of the oxygen molecule to water. The overall equation of the mono-oxygenation reaction is:[102]

$$S + O_2 + DH_2 \rightarrow SO + D + H_2O ,$$

where S is the substrate and $DH_2$ the reducing agent. The respiratory chain of mitochondria, NADH (nicotinamide-adenine dinucleotide) or NADPH (nicotinamide-adenine dinucleotide phosphate), reduced flavins, and tetrahydropteridines can play the role of reductants.

It is striking that the modelling of the mono-oxygenating activity of cytochromes P-450 by metalloporphyrin complexes has been achieved only in the presence of a suitable electron donor. The results of these studies are presented in Table 1. Only in the presence of a reductant in the system does the metalloporphyrin act as an agent transferring one of the atoms of molecular oxygen to the oxidisable substrate. In the absence of a reductant, the free-radical chain autoxidation is initiated with formation of a set of products characteristic of this process.[110]

The mechanism of the processes occurring in model systems consisting of a metalloporphyrin, oxygen, and an oxidisable substrate can be represented as follows. A superoxide (or peroxide) complex, which is capable of initiating the free-radical chain oxidation by abstracting a mobile hydrogen atom from the substrate molecule (or by adding to the double bond of the olefin) (pathway *b* in the scheme below), is formed initially. In addition, the complex functions as an agent transferring oxygen to the oxidisable compound (pathway *a*), although this process cannot be regarded as truly catalytic because the metalloporphyrin is then converted into the oxidised form and is immediately eliminated from the system. The added reductant regenerates the active form of the metalloporphyrin and completes the catalytic cycle of the model oxygenation reaction. However, under these conditions there is a possibility of the formation of secondary products via the interaction of the oxidation product with the reductant.




The model mono-oxygenating systems are much less active than the natural enzymes. Thus in the presence of TPhP-MnCl the yields of the olefin oxidation products range from 3 to 32% after 24 h and between 1.7 and 32 catalytic cycles are accomplished during this period (Table 1). TPP-MnCl is most active in the oxidation of steroids, where 170–230 catalytic cycles take place in 1–3 h and the yield of the product reaches 78–82%.[48,49] The activity of haemin in the oxidation of cyclohexane in an aqueous acetone medium is less than that of the natural hydroxylating system by a factor of 50,[108] while in the hydroxylation of aniline in a highly alkaline medium it is less by a factor of 4.[109] The higher effectiveness of natural cytochromes P-450 compared with the model systems is apparently associated with the fact that the protein component of the enzyme ensures the optimum spatial orientation of the substrate with respect to the oxygen complex of

haem and at the same time creates the optimum micro-environment for the active centre (for example, the necessary basicity).[109]

Table 1 shows that the character of the products and the selectivity of the oxidation reactions in the presence of the model catalytic system depend significantly on the nature of the reductant. A mild reducing agent, such as sodium ascorbate, makes it possible to achieve the epoxidation of olefins (cyclohexene, hex-1-ene, 2,3-dimethylbut-2-ene, and styrene) with 100% selectivity,[77] while in the presence of powerful reducing agents, namely sodium and tetra-n-butylammonium tetrahydroborates, the reaction usually results in the formation of a mixture of saturated alcohols and ketones[48, 49, 106] (only $\Delta^5$-steroids give rise to single products—5-α-hydroxysteroids).

Cyclohexene differs from other unsaturated hydrocarbons by the presence of allyl oxidation products—cyclohex-2-en-1-ol,[84, 105, 106] and cyclohex-2-en-1-one.[107] The influence of the nature of the reductant on the composition of the reaction products has also been traced in relation to cyclohexene: a

**Table 1.** Oxidation of organic compounds by oxygen at room temperature in the presence of TPhP-MnCl and a reductant.

| No. | Substrate | Reductant | Solvent | τ, h | Products | Yield, % | | Refs. |
|---|---|---|---|---|---|---|---|---|
| | | | | | | $\alpha_o$ | $\alpha_c$ | |
| 1 | Cyclohexene | $NaBH_4$ | Benzene–ethanol | — | Cyclohexanol | 2.0 | 1 224 | [105] |
| | | | | | Cyclohex-2-en-1-ol | 0.5 | 306 | |
| 2 | Cyclohexene* | $NaBH_4$ | THF | 48—130 | Cyclohexanol | 10 | 20 000 | [84] |
| | | | | | Cyclohex-2-en-1-ol | 0.2 | 400 | |
| 3 | Cyclohexene | $(NBu_4)BH_4$ | $CH_2Cl_2$ | 24 | Cyclohexanol | 16 | 1 600 | [106] |
| | | | | | Cyclohex-2-en-1-ol | 8 | 800 | |
| 4 | Cyclohexene** | $H_2$-colloidal Pt | Ethanol | 63 | Epoxycyclohexane | 19 | 6 470 | [107] |
| | | | | | Cyclohex-2-en-1-one | 13 | 440 | |
| 5 | Cyclohexene*** | Na ascorbate | Benzene–water (pH 8.5) | 10 | Epoxycyclohexane | — | 230 | [77] |
| 6 | Cyclo-octene | $(NBu_4)BH_4$ | $CH_2Cl_2$ | 24 | Cyclo-octanone | 20 | 2 000 | [106] |
| | | | | | Cyclo-octanol | 8 | 800 | |
| 7 | Oct-1-ene | $(NBu_4)BH_4$ | $CH_2Cl_2$ | 24 | 2-Octanone | 7 | 700 | [106] |
| | | | | | 2-Octanol | 9 | 900 | |
| 8 | Styrene | $(NBu_4)BH_4$ | $CH_2Cl_2$ | 24 | Acetophenone | 7 | 700 | [106] |
| | | | | | 1-Phenylethanol | 17 | 1 700 | |
| 9 | Styrene*** | Na ascorbate | Benzene–water (pH 8.5) | 10 | Styrene oxide | — | 600 | [77] |
| | | | | | 2-Phenylethanal | — | 80 | |
| 10 | 1-Phenylpropene | $(NBu_4)BH_4$ | $CH_2Cl_2$ | 24 | Propiophenone | 12 | 1 200 | [106] |
| | | | | | 1-Phenyl-1-propanol | 20 | 2 000 | |
| 11 | Ethylene | $NaBH_4$ | DMF | 24 | Ethanol | 3 | 167 | [48, 49] |
| 12 | Propene | $NaBH_4$ | DMF | 24 | 2-Propanone | 4 | 222 | [48, 49] |
| | | | | | 2-Propanol | 6 | 333 | |
| 13 | Hex-1-ene | $NaBH_4$ | DMF | 24 | 2-Hexanone | 9.8 | 975 | [48, 49] |
| | | | | | 2-Hexanol | 3.2 | 325 | |
| 14 | Hex-1-ene | $NaBH_4$ | Benzene–ethanol | 24 | 2-Hexanone | 2.0 | 110 | [48, 49] |
| | | | | | 2-Hexanol | 7.6 | 420 | |
| | | | | | 1,2-Epoxyhexane | 0.5 | 28 | |
| 15 | Hex-2-ene | $NaBH_4$ | DMF | 24 | 2-Hexanone | 6.0 | 600 | [48, 49] |
| | | | | | 3-Hexanone | 6.0 | 600 | |
| | | | | | 2-Hexanol | 1.5 | 150 | |
| | | | | | 3-Hexanol | 1.5 | 150 | |
| 16 | Hex-2-ene | $NaBH_4$ | Benzene–ethanol | 24 | 2-Hexanone | 0.5 | 26.6 | [48, 49] |
| | | | | | 3-Hexanone | 0.5 | 26.6 | |
| | | | | | 2-Hexanol | 5.2 | 287 | |
| | | | | | 3-Hexanol | 5.2 | 287 | |
| | | | | | 2,3-Epoxyhexane | 0.7 | 40 | |
| 17 | Hex-1-ene*** | Na ascorbate | Benzene–water (pH 8.5) | 10 | 1,2-Epoxyhexane | — | 30 | [77] |
| 18 | 2,3-Dimethylbut-2-ene*** | Na ascorbate | Benzene–water (pH 8.5) | 10 | 2,3-Epoxy-2,3-dimethylbutane | — | 340 | [77] |
| 19 | D-Androst-5-en-3β-ol | $NaBH_4$ | Benzene–ethanol | 2 | D-Androstane-3β,5α-diol | 78 | 22 000 | [48, 49] |
| 20 | D-Cholest-5-en-3β-ol | $NaBH_4$ | DMF | 2 | D-Cholestane-3β,5α-diol | 80 | 17 900 | [48, 49] |
| 21 | D-Cholest-5-en-3β-ol | $NaBH_4$ | Benzene–ethanol | 2 | D-Cholestane-3β,5α-diol | 82 | 23 000 | [48, 49] |
| 22 | Cyclohexane*** | Na ascorbate | Benzene–water (pH 8.5) | 10 | Cyclohexanol | — | 40 | [77] |
| | | | | | Cyclohexanone | — | 300 | |
| 23 | Cyclohexane**** | *o*-HS—$C_3H_4$—$CO_2H$ | Water–acetone | 0.4 | Cyclohexanol | 0.8 | 200 | [108] |
| | | | | | Cyclohexanone | 0.4 | 100 | |
| 24 | Heptane*** | Na ascorbate | Benzene–water (pH 8.5) | 10 | 4-Heptanone | — | 300 | [77] |
| | | | | | 3-Heptanone | — | 130 | |
| | | | | | 2-Heptanone | — | 70 | |
| 25 | Adamantane | $H_2$-colloidal Pt | Ethanol | 14 | 1-Adamantanol | 1.8 | 314 | [107] |
| | | | | | 2-Adamantanol | 0.2 | 36 | |
| | | | | | 2-Adamantanone | 0.12 | 21 | |
| 26 | Toluene*** | Na ascorbate | Benzene–water (pH 8.5) | 10 | Benzaldehyde | — | 400 | [77] |
| 27 | Aniline**** | NADH (or NADPH) | Water (pH > 11) | | *p*-Aminophenol | 1.5 | 300 | [109] |
| 28 | Cyclohexanol*** | Na ascorbate | Benzene–water (pH 8.5) | 10 | Cyclohexanone | — | 1 500 | [77] |
| 29 | 4-Heptanol*** | Na ascorbate | Benzene–water (pH 8.5) | 10 | 4-Heptanone | — | 1 300 | [77] |
| 30 | Benzyl alcohol*** | Na ascorbate | Benzene–water (pH 8.5) | 10 | Benzaldehyde | — | 8 700 | [77] |

Notation: τ is the reaction time and $\alpha_o$ and $\alpha_c$ are the yields of the product recalculated in terms of the compound oxidised and the catalyst respectively.

*The catalyst was OEP-RhCl, where OEP = octaethylporphyrin ligand.
**1-Methylimidazole was added to the system.
***Two-phase system containing a phase transfer agent (methyltrioctylammonium chloride).
****The catalyst was haemin.

mixture of cyclohexanol and allyl alcohol is obtained in the presence of $NaBH_4$,[105] when gaseous hydrogen and colloidal platinum are used, the products are epoxycyclohexane and an αβ-unsaturated ketone,[107] while epoxycyclohexane is formed on treatment with sodium ascorbate.[77] Saturated hydrocarbons are oxidised in the presence of the model catalytic systems with formation of alcohols and ketones.[77,107,108]

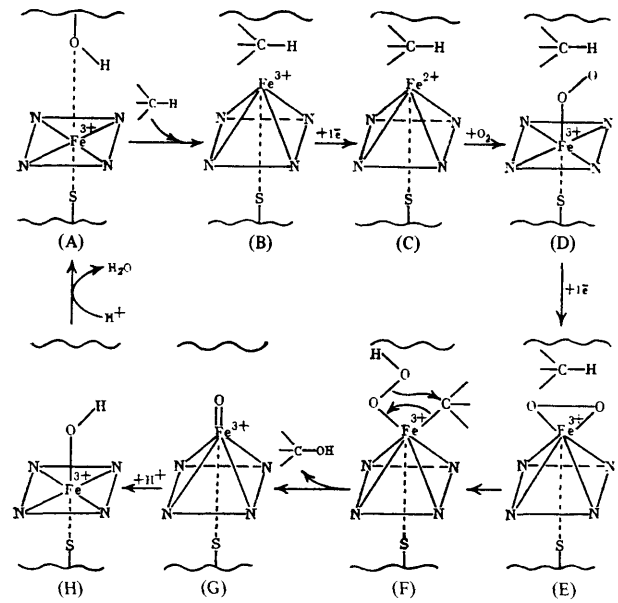
A characteristic feature of the oxidation of olefins on treatment with the model systems is an increase in the rate of reaction with increasing nucleophilicity of the double bond. Thus the rate of oxidation in the $O_2$–TPhP–MnCl–$NaBH_4$ system increases in the sequence ethylene < propene < hex-1-ene < hex-2-ene;[48,49] in the $O_2$-TPhP–MnCl–sodium ascorbate two-phase system containing a phase-transfer agent, the reactivity of olefins increases in the following sequence: hex-1-ene < cyclohexene < 2,3-dimethylbut-2-ene < styrene;[77] in the $O_2$–TPhP-MnCl–$(NBu_4)BH_4$ system 1-phenylpropene is more reactive than styrene;[106] in the $O_2$–TPhP-MnCl–$H_2$–colloidal platinum system, *cis*-oct-2-ene is oxidised approximately 18 times faster than hex-1-ene.[107] The very high reactivity of trisubstituted steroid olefins in oxidation by the $O_2$–TPhP-MnCl–$NaBH_4$ system cannot apparently be explained solely by the nucleophilic properties of the double bond. We shall return to this problem later. The analogous influence of electron-donating substituents on the rate of mono-oxygenation has been noted also for enzyme systems.[111]

Another feature of the oxidation of olefins in the presence of the model catalytic systems is the regioselectivity of the process. The oxidation involves the most substituted carbon atom: only secondary alcohols and ketones are formed from asymmetrically substituted olefins (oct-1-ene, styrene, 1-phenylpropene,[106] propene, and hex-1-ene[48,49]).

The third feature is the significant role of steric factors, which is indicated by the activity of *cis*-oct-2-ene being greater by an order of magnitude than that of its *trans*-isomer in the oxidation reaction catalysed by the $O_2$–TPhP-MnCl–$H_2$–colloidal platinum system.[107]

The mechanism of the action of hydroxylating enzyme systems based on cytochromes P-450 has not so far been established. The nature of the oxidising agent has not been determined by direct procedures in any of the systems. Several mechanisms have been discussed in the literature.[41,102,112–118] One of these, presented below (Scheme 1),[102] reflects in our view the electrophilic nature of the reaction most convincingly. The catalytic cycle begins with the conversion of the hexacoordinate $Fe^{3+}$ complex in a low-spin state (A) into a pentacoordinate $Fe^{3+}$ complex in a high-spin state (B) as a result of the binding of the hydrocarbon to be oxidised by the protein component of the enzyme. The one-electron reduction of compound (B) leads to a pentacoordinate $Fe^{2+}$ complex in a high-spin state (C) capable of binding oxygen with formation of a low-spin $Fe^{3+}$ superoxide complex (D). The states (A), (B), (C), and (D) have been thoroughly characterised,[115,119] but the mechanism of the transfer of oxygen from the complex (D) to the substrate being oxidised has not been finally elucidated.

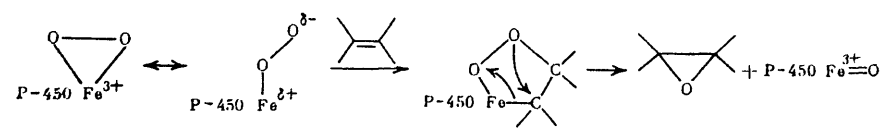
Scheme 1




The addition of a second electron to (D) can lead to the formation of the $Fe^{3+}$ peroxide complex (E). The mechanism of this addition has also not been established hitherto. Presumably the porphyrin ligand gives up an electron, being converted simultaneously into a porphyrin radical-cation. The heterolytic cleavage of the C–H bond is accompanied by the simultaneous opening of the $Fe^{3+}$–peroxo bond and leads to a very unstable alkyl $Fe^{3+}$ hydroperoxide (F), which decomposes with formation of the oxidation product – an alcohol and the $Fe^{3+}$ oxo-complex (G). The latter hydrolyses to the $Fe^{3+}$ hydroxo-complex (H), the initial complex (A), and water.

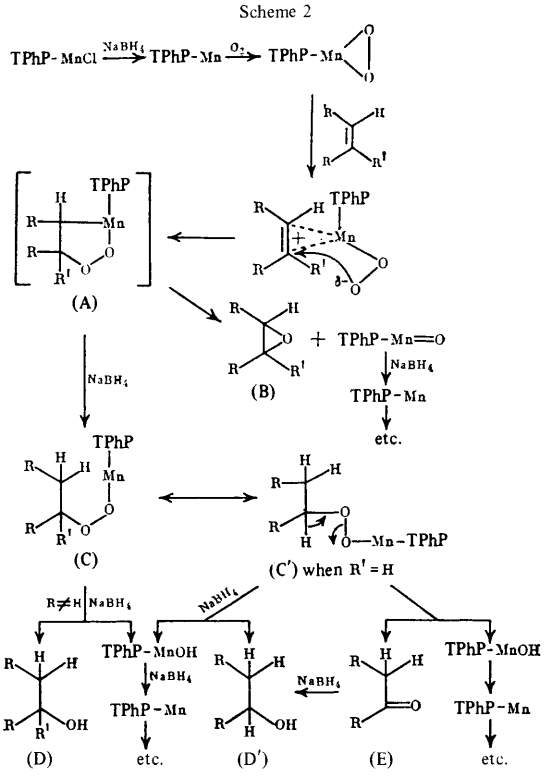
This mechanism agrees with the large isotope effect ($k_H/k_D$ = 11.5) in the norbornane hydroxylation reaction in the presence of cytochromes P-450,[120] which presupposes the activation and cleavage of the C–H bond. This scheme also agrees with the formation of the $Fe^{3+}$ oxo-complex, detected in the two-electron oxidation of chloroperoxidase.[121] The intermediate formation of the same complex has been postulated in the hydroxylation of hydrocarbons by hydrogen peroxide in the presence of iron ions.[122]

The mechanism of the epoxidation of olefins and aromatic compounds in the presence of cytochromes P-450 presupposes[102] the insertion of an olefin molecule in the 1,3-dipolar metal–peroxo bond of the complex (E) (Scheme 1) with formation of an intermediate five-membered ring, which decomposes into an epoxy-compound and an oxo-complex. Aromatic epoxides then rearrange to phenols.



A mechanism of the oxidation of olefins in the presence of the $O_2$–TPhP-MnCl–reductant model system has been proposed,[49] which takes into account all the characteristic features of this process, namely the influence of the nature of the reductant on the composition of the reaction products, the formation of a single product (a tertiary alcohol from trisubstituted olefins and a ketone and a secondary alcohol from mono- and di-substituted olefins) when powerful reductants are used, and the regioselectivity of the oxidation and the dependence of the rate of the latter on the nucleophilicity of the double bond and steric factors (Scheme 2).

Scheme 2




In the first stage of the process the reductant (in the given instance $NaBH_4$) converts TPhP-$Mn^{3+}$Cl into TPhP-$Mn^{2+}$, which interacts with molecular oxygen to form an oxygen complex having the peroxide structure: TPhP-$Mn^{4+}$...$O_2^{2-}$;[98-101] according to Hansen and Hoffman,[100] the $Mn^{4+}$ ion in this complex lies 0.5 Å above the plane of the porphyrin ligand. The nucleophilic olefin is coordinated to the most electrophilic component of this complex – the $Mn^{4+}$ ion, after which the olefin molecule is inserted in the dipolar Mn-peroxo bond with formation of the cyclic intermediate (A). The regioselectivity of the reaction is determined by the laws governing electrophilic addition. The epoxide (B) can be formed as a result of the disproportionation of the intermediate (A). When weak reductants are used, the epoxide is the only product of the reaction. However, in model systems containing a powerful reductant, the reductive cleavage of the Mn–C bond in the cyclic intermediate (A) apparently takes place with formation of a peroxide complex (C or C'). The subsequent reactions of this complex should depend on the degree of substitution of the carbon atom linked to the peroxy-group. The reduction of the O–O bond in the complex (C) with a tertiary carbon atom by sodium tetrahydroborate leads to the tertiary alcohol (D) and TPhP-MnOH, which enters into a new catalytic cycle. The peroxide complex for the secondary carbon atom (C') is capable, on the one hand, of being reduced by $NaBH_4$ to the secondary alcohol (D') and TPhP-MnOH and, on the other hand, it can disproportionate to the ketone (E) and TPhP-MnOH. An alternative pathway to the formation of secondary alcohols involves the reduction of the ketone (E) by sodium tetrahydroborate.

The order in which the Mn–C and O–O bonds are ruptured in the cyclic intermediate (A) is unimportant, since in both cases the ketone (E) and the alcohols (D) and (D') are formed as primary products without manganese.

Although this mechanism is so far only tentative, it must be emphasised that all its stages have reasonable analogies. Thus reactions involving the disproportionation of secondary peroxides to the carbonyl compounds (C') → (E) and the reduction of M–C bonds by tetrahydroborate (A) → (C) are known.[123,124]

Analysis of the products of the oxidation of olefins in the presence of model catalytic systems (Table 1) permits the conclusion that model systems containing milder reductants, for example, sodium ascorbate, are closer in their action to natural cytochromes P-450: the intermediate (A) disproportionates in their presence with formation of epoxy-compounds via the reaction (A) → (B).

The oxidation of tertiary olefins, in particular of the steroids D-androst-5-en-3β-ol and D-cholest-5-en-3β-ol, by the $O_2$-TPhP-MnCl–$NaBH_4$ system leads to a single product (corresponding to a tertiary alcohol) via the reaction (C) → (D), since the formation of a ketone is in this instance impossible. The high reactivity of steroids in this reaction is apparently associated not only with the enhanced nucleophilicity of the double bond owing to the presence of substituents but also with the reduced energy of the C=C bond owing to the strain in the molecular structure of the steroids. This facilitates the formation of the cyclic intermediate complex (A), i.e. diminishes the activation barrier to the reaction.

Presumably the oxidation of saturated hydrocarbons in the presence of metallo-porphyrin catalytic systems proceeds via the intermediate formation of a hydroperoxy-compound, which then decomposes and is converted into an alcohol or ketone. It may be that this mechanism is also responsible for the formation of the products of the allyl oxidation of cyclohexene by the $O_2$–TPhP-MnCl–$NaBH_4$ system.

In conclusion of this Section, it must be emphasised that the above mechanisms make it possible to regard the selective oxidation of hydrocarbons by molecular oxygen in the presence of cytochromes P-450 and synthetic metalloporphyrins as a special case of reactions which are accelerated in the presence of transition metal complexes and involves the insertion of a molecule of the coordinated substrate in the metal–nucleophile bond (polymerisation, hydrogenation, hydroformylation and other processes belong to reactions of of this kind).[125]

## III. OXIDATION BY IODOSO-COMPOUNDS

Metalloporphyrins catalyse the oxidation of hydrocarbons by iodosobenzene[126-134] without the involvement of reductants (Table 2). The results presented show that the catalytic effects of the Mn-porphyrins, on the one hand, and Fe- and Cr-porphyrins, on the other, are different. The difference is manifested in the first place in the composition of the reaction product. Fe- and Cr-porphyrins usually catalyse the selective epoxidation of olefins and the hydroxylation of saturated and aromatic hydrocarbons. Cyclohexene is an exception, being oxidised in the presence of Fe-porphyrins predominantly to an epoxide (75–95%) with formation of a small amount of cyclohex-2-en-1-ol (5–25%);[126,127] mainly

**Table 2.** Oxidation of hydrocarbons by iodosobenzene in the presence of metalloporphyrins at 25 °C in solution in $CH_2Cl_2$.

| Substrate | Catalyst | Products | W, % | α, %* | Refs. |
|---|---|---|---|---|---|
| Cyclohexene | TPhP-FeCl | Epoxycyclohexane | 78 | 70 (430)** | [126] |
| | | Cyclohex-2-en-1-ol | 22 | | |
| Cyclohexene | TPhP-FeCl | Epoxycyclohexane | 75 | 65 (650) | [127] |
| | | Cyclohex-2-en-1-ol | 25 | | |
| Cyclohexene | TFPhP-FeCl | Epoxycyclohexane | 95 | 100 (1000) | [126] |
| | | Cyclohex-2-en-1-ol | 5 | | |
| Cyclohexene | TPhP-CrCl | Epoxycyclohexane | 4 | 66 | [128] |
| | | Cyclohex-2-en-1-ol | 75 | | |
| | | Cyclohex-2-en-1-one | 21 | | |
| Cyclo-octene | TPhP-CrCl | Epoxycyclo-octane | 100 | 28 | [128] |
| Norbornene | TPhP-CrCl | Norbornene oxide | 100 | 90 | [128] |
| Sytrene | TPhP-CrCl | Styrene oxide | 100 | 65 | [128] |
| *cis*-Stilbene | TPhP-FeCl | *cis*-Stilbene oxide | 100 | 82 | [126, 129] |
| *cis*-Stilbene | TPhP-CrCl | *cis*-Stilbene oxide | 100 | 23 | [128, 129] |
| *cis*-Stilbene | TPhP-MnCl | *cis*-Stilbene oxide | 49 | 88 | [130] |
| | | *trans*-Stilbene oxide | 61 | | |
| *cis*-Stilbene | T(*o*-$CH_3O$-Ph) P-MnCl | *cis*-Stilbene oxide | 74 | | |
| | | *trans*-Stilbene oxide | 26 | 87 | [130] |
| *trans*-Stilbene | TPhP-FeCl | *trans*-Stilbene oxide | 100 | traces | [126, 129] |
| *trans*-Stilbene | TPhP-CrCl | *trans*-Stilbene oxide | 100 | 17 | [128, 129] |
| *trans*-Stilbene | TPhP-MnCl | *trans*-Stilbene oxide | 100 | 53 | [130] |
| Cyclohexa-1,3-diene | TPhP-FeCl | 1,2-Epoxycyclohex-3-ene | 100 | 74 | [126] |
| Cyclohexane | TPhP-FeCl | Cyclohexanol | 100 | 8 | [126] |
| Cyclohexane | TPhP-FeCl | Cyclohexanol | 100 | 5 (50) | [127] |
| Cyclohexane | TFPhP-FeCl | Cyclohexanol | 100 | 71 (710) | [127] |
| Cyclohexane | TPhP-MnCl | Cyclohexanol | 71 | 70 | [130] |
| | | Cyclohexyl chloride | 29 | | |
| Cyclohexane | TPhP-MnBr | Cyclohexanol | 65 | | |
| | | Cyclohexanone | 8 | 40 | [131] |
| | | Cyclohexyl chloride | 25 | | |
| | | Bicyclohexyl | 2 | | |
| Cyclohexane*** | TPhP-FeCl | Cyclohexanol | 91 | | |
| | | Cyclohexanone | 9 | 26.5 (530) | [133] |
| Cyclohexane*** | TPhP-MnCl | Cyclohexanol | 91 | | |
| | | Cyclohexanone | 9 | 33 (660) | [133] |
| Cyclohexane*** | TPhP-CrCl | Cyclohexanol | 50 | 8 (160) | [133] |
| | | Cyclohexanone | 50 | | |
| Cyclohexane*** | TPhP-CoCl | Cyclohexanol | 77 | | |
| | | Cyclohexanone | 23 | 6.5 (130) | [133] |
| n-Heptane*** | TPhP-FeCl | 2-Heptanol | 33 | | |
| | | 3-Heptanol | 38 | | |
| | | 4-Heptanol | 19 | 20 (400) | [133] |
| | | 2-Heptanone | 3 | | |
| | | 3-Heptanone | 4 | | |
| | | 4-Heptanone | 2 | | |
| Adamantane | TPhP-FeCl | 1-Adamantanol | 92 | 13 | [126] |
| | | 2-Adamantanol | 8 | | |
| Adamantane | TPhP-MnCl | 1-Adamantanol | 59 | | |
| | | 2-Adamantanol | 18 | | |
| | | 1-Chloroadamantane | 11 | 80 | [130] |
| | | 2-Chloroadamantane | 12 | | |
| Norcarane | TPhP-MnCl | 2-Norcaranol | 50 | | |
| | | 2-Hydroxymethylnorcarane | 20 | | |
| | | 2-Chloromethylnorcarane | 22 | — | [130] |
| | | 2-Chlorononcarane | 5 | | |
| | | 2-Norcaranone | 1 | | |
| Anisole**** | TPhP-FeCl | *o*-Methoxyphenol | 10 | | |
| | | *p*-Methoxyphenol | 50 | 2 | [127] |
| | | Phenol | 40 | | |
| Anisole**** | TFPhP-FeCl | *o*-Methoxyphenol | 26 | 11.4 | [127] |
| Anisole**** | TFPhP-FeCl | *p*-Methoxyphenol | 70 | 11.4 | [127] |
| | | Phenol | 4 | | |
| Anisole**** | TPhP-MnCl | Phenol | 74 | | |
| | | *p*-Methoxyphenol | 1 | 16.1 | [127] |
| | | Diphenyl ether of ethylene glycol | 25 | | |

Notation: TFPhP-FeCl = Fe-tetra(pentafluorophenyl)-porphin chloride; T(o-$CH_3O$-Ph)P-MnCl = Mn-tetra-(*o*-methoxyphenyl)porphin chloride; α = yield of products; *W* = proportion of product.

*Yield expressed as a percentage relative to iodosobenzene; the yield expressed in relation to the catalyst is given in brackets (our calculation based on the authors' data).

**The overall yield with respect to cyclohexene is 2.2%.

***Solution in benzene.

****Without a solvent.

cyclohex-2-en-1-ol (75%) is formed in the presence of TPhP-CrCl with a smaller amount of cyclohex-2-en-one (21%) and only 4% of epoxycyclohexane.[128] On the other hand, Mn-porphyrins catalyse the non-stereospecific epoxidation of stilbene[130] and the oxidation of saturated and aromatic hydrocarbons[127,130,131,133] with formation of a large set of products and, when the reaction is carried out in chlorinated solvents, chloro-products are also formed. Another difference between the effects of Mn-porphyrins, on the one hand, and Fe- and Cr-porphyrins, on the other, concerns the stereospecificity of the olefin epoxidation reaction. The epoxidation of *cis*-stilbene in the presence of TPhP-FeCl and TPhP-CrCl[126,128,129] results in the exclusive formation of *cis*-stilbene oxide: *trans*-stilbene is converted in the presence of TPhP-CrCl solely into the *trans*-oxide (the reaction does not occur in the presence of TPhP-FeCl). In this reaction the Mn-porphyrin catalysts[130] do not exhibit stereospecificity – a mixture of the *cis*- and *trans*-oxides is formed in the oxidation of *cis*-stilbene.

The above data permit the conclusion that the mechanisms of the catalytic action of Mn-porphyrins, on the one hand, and the Fe- and Cr-porphyrins, on the other, in the oxidation of hydrocarbons by iodosobenzene are different: Mn-porphyrins catalyse a radical process, while Fe- and Cr-porphyrins act as oxygen atom-transferring agents. The hydroxylating and epoxidising iodosobenzene–P-FeCl (or P-CrCl) system constitutes a functional model of cytochrome P-450. Additional evidence of this is provided by the following facts: the TPhP-FeCl–PhIO system is effective in the dealkylation reactions of *NN*-dimethylaniline[135] and anisole,[43,136] which are characteristic of cytochromes P-450;[43, 137,138] in the hydroxylation of anisole by iodosobenzene and TFPhP-FeCl, it has been established by the isotope tracer method that hydrogen atoms migrate[127] [see Eqn.(1)], which is characteristic of the hydroxylation of aromatic hydrocarbons in the presence of cytochromes P-450;[104] furthermore, iodosobenzene successfully substitutes molecular oxygen and the reductant in oxidation reactions catalysed by these enzymes.[44,47]

In the PhIO–P-MCl systems agents responsible for direct oxygen transfer to the substrate are oxo-complexes of metalloporphyrins containing the metal in a high oxidation state.[126,128-131,139-144] It has been shown that the reaction of P-MCl with PhIO results in the formation of iodobenzene (absorption bands at 1018 and 999 $cm^{-1}$ appear in the infrared spectra)[128,129] and the oxo-complex of the metalloporphyrin (the absorption band at 1026 $cm^{-1}$ corresponds to the vibrations of the Cr=O bond[128] and that at 1060 $cm^{-1}$ to the vibrations of the Mn=O bond[145]). The addition of labelled water $H_2^{18}O$ to the PhIO–TPhP-CrCl system results in the disappearance of the 1026 $cm^{-1}$ band from the infrared spectrum and the appearance of a band at 982 $cm^{-1}$ corresponding to the vibration of the $Cr=^{18}O$ bond. When norbornene is introduced, the epoxide containing 94% of $^{18}O$ is formed. Special experiments demonstrated that PhIO is not involved in oxygen exchange with $H_2^{18}O$ under these conditions.

Analogous results have been obtained in the presence of TPhP-MnCl[130] and TMP-FeCl (TMP is the tetramesitylporphin ligand).[141] In addition, a reliable instance of the transfer of an oxygen atom to the substrate undergoing oxidation from an oxo-metalloporphyrin is known. This is the reaction involving the oxidation of substituted phosphine by *cis*-dioxomolybdenum(VI)-tetra-*p*-tolylporphin:[146,147]

$$T\,(p\text{-}CH_3\text{-}Ph)\,P\text{-}Mo^{VI}\!\!\begin{matrix}O\\O\end{matrix} + PR_3 \rightarrow T\,(p\text{-}CH_3\text{-}Ph)\,P\text{-}Mo^{IV}{=}O + OPR_3.$$

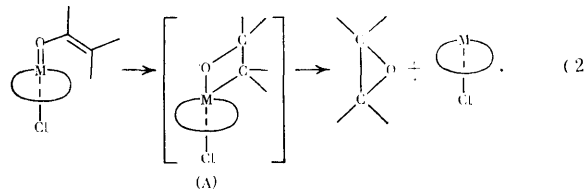
It has been shown recently[148] that the imido-complex of Mn-porphyrin effects direct oxidative amination of olefins, which leads to nitrogen-containing analogues of epoxides.

The oxo-complexes of metalloporphyrins formed when P-MCl interacts with iodosobenzene in solution in methylene chloride have been isolated at reduced temperatures; their structure and properties have been characterised by various methods (infrared, EPR, NMR, and Mössbauer spectroscopy, the spectroscopy in the visible region, and measurements of magnetic susceptibility.[128-131,140,141,149] The oxo-complex of chromium is stable at room temperature for several hours.[129] In the solid state the oxo-complex of manganese is stable for several days at 25 °C, but, on dissolution in aromatic and chlorinated hydrocarbons, it is rapidly reduced with formation of P-$Mn^{3+}$Cl.[130,131] Solutions of oxo-complexes of iron are unstable at room temperature.[140,141]

The entire set of data shows that the oxo-complexes of chromium and manganese contain a quintuply charged metal ion: Cl(TPhP)$Cr^{5+}$=O and Cl(TPhP)$Mn^{5+}$=O. However, it has been suggested[145] that, when TPhP-MnOAc reacts with iodosobenzene in solution in methanol, the oxo-complex of quadrivalent manganese, i.e. TPhP-$Mn^{4+}$=O, is formed. Study of the structure of the oxo-complex of iron,[141,150] permits the conclusion that it contains quadrivalent iron and the radical-cation derived from the porphyrin ligand: Cl(TMP)$^{\cdot}$. .$Fe^{4+}$=O. Although this structure does not in fact account for all the observed spectroscopic properties, it agrees with the results of a study[151] showing that the electrochemical oxidation of TPhPF$e^{4+}$(Cl)(OH) involves the porphyrin ligand and not the central metal ions; the process results in the formation of (TPhP)$^{\cdot}$F$e^{4+}$(Cl)(OH). This behaviour of Fe-porphyrin arises because, according to theoretical calculations,[152] the energies of the lowest *d* orbitals of the iron ion and the $a_{2u}$ orbitals of the TPhP ligand are similar. The energies of the *d* orbitals of the chromium and manganese ions are higher than those of the $a_{2u}$ orbitals of TPhP and these complexes are therefore oxidised with participation of the central metal ion. It is noteworthy that the spectrum of the oxo-complex of iron, obtained by Groves et al.,[141] is analogous to that of compound I of horseradish peroxidase.

The mechanisms of oxygen transfer from the oxo-complexes of Mn-porphyrin, on the one hand, and Cr- and Fe-porphyrins, on the other, are apparently different. The PhIO–P-CrCl (or P-FeCl) oxidising system is characterised, apart from the features described above, also by a high specificity of the reaction in relation to *cis*-olefins, which indicates a major role of steric factors. Thus the PhIO–TPhP-FeCl system oxidises a mixture of *cis*- and *trans*-stilbenes with formation of only *cis*-stilbene oxide in 80% yield; *cis*-but-2-ene is six times more reactive than *trans*-but-2-ene; *cis*, *trans*, *trans*-cyclododecatriene gives rise to a 2:1 mixture of the *trans*- and *cis*-epoxides (i.e. the reactivities of both types of bonds are approximately the same), while the oxidation of this compound by *m*-chloroperbenzoic acid results in the formation of 98% of the *trans*-isomer.[129] In addition, data have been obtained[128] showing an increase of the reactivity of olefins with increasing nucleophilicity of the double bond (the reaction rates increase in the sequence stilbene < styrene < norbornene).

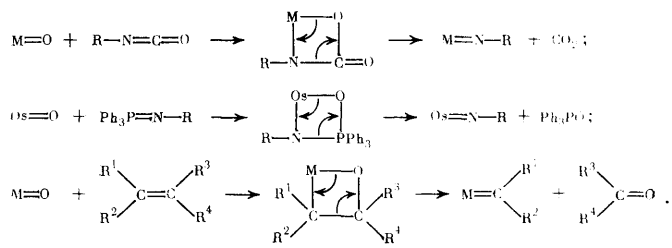
Taking into account all these features, one can put forward the following mechanism of the transfer of an oxygen atom from the oxo-complexes of Cr- and Fe-porphyrins to olefins. In the first stage an olefin molecule is coordinated to the central metal ion of the oxo-complex, after which the olefin is inserted in the metal–oxygen bond, with formation of a four-membered cyclic intermediate complex (A), which then disproportionates to the epoxide and a metalloporphyrin, the latter entering a new catalytic cycle:



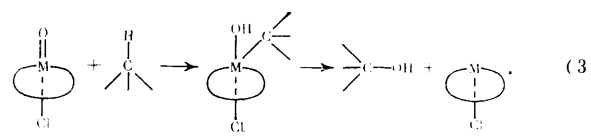
(2)

(A)

The formation of four-membered transition states has been postulated in a number of reactions of the oxo-complexes of metals,[102] including isocyanates, phosphine imines, and olefins:



The mechanism of the oxidation of saturated hydrocarbons by the oxo-complexes of Fe- and Cr-porphyrins can be represented analogously. The heterolytic cleavage of the C–H bond leads simultaneously to the rupture of the metal–oxygen bond. The complex (B) formed as a result of the reaction then decomposes into an alcohol and the metalloporphyrin:



(3)

(B)

It is difficult to account for the characteristic features of the cyclohexene oxidation reaction in the presence of Fe- and Cr-porphyrins, which deviates from this picture. An alcohol and even a ketone are formed together with the epoxide in the presence of Fe- and Cr-porphyrins, the proportions of the products being different in the two cases (Table 2). It may be that the competitive activation of the double bond [reaction (2)] and the allyl C–H bond [reaction (3)] takes place and the contributions of these reactions depend significantly on the nature of the metal in the oxo-complex.

According to the proposed mechanisms of the oxidation of olefins and alkanes by the oxo-complexes of Fe- and Cr-porphyrins, the transition complexes (A) and (B) are formed via reactions (2) and (3) without changes in the oxidation state of the metal ion but with dissociation of the M=O bond. Consequently the M=O bond in the porphyrin complex must be fairly labile in relation to heterolytic cleavage for reactions (2) and (3) to occur. There is reason to suppose that the M=O bond in the complex Cl(TPhP)Mn=O is more stable than in the corresponding iron and chromium complexes. The $Mn^{5+}$ ion is apparently more electrophilic than the $Cr^{5+}$ ion, since the $Mn^{5+}$ radius should probably be smaller than the $Cr^{5+}$ radius (in view of the lack of data for the dimensions of these ions owing to their extreme instability, we shall quote for the purposes of the comparison the radii of the $Mn^{3+}$ and $Cr^{3+}$ ions, which are respectively 0.62 and 0.64 Å or 0.68 and 0.71 Å.[153] Consequently the $Mn^{5+}$=O bond should be stronger than the $Cr^{5+}$=O bond. This is confirmed by the infrared spectroscopic data for the corresponding oxo-porphyrin complexes of manganese and chromium. The

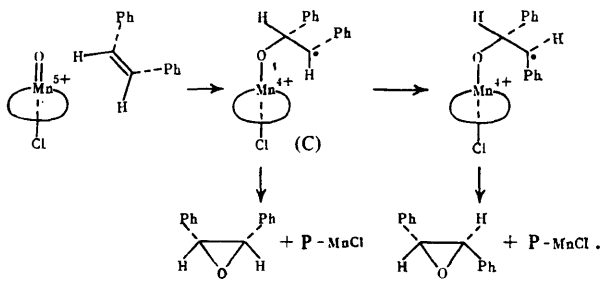
higher absorption frequency corresponding to the vibrations of the Mn=O group ($\nu$ = 1060 $cm^{-1}$)[143] compared with the Cr=O group ($\nu$ = 1026 $cm^{-1}$)[126,127] shows that the Mn=O bond is stronger and shorter. The quadrivalent iron ion present in the complex $Cl(TPhP)^{+}Fe^{4+}=O$ is less electrophilic than the quinquevalent manganese ion and the $Fe^{4+}=O$ bond is therefore stronger than the $Mn^{5+}=O$ bond. Although there are no infrared spectroscopic data for the vibration frequency of the $Fe^{IV}=O$ bond, the higher activity of $Cl(TPhP)^{+}Fe^{IV}=O$ compared with $Cl(TPhP)Cr^{V}=O$ in the olefin epoxidation reaction (Table 2), suggests that the $Fe^{IV}=O$ bond is more labile than the $Cr^{V}=O$ bond.

In the $Cr^{5+}$, $Mn^{5+}$, $Fe^{4+}$ series, the best oxidant should be the manganese ion, which is indicated by the calculated ionisation potentials (the following ionisation potentials correspond to the $M^{4+} - e \rightarrow M^{5+}$ process: 76V for M = Mn and 73 V for M = Cr; 56 V for the process $Fe^{3+} - e \rightarrow Fe^{4+}$.[154] (The oxidation-reduction potentials of the corresponding porphyrin complexes have not been determined.) This suggests that there is a possibility of the reduction of quinquevalent manganese in the oxo-complex which leads to a radical species. This can be represented conventionally in the following manner:

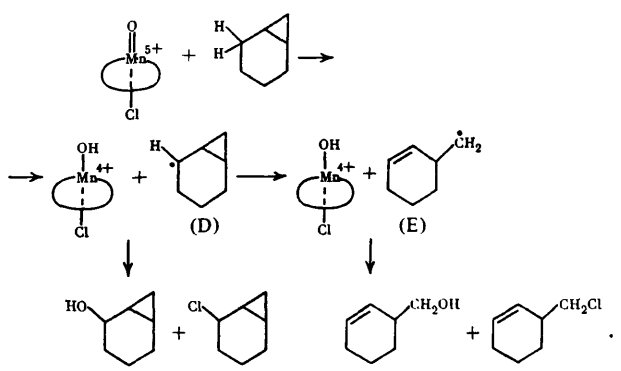
$$TPhP\text{-}Mn^{5+}\quad O \quad \cdot\cdot TPhP\text{-}Mn^{4+}\text{--}O\cdot .$$

Apparently these distinctive properties of the oxo-complex of Mn-porphyrin actually determine the radical mechanism of the transfer of an oxygen atom to the substrate undergoing oxidation, a characteristic feature of which is a change in the oxidation state of manganese on formation of the transition complex.

The homolytic rupture of the double bond of the olefin occurring in the reaction with (Cl)TPhP-Mn=O leads to the radical intermediate (C), the free rotation about the C–C bond in which is apparently responsible for the formation of a mixture of *cis*- and *trans*-isomeric products in the oxidation of *cis*-stilbene.[130]




On interaction with saturated hydrocarbons, the oxo-complex of the Mn-porphyrin apparently abstracts from them a mobile hydrogen atom. A tentative reaction mechanism is presented below for norcarane:[130]

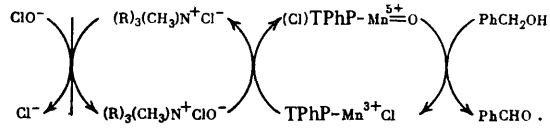



The norcaranyl free radical (D) formed can subsequently abstract one of the axial ligands from the complex TPhP-Mn.(Cl)(OH) or a chlorine atom from the chlorinated solvent and can also rearrange to the radical (E). The reactions of the radical (D) via several pathways are in fact responsible for the large assortment of reaction products.

It is seen from the foregoing that the specificity of the action of metalloporphyrins in the oxidation of hydrocarbons by iodosobenzene depends significantly on their structure and in particular on the nature of the central metal ion: thus, whereas Fe- and Cr-porphyrins catalyse selective oxidation, Mn-porphyrin initiates a radical process.

## IV. REACTIONS OF ORGANIC COMPOUNDS WITH SODIUM HYPOCHLORITE

Metalloporphyrins are also effective catalysts of the oxidation of organic compounds by sodium hypochlorite in immiscible solvents in the presence of a phase transfer agent[155–158] (Table 3). The use of a porphyrin catalyst combined with a phase transfer agent gives rise to a powerful synergistic effect. Table 4 shows that, in the absence of one of the components of the catalytic system, the rate of oxidation of benzyl alcohol is appreciably reduced. The function of the phase transfer agent consists in transporting the oxidising ion $ClO^{-}$ from the aqueous phase to the organic phase containing the substrate to be oxidised,[155] where the catalytic process actually takes place:




This oxidising system is very effective in the oxidation of alcohols and ethers to the corresponding aldehydes. Saturated hydrocarbons and olefins are oxidised fairly rapidly; for example, the degree of conversion of styrene in the presence of TPhP-MnOAc is 68% in 1 h,[156] the epoxide and other products being formed (Table 3).

The mechanism of the oxidation reaction involving sodium hypochlorite has not been investigated hitherto. However, one may suppose that it proceeds via the intermediate formation of the oxo-complex of the metalloporphyrin. Thus it has been shown[145] that the interaction of TPhP-MnOAc with NaClO results in the formation of a compound whose spectrum is analogous to that of the product of the reaction of TPhP-MnOAc with PhIO. Furthermore, the presence of chlorinated alkanes in the products of the oxidation of saturated hydrocarbons by the TPhP-MnCl–NaClO system[155] as well as the complete suppression of the reaction in the presence of the radical inhibitor 2,6-di-t-butyl-*p*-cresol[155] indicate a radical mechanism of the reaction. A similar mechanism is also characteristic of the TPhP-MnCl–PhIO system, which suggests that the active species involved in the two systems are identical.

## V. THE INTERACTION OF OLEFINS WITH HYDROPEROXIDES AND PERACIDS

The reactions involving oxidation by hydroperoxide compounds and peracids in the presence of metalloporphyrins and metallophthalocyanines[133,136,141,159–168] (Tables 5–7) apparently proceed with participation of active species of a different kind than in the case of iodoso-compounds and sodium

**Table 3.** Oxidation of organic substrates by sodium hypochlorite in immiscible solvents in the presence of metalloporphyrin catalysts and a phase transfer agent at 25 °C.

| Substrate | Catalyst | Solvent | Phase transfer agent | $\tau$, min | Products | W, % | $\chi$, % | Refs. |
|---|---|---|---|---|---|---|---|---|
| Styrene | TPhP-MnOAc | $CH_2Cl_2$:$H_2O$ = 2:1 | BMDAC | 180 | Styrene oxide<br>Other products | 45<br>55 | 80 (3200)** | [156] |
| Styrene*** | TPhP-MnOAc | $CH_2Cl_2$:$H_2O$ = 1:2 | BMDAC | 30 | Styrene oxide<br>Other products | 80<br>20 | 100 (16 000)** | [158] |
| Styrene | TPhP-FeCl | $CH_2Cl_2$:$H_2O$ = 2:1 | BMDAC | 180 | Styrene oxide<br>Other products | 6<br>94 | 33 (1340)** | [156] |
| Styrene | TPhP-CoBr | $CH_2Cl_2$:$H_2O$ = 2:1 | BMDAC | 180 | Styrene oxide<br>Other products | 11<br>89 | 53 (2120)** | [156] |
| Cyclohexene | TPhP-MnOAc | $CH_2Cl_2$:$H_2O$ = 2:1 | BMDAC | 180 | Epoxycyclohexane<br>Other products | 21<br>79 | 70 (2800)** | [156] |
| Cyclohexene**** | TPhP-MnOAc | $CH_2Cl_2$:$H_2O$ = 1:2 | BMDAC | 240 | Epoxycyclohexane<br>Other products | 85<br>15 | 95 (15 200)** | [158] |
| Cyclohexane | TPhP-MnCl | $CH_2Cl_2$:$H_2O$ = 3:2 | TOMAC | 20 | Cyclohexanone<br>Cyclohexyl chloride | 5<br>95 | 80 (1155) | [155] |
| Adamantane | TPhP-MnCl | $CH_2Cl_2$:$H_2O$ = 3:2 | TOMAC | 200 | 1-Chloroadamantane<br>1-Adamantanol<br>2-Chloroadamantane<br>2-Adamantanol<br>2-Adamantanone | 47<br>17<br>21<br>11<br>4 | 20 (430)** | [155] |
| Benzyl alcohol | TPhP-MnCl | $CH_2Cl_2$:$H_2O$ = 3:2 | TOMAC | 5 | Benzaldehyde | — | 94 (150) | [155] |
| Dibenzyl ether | TPhP-MnCl | $CH_2Cl_2$:$H_2O$ = 3:2 | TOMAC | 1 | Benzaldehyde | — | 85 (189) | [155] |
| Benzyl isopropyl ether | TPhP-MnCl | $CH_2Cl_2$:$H_2O$ = 3:2 | TOMAC | 1 | Benzaldehyde | — | 79 (239) | [155] |

Notation: BMDAC = benzyldimethyltetradecylammonium chloride; TOMAC = trioctylmethylammonium chloride.

*Yield relative to the substrate oxidised; the yield relative to the catalyst is given in brackets.
**Yield relative to the catalyst calculated by ourselves from authors' data.
***In the presence of added pyridine.
****In the presence of added 4-methylpyridine.

hypochlorite. This is indicated, in particular, by the dependence of the proportions of the oxidation products on the nature of the oxidant (Table 7). In addition, according to Groves et al.,[141] the interaction of tetramesitylporphinatoiron chloride (TMP.FeCl) with perbenzoic acid and iodosobenzene results in the formation of compounds of different nature, manifesting different reactivities in the epoxidation of olefins.

It has been suggested recently that the reactions involving the transfer of oxygen from peroxy-compounds to the substrate being oxidised, catalysed by cytochromes P-450, proceed via the formation of a cytochrome–peroxy-compound complex.[169-171]

**Table 4.** The rate constants for the oxidation of benzyl alcohol in immiscible solvents ($CH_2Cl_2$ : $H_2O$ = 3 : 2) at room temperature.[155]

| Oxidising system | $10^3 d[PhCHO]/dt$, mol litre $min^{-1}$ | $k$ |
|---|---|---|
| NaClO* | 1.5 | 0.0083 litre $mol^{-1}$ $min^{-1}$ |
| NaClO + TOMAC | 4.5 | 0.930 litre$^2$ $mol^{-2}$ $min^{-1}$ |
| NaClO + TPhP-MnCl | 4.4 | 1.460 litre$^2$ $mol^{-2}$ $min^{-1}$ |
| NaClO + TOMAC + TPh-MnCl MnCl | 65 | 375 litre$^3$ $mol^{-3}$ $min^{-1}$ |

*$3.6 \times 10^{-4}$ mol of NaClO in a mixture of 3 ml of $CH_2Cl_2$ and 2 ml of an aqueous solution of alkali (pH 12.8).

**Table 5.** Selectivity of the epoxidation of olefins by hydroperoxides and peracids in the presence of various metalloporphyrin and metallophthalocyanine catalysts.

| Olefin | Catalyst | Oxidant | $W_e$, % | Refs. |
|---|---|---|---|---|
| Cyclohexene | (Py)(Cl)(TPhP) Mo = O | $(CH_3)_3COOH$* | 68 | [159] |
| Cyclohexene | $(CH_3O)$(TPhP) Mo = O | $(CH_3)_3COOH$* | 84 | [159] |
| Cyclohexene | TPhP-$MoO_2$ | $(CH_3)_3COOH$* | 85 | [159] |
| Cyclohexene | Pc-$MoO_2$ | $(CH_3)_3COOH$ | >90 | [160] |
| Oct-1-ene | Pc-$MoO_2$ | $(CH_3)_3COOH$ | >90 | [160] |
| Cyclohexene | T(*p*-$CH_3O$-Ph) P-FeCl | $(C_6H_5)(CH_3)_2COOH$ | <1 | [161] |
| Cyclohexene | T(*p*-$CH_3O$-Ph) P-FeCl | (*m*-Cl-$C_6H_4$)$CO_3H$ | <1 | [161] |
| Cyclohexene | T(*p*-$CH_3O$-Ph) P-FeCl | (*p*-$NO_2$-$C_6H_4$)$CO_3H$ | <1 | [161] |

Notation: Pc = phthalocyanine ligand; $W_e$ = content of epoxide in products.
*In benzene at 80 °C.

In the selective epoxidation of cyclohexene, *cis*- and *trans*-hex-2-enes, and isoprene with t-butyl hydroperoxide in the presence of the Cl(TPhP)$Mo^{V}$=O catalyst, towards the end of the induction period a complex was detected in the system by spectroscopy in the visible region, to which the structure (t-Bu–O–O)(TPhP)Mo=O was attributed.[159]

All these factors suggest that the first stage in the oxidation of hydrocarbons by hydroperoxides and peracids in the presence of metalloporphyrins and metallophthalocyanines is the formation of a catalyst–oxidant complex:

$$P\text{-}M^{n+} + ROOH \rightleftarrows [P\text{-}M^{n+}\cdot ROOH].$$

Such complexes have been described in the literature – these are the complexes of tetra(*p*-methoxyphenyl)porphinatoiron chloride T(*p*-$CH_3O$-Ph)P-FeCl with cumenyl hydroperoxide and substituted perbenzoic acids,[161] of T(p-X-Ph)P-Co (X = $OCH_3$, H, or Cl) with 1,2,3,4-tetrahydro-1-naphthyl, 1-methyl-1-phenylethyl, and t-butyl hydroperoxides,[172] of tetramesitylporphinatomanganese chloride with *m*-chloroperbenzoic acid,[173] and of Pc-Cu with cumenyl hydroperoxide.[174] In the last case it is assumed that the copper ion is not directly involved in the formation of the complex and that the complex formation reaction proceeds via the phthalocyanine ligand.[175]

The porphyrin and phthalocyanine complexes of molybdenum exhibit a high selectivity and stereospecificity in the epoxidation of olefins by hydroperoxides[159,160] (Table 5): the epoxidation of *cis*- and *trans*-hex-2-ene by t-butyl hydroperoxide in the presence of Cl(TPhP)Mo=O results in the formation of 97 and 99% of the *cis*- and *trans*-2,3-epoxides respectively;[159] the rate of epoxidation then depends on the nature of the olefin and increases with increasing nucleophilicity of the double bond.[160] On the other hand, in the presence of Fe-porphyrin catalysts the oxidation of olefins by hydroperoxides and peracids leads to the preferential formation of allyl oxidation products – unsaturated alcohols and ketones, and the content of epoxides is less than 1%[161] (Table 6).

Table 6. Dependence of the proportions of the cyclohexene oxidation products on the nature of the oxidant (catalyst–tetra-*p*-methoxyphenylporphinatoiron chloride).[161]

| Oxidant | Proportions of products, % | | |
|---|---|---|---|
| | epoxycyclohexane | cyclohex-2-en-1-one | cyclohex-2-en-1-ol |
| $(C_6H_5)(CH_3)_2CO_2H$ | 1 | 18 | 81 |
| $(m\text{-}Cl-C_6H_4)CO_3H$ | 1 | 59 | 40 |
| $(p\text{-}NO_2-C_6H_4)CO_3H$ | 1 | 51 | 49 |
| $C_6H_5IO$ | 20 | 12 | 67 |

The complex of the metalloporphyrin or metallophthalocyanine with the hydro-peroxy-compound formed in the reaction system is converted via two pathways. On the one hand, it can epoxidise the olefin via a heterolytic mechanism (the oxidation state of the central metal ion does not change):

$$[P\text{-}M^{n+} \cdot ROOH] + \text{>C=C<} \rightarrow \text{>C(O)C<} + ROH + P\text{-}M^{n+}, \quad (4)$$

and, on the other hand, there is a possibility of the homolytic decomposition of the hydroperoxide via the following oxidation-reduction process:

$$[P\text{-}M^{n+} \cdot ROOH] \rightarrow P\text{-}M^{(n-1)+} + RO_2^{\cdot} + H^+, \quad (5)$$

followed by the oxidation of the olefin via a radical mechanism.

It is noteworthy that a homolytic oxidation pathway is postulated together with the heterolytic pathway in the reactions involving the oxidation of organic substrates by hydroperoxides and peracids and catalysed by cytochromes P-450.[40,45,115,176–179]

The selectivity of the epoxidation of olefins is determined by the relative contributions of the two competing pathways (4) and (5). The ratio of the Lewis acidity and oxidising capacity of the central metal ion determines its preferential involvement in a particular reaction. The more pronounced are the acidic properties of the metal ion the higher is the activity which it should exhibit in the heterolytic epoxidation reaction [reaction (4)] and the higher its oxidation-reduction potential the more effective should be its involvement in reaction (5). Electron-accepting substituents in the porphin ring of the catalyst and electron-accepting *trans*-ligands should enhance the acid properties of the central metal ion and hence should increase the activity of the catalyst in reaction (4).

Table 7. Dependence of the proportions of cyclohexane oxidation products on the nature of the oxidant.

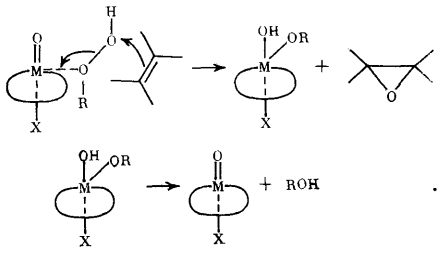
| Catalyst | Oxidant | Proportions of products, % | | Overall yield, % | Refs. |
|---|---|---|---|---|---|
| | | cyclohexanol | cyclohexanone | | |
| TPhP-FeCl | $(CH_3)_3CO_2H$ | 66.5 | 33.5 | 32 | [162] |
| TPhP-FeCl | $(C_6H_5)(CH_3)_2CO_2H$ | 67 | 33 | 60 | [162] |
| TPhP-MnCl | $(C_6H_5)(CH_3)_2CO_2H$ | 67.5 | 32.5 | 37 | [133] |
| TPhP-CoCl | $(C_6H_5)(CH_3)_2CO_2H$ | 66.5 | 33.5 | 60 | [133] |
| TPhP-CrCl | $(C_6H_5)(CH_3)_2CO_2H$ | 72 | 28 | 46 | [133] |
| TPhP-FeCl | $C_6H_5IO$ | 92 | 8 | 13 | [162] |
| TPhP-MnCl | $C_6H_5IO$ | 91 | 9 | 33 | [133] |
| TPhP-CrCl | $C_6H_5IO$ | 50 | 50 | 8 | [133] |
| TPhP-CoCl | $C_6H_5IO$ | 77 | 23 | 6.5 | [133] |

*Relative to the oxidant.

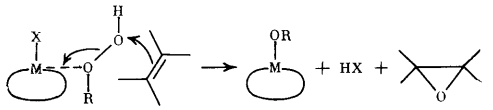
The higher selectivity of the epoxidation of olefins in the presence of the oxomolybdenum complexes of porphyrins and phthalocyanine compared with the Fe-porphyrin complexes (Table 5) is apparently associated with the fact that the $Mo^{5+}$ ion, linked to the electron-accepting oxo-group, possesses a much higher Lewis acidity than tervalent iron (according to theoretical calculations,[180] the effective charge on the iron ion in TPhP-FeCl is +0.27).

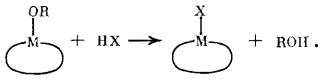
Oxomolybdenumporphyrins and oxomolybdenumphthalocyanines also catalyse the radical oxidation of olefins by a hydroperoxy-compound; this is indicated by the fact that the selectivity of the epoxidation is not 100% (Table 5). This finding agrees with the fairly high oxidising capacity of the catalyst–$E_{1/2}(Mo^{5+}/Mo^{4+})$ = +0.11 V relative to the saturated calomel electrode has been obtained for (OH).(TPhP)Mo=O in DMF[181] [under the same conditions, $E_{1/2}$.$(Fe^{3+}/Fe^{2+})$ = −19 V [sic] for TPhP-FeCl [181]]. Fe-porphyrins catalyse preferentially the homolytic cleavage of the peroxide linkage [reaction (5)] and are almost inactive in the epoxidation reaction [reaction (4)].

By analogy with the mechanism of the action of molybenum oxide and vanadium oxide catalysts,[160,182–185] the mechanism of the transfer of peroxide oxygen from the complex P-M.ROOH to the olefin can be represented as follows. The function of the catalyst consists in displacing the electron density from the peroxide oxygen atoms, which increases the electrophilicity of the hydroperoxide and thus activates it with respect to the electrophilic attack by the olefin double bond:



The oxo-group of the catalyst fulfills the role of an intramolecular proton acceptor. In the absence of the M=O group, this role is apparently assumed by the axial ligand.





The olefin is apparently not coordinated to the metal ion of the catalytic centre. The reactivity of olefins having bulky substituents is determined mainly by steric factors and not by the nucleophilic properties of the double bond. Thus the epoxidation of isoprene by t-butyl hydroperoxide in the presence of (Cl)(TPhP)Mo=O results in the formation of 3,4-epoxy-3-methylbut-1-ene and 3,4-epoxy-2-methylbut-1-ene in proportions of 0.7 : 1.0, whereas in the reaction where $Mo(CO)_6$ is used as the catalyst the ratio is 4 : 1.[159] Similar steric effects have been noted in the oxidation of phosphines in the presence of TPhP.$MoO_2$: it has been shown that the rate constant is sensitive not to the electron-donating properties of the substituents R in the $PR_3$ molecule but to their size.[146]

According to kinetic data,[160] the reactions involving the epoxidation of cyclohexene and oct-1-ene by t-butyl hydroperoxide in the presence of Pc-$MoO_2$ in methylcyclohexane are of first order with respect to the hydroperoxide, the olefin, and the catalyst, i.e. epoxidation in accordance with reaction (4) takes place preferentially in the system. Apparently, apart from the fact that Pc-$MoO_2$ exhibits only a weak activity in reaction (5), the homolytic decomposition of the hydroperoxide is inhibited by the olefin and the solvent.

After the formation of the primary radical via reaction (5), the hydroperoxide decomposition process proceeds via the following mechanism:

$$2RO_2^{\cdot} \rightarrow 2RO^{\cdot} + O_2;\ RO^{\cdot} + RO_2H \rightarrow ROH + RO_2^{\cdot}.$$

In the presence of a solvent SH containing active C–H bonds or of an olefin, the kinetic hydroperoxide decomposition chain terminates:[160]

$$RO^{\cdot}(RO_2^{\cdot}) + SH \rightarrow ROH\,(RO_2H) + S^{\cdot},$$
$$S^{\cdot} + RO_2^{\cdot} \rightarrow SO_2R \rightarrow \text{products},$$
$$S^{\cdot} + O_2 \rightarrow SO_2^{\cdot} \rightarrow \text{products},$$

or

$$RO^{\cdot}(RO_2) + -CH_2-CH=CH_2 \rightarrow ROH\,(RO_2H) + -\dot{C}H-CH=CH_2,$$
$$-\dot{C}H-CH=CH_2 + RO_2^{\cdot} \rightarrow -CH\,(O_2R)-CH=CH_2 \rightarrow \text{products},$$
$$-\dot{C}H-CH=CH_2 + O_2 \rightarrow -CH\,(O_2^{\cdot})-CH=CH_2 \rightarrow \text{products}.$$

Indeed the rate of decomposition of t-butyl hydroperoxide in benzene and chlorobenzene is 8 times higher than in cyclohexane and methylcyclohexane.[160]

The formation of the products of the allyl oxidation of olefins, characteristic of catalysts active in the homolytic decomposition of hydroperoxide [reaction (5)], can be represented as follows:

$$-CH\,(O_2R)-CH=CH_2 \xrightarrow{\text{catalyst}} -CH\,(\dot{O})-CH=CH_2,$$
$$2-CH\,(\dot{O})-CH=CH_2 \rightarrow -\underset{\underset{O}{\|}}{C}-CH=CH_2 + -CH\,(OH)-CH=CH_2.$$

It is known that peracids effectively epoxidise unsaturated hydrocarbons.[186,187] Thus the selectivity of the epoxidation of cyclohexene by *m*-chloro- and *p*-nitroperbenzoic acids via the stoichiometric reaction is very high, amounting to 82–92% (Table 8). The introduction of the Fe-porphyrin catalyst into the system alters sharply the composition of the oxidation product and lowers their epoxide content to 1%. This is associated with the fact that the active decomposition of the peracids via reaction (5) in the presence of T(OCH$_3$-.Ph)P-FeCl suppresses the epoxidation reaction.

**Table 8.** Proportions of the products of the oxidation of cyclohexene by peracids.[161]

| Catalyst | Oxidant | Yield*, % | Proportions of products, % | | |
|---|---|---|---|---|---|
| | | | epoxycyclohexane | cyclohex-2-en-1-one | cyclohex-2-en-1-ol |
| — | (*m*-Cl—$C_6H_4$)$CO_3H$ | 63 | 92 | 3 | 4 |
| | (*p*-$NO_2$—$C_6H_4$)$CO_3H$ | 86 | 82 | 9 | 8 |
| T(*p*-$CH_3O$-Ph)P-FeCl | (*m*-Cl—$C_6H_4$)$CO_3H$ | 60 | <1 | 59 | 40 |
| T(*p*-$CH_3O$-Ph)P-FeCl | (*p*-$NO_2$—$C_6H_4$)$CO_3H$ | 56 | <1 | 51 | 49 |

*Relative to the oxidant.

**Table 9.** The yield* (%) of the products of the oxidation of cyclohexane by cumenyl hydroperoxide.[162]

| Catalyst | TPhP-CoCl | TPhP-FeCl | THp-MnCl | TPhP-Os(CO)(Py) |
|---|---|---|---|---|
| Cyclohexanol | 45 | 40 | 1 | 5 |
| Cyclohexanone | 23 | 20 | 0.5 | 2.5 |

*Relative to the hydroperoxide.

According to Mansuy and coworkers,[133,162] TPhP-FeCl, TPhP-CoCl, and TPhP-RhI effectively catalyse the oxidation of cyclohexane by cumenyl hydroperoxide with formation of cyclohexanol and cyclohexanone in proportions of 2 : 1. (CO)(Py)(TPhP)Os, TPhP-CrCl, and TPhP-MnCl show a lower activity in this reaction, while $Cu^{II}$–, $Ni^{II}$–, $Zn^{II}$–, and $Mg^{II}$-TPhP, TPhP-$V^{IV}$=O, and TPhP-$Ti^{IV}$=O are inactive (Table 9). It has been observed that Fe-porphyrins catalyse the oxidation of n-heptane by cumenyl hydroperoxide[133] with formation of alcohols and ketones. Presumably in these systems, the hydroperoxide undergoes homolytic decomposition via reaction (5) with subsequent involvement of cyclohexane and n-heptane in the radical process. This is indicated by a number of factors – the rapid decomposition of cumenyl hydroperoxide at the beginning of the reaction[162] and the activity of only those catalysts whose central metal ion is capable of undergoing a change in the oxidation state, which is essential for the occurrence of reaction (5). Indeed the central metal ion is involved in the oxidation-reduction cycles of Cr-, Mn-, Fe-, Co-, and Os-porphyrins, while the oxidation-reduction of Cu-, Zn-, Mg-, TiO-, and VO-porphyrins involves the porphyrin ring. In the case of TPhP-Ni the $Ni^{2+}$ ion and the TPhP ligand are oxidised at the same potential (Table 10); according to Yamada and Kamiya,[172] TPhP-Ni and TPhP-Cu do not form complexes with hydroperoxides. Furthermore, the increase of the activity of the catalysts containing a tervalent metal ion with increase of their oxidising

capacity is consistent with the proposed homolytic decomposition of the hydroperoxide, i.e. TPhP-MnCl < TPhP-FeCl < TPhP-CoCl (Table 10).

Table 10. Oxidation-reduction potentials of metalloporphyrins ($E_{1/2}$, V)*.[181]

| Compound | Oxidation of ring | | Metal | Reduction of ring | |
|---|---|---|---|---|---|
| | $-2\bar{e}$ | $-\bar{e}$ | | $+\bar{e}$ | $+2\bar{e}$ |
| TPhP-CrCl | — | — | III/II—1.06 | —1.69 | —1.91 |
| TPhP-MnCl | — | — | III/II—0.23 | —1.52 | |
| TPhP-FeCl | — | 1.4** | III/II—0.19 | —1.61 | — |
| TPhP-Co | 1.26 | 1.06 | II/III+0.32 | —1.87 | — |
| TPhP-Ni | 1.40 | 1.10 | II/III+1.04 | —1.18 | —1.75 |
| TPhP-Cu | 1.16 | 0.90 | — | —1.20 | —1.68 |
| TPhP-Zn | 1.03 | 0.71 | — | — | —1.80 |
| TPhP-Mg | 0.86 | 0.54 | — | —1.35 | —1.80 |
| OEP-Ti = O | 1.32 | 1.03 | — | —1.21 | —1.69 |
| TPhP-V = O | 1.22 | 1.00 | — | —0.94 | —1.32 |
| OEP-Os(CO)(Py) | — | — | II/III+0.48 | — | — |

*Potentials relative to the saturated calomel electrodes; reduction in DMF or dimethyl sulphoxide; oxidation in $CH_2Cl_2$ or butyronitrile.
**Irreversible oxidation.

Thus the mechanism of the oxidation of olefins by hydroperoxides is determined by the nature of the metalloporphyrin or metallophthalocyanine catalyst – the acid and oxidation-reduction properties of the central metal ion determine the reaction pathway, which involves either the activation of the hydroperoxide for electrophilic attack on the olefin or the homolytic decomposition of the hydroperoxide and subsequent free-radical oxidation of the olefin.

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In conclusion, it must be emphasised that the presence in metalloporphyrin molecules of a central metal ion in different oxidation states and having in the *d* shell electrons with unpaired spins together with a planar porphyrin ligand having an extensive π-conjugation system gives rise to the possibility of a wide variety of different types of action by metalloporphyrins in reactions involving the oxidation of organic compounds by molecular oxygen and oxygen-containing oxidants: they can catalyse a selective oxidation reaction and can initiate free-radical oxidation.

The behaviour of metalloporphyrins in oxidation reactions depends very greatly on their structure, i.e. on the nature of the central metal ion and the porphyrin ligand. In particular, the replacement of the metal ion can alter radically the mechanism of the oxidation of organic substrates by oxygen-containing compounds.

Strictly speaking, metalloporphyrins are not true catalysts of the selective oxidation of organic compounds by molecular oxygen because a reductant is necessary for the regeneration of the catalyst and the completion of the catalytic cycle.

The reactions involving the epoxidation of olefins by iodosobenzene, sodium hypochlorite, and hydroperoxides, and other oxygen donors[188] in the presence of certain metalloporphyrins and phthalocyanines do not require a reductant and they can be regarded as truly catalytic.

The proposed mechanisms of the selective oxidation of organic substrates by molecular oxygen and iodosobenzene presuppose the formation of the peroxo- or oxo-complex of the metalloporphyrin respectively, the coordination of the substrate being oxidised to the metal ion in this complex, and its subsequent insertion in the metal-peroxo or metal-oxo bond. The porphyrin ligand apparently plays the very important role of an electron "buffer", stabilising the transition states of the catalytic process.

It is significant that the nature of the reductant determines the composition of the products of the oxidation of olefins by molecular oxygen. When weak reducing agents are used, the corresponding epoxy-derivatives are formed. Strong reductants effect the reductive cleavage of the M–C and O–O bonds in the cyclic intermediate complex, which leads to the formation of saturated alcohols and ketones.

From the standpoint of the solution of the problem of the creation of new catalytic systems for mild selective oxidation, we believe it is useful to investigate reactions involving the oxidation of organic compounds by molecular oxygen in the presence of metalloporphyrins and reductants. The choice of a suitable reductant is then crucial, since it determines the nature of the resulting oxidation product.

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Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow

Pavlov Samarkand Medical
Institute