

MONOOXYGENASE ACTIVITY OF METALLOPORPHYRINS AND MECHANISM  
OF ACTIVATION OF MOLECULAR OXYGEN

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Reaction rate constants have been measured for the oxidation of cholesterol by atmospheric oxygen in the presence of tetra-meso-substituted metalloporphyrins [MP] (M = Ni, Cr, Mn, Fe, Co). The results have been interpreted by the use of data on the structure of metal complexes and reaction mechanisms. It has been established that the reaction proceeds at a high rate when the oxygen in the composition of the intermediate complex [MO<sub>2</sub>P] is in the singlet spin state. The singlet state of O<sub>2</sub> is occupied in the case in which the metal ion in the porphyrin complex is in a high-spin state. The spin state and related catalytic activity of the metalloporphyrin is regulated by meso-substituents in the porphine ring. The influence of meso-substituents is predicted theoretically within the framework of a generalized orienting effect, the presence of which is supported by an analysis of <sup>13</sup>C NMR data for meso-substituted metalloporphyrins.

Activation of molecular oxygen is one of the decisive stages in enzyme oxidation processes that are catalyzed by monooxygenases [1]. Even though the most significant directions in the action, functions, and structure of monooxygenases have been studied in detail, one of the key questions remains essentially unanswered - the question of the mechanism of activation of molecular oxygen and the nature of the active species of oxygen that accomplishes the oxidation. Since synthetic metalloporphyrins (MPs) can activate molecular oxygen in the presence of a reducing agent, thus catalyzing oxidation reactions [2-4], these metalloporphyrins can be used as model compounds in studying the individual stages in the mechanism of monooxygenase action. In the work reported here, we investigated manganese, iron, and cobalt porphyrin complexes, similar in structure to the prosthetic group of monooxygenases. Experimental results on the variation of rate constant in the oxidation of cholesterol (Table 1) indicate that manganese porphyrin complexes differ substantially in catalytic activity from the complexes of other metals.

It had been shown previously that tetra-p-methoxyphenylporphinatomanganese chloride (TMPPMnCl) in the presence of excess sodium borohydride (NaBH<sub>4</sub>) catalyzes rapid and quantitative oxidation of cholesterol (cholest-5-en-3β-ol) to 3β-5α-cholestanediol [5]. The process is 100% regioselective and stereoselective. For aliphatic olefins with electron-donor substituents, the rate of such oxidation increases from monosubstituted to disubstituted and trisubstituted olefins, the process maintaining 100% regioselectivity throughout. The observed kinetic relationships in the oxidation process have been described within the framework of a formal kinetic scheme [6]. However, the source of the differences in catalytic activity of complexes of different metals remained unexplained, and this has provided the impetus for the present investigation. The only statements found in the literature are general hypotheses that the MP is coordinated either with molecular oxygen (with transfer of one or two electrons and the formation of a superoxo MO<sub>2</sub><sup>-</sup> or peroxo MO<sub>2</sub><sup>2-</sup> complex) or with the substrate (with partial transfer of electron density to the MP).

A general scheme for the mechanism of catalytic oxidation of olefins in the presence of MP is shown in Fig. 1. The first stage of olefin oxidation in the presence of MP and excess reducing agent has been described in [2, 7]; it consists of binding of atmospheric oxygen with a reduced metalloporphyrin complex, the nature of which is the decisive factor in determining whether the catalytic oxidation occurs at all. Reversible binding of oxygen

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TABLE 1. Specific Effective Rate Constant\* k for Oxidation of Cholesterol (0.1 M) by Molecular Oxygen (0.2 M) in the Presence of Transition-Metal Porphyrinates ( $6 \cdot 10^{-3}$  M) and Sodium Borohydride ( $5 \cdot 10^{-2}$  M) in Ethanol at Room Temperature

Porphyrin	k, liters/ mole·sec	Porphyrin	k, liters/ mole·sec
TPPMnOAc	0.48	TPPCo	0.017
TPPFeCl	0.07	TPPNi	0.01
TPPCrOAc	0.01		

\*Rate constants were determined from slope of kinetic curves for oxygen absorption at the start of oxidation.

by the manganese complex [TMPPMn(II)] at 203°K was registered in [8] by means of ESR. The total spin of the complex [TMPPMnO<sub>2</sub>] is 3/2, the unpaired electrons being localized to a considerable degree on the central ion [8, 9]. Double-bond addition of an olefin molecule to [TMPPMnO<sub>2</sub>] leads to the formation of an intermediate complex [TMPPMnO<sub>2</sub>(olefin)]. Decomposition of this complex, with the formation of the final products and the oxidized form of the catalyst [TMPPMn(III)]<sup>+</sup>, takes place only if the reducing agent BH<sub>4</sub><sup>-</sup> is present [6]. The complex [TMPPMn(III)]<sup>+</sup> is reduced to [TMPPMn(II)], thereby closing the catalytic cycle.

Porphinatocobalt(II) with atmospheric oxygen forms a complex with total spin 1/2, the unpaired electron being localized on the oxygen atom [10]. It is also known that the complex [TMPPCo] does not catalyze olefin oxidation under the conditions investigated [11]. The significant difference in catalytic activity between the complexes [TMPPCo] and [TMPPMn] in oxidation reactions is apparently related mainly to a difference in states in which the oxygen molecule exists in the complexes [TMPPCoO<sub>2</sub>] and [TMPPMnO<sub>2</sub>].

In order to elucidate the nature of these states, let us examine the mechanisms of interaction of a "free" O<sub>2</sub> molecule with olefins. Direct oxidation of an olefin by atmospheric oxygen through the double bond is forbidden by spin selection rules, since the ground state of the oxygen molecule is triplet (<sup>3</sup>Σ), and the reaction products are in the singlet spin state. Such reactions are known to proceed either very slowly or nonspecifically [12].

The reaction of singlet oxygen O<sub>2</sub>(<sup>1</sup>Δ) with olefins in the gas phase has been subjected to extensive theoretical study [13-16]. With a symmetrical position of the reactants (olefin double bond and oxygen), the following path has been proposed for the reaction of singlet oxygen with an olefin:

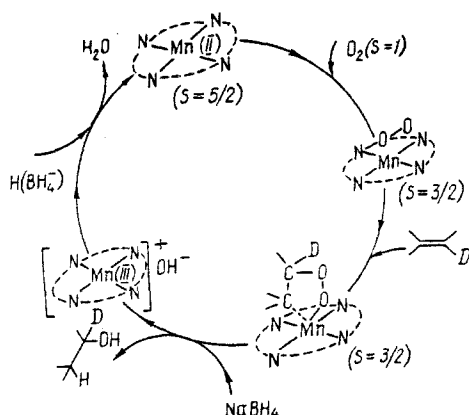
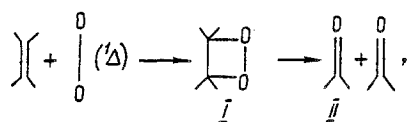
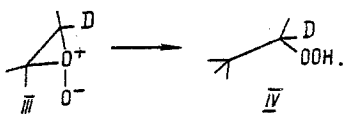
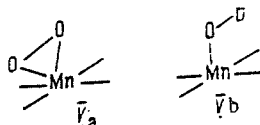


Fig. 1. Catalytic reaction cycle in oxidation of cholesterol (olefin) with the participation of Mn porphyrin.

proceeding with complete rupture of the C=C bond [14, 15]. Calculations show that with a nonsymmetrical position of the reactants relative to each other, the gas-phase reaction gives the primary product III, which decomposes through an ene mechanism:



Experiments reported in [17] support the possibility of such a mechanism, simultaneously demonstrating the presence of regioselectivity in the reaction of a free molecule of olefin with singlet oxygen. In an examination of features of geometric structure of complexes with oxygen, it was established in [18, 19] by means of ab initio calculations that of the two hypothetical structures of the intermediate complex [TMPPMnO<sub>2</sub>]



the "unsymmetrical" structure Vb is energetically more favorable. We have used these data in explaining the mechanism of the reaction we are considering.

We believe that the oxygen bound in the complex Vb in certain ratios is similar to free singlet oxygen O<sub>2</sub>(<sup>1</sup>Δ). Actually, from an analysis of the results obtained in quantum-chemical calculations and the results of experiments, we can conclude that all of the unpaired electrons are localized on the metal (or on the metalloporphyrin fragment) and that there is no spin density or appreciable negative charge on the O<sub>2</sub>, such that the oxygen molecule O<sub>2</sub> is, in effect, in the singlet state <sup>1</sup>Δ.

Our hypothesis is based on the following theoretical and experimental results. Ab initio calculations of individual electronic configurations of the complex [MnO<sub>2</sub>Por] have shown [18, 19] that the most energy-favorable electronic configuration is that with the structure Mn(III)O<sub>2</sub><sup>-</sup> with one unpaired electron on the O<sub>2</sub>. This result contradicts the experimental data reported in [8, 10, 20] on the distribution of spin density in the complex [TMPPMnO<sub>2</sub>], according to which the spin density on the O<sub>2</sub> is close to zero. It was established in [18, 19] that the electronically excited configurations of the complex [MnO<sub>2</sub>Por] that are the closest in energy correspond to structures of Mn(II)O<sub>2</sub> with zero spin density on the O<sub>2</sub>. At the same time, configurations with the structure Mn(IV)O<sub>2</sub><sup>2-</sup> correspond to far greater excitation energies. Since a more accurate calculation must take into account the interaction of all of the electronic configurations considered in [18] and their contributions to the ground state, which will be greater for configurations with lower energy, we can then conclude, when we consider experimental data on the spin state of O<sub>2</sub> in the complex, that the exact (true) state of [MnO<sub>2</sub>Por] corresponds to the structure Mn(II)O<sub>2</sub> without any appreciable charge transfer to O<sub>2</sub>.

This view of the electronic structure of the oxygen-containing manganese porphyrin complex is supported by semiempirical calculations of the complex [FeO<sub>2</sub>Por]. The results from a calculation of this complex in the PPP approximation, taking configuration interaction into account [21, 22], indicate that in this complex the O<sub>2</sub> is similar in certain characteristics (magnitude of bond order and near-zero charge) to molecular oxygen in the singlet spin state. According to these calculations, when the O<sub>2</sub>-Fe(Por) bond is formed, electrons are redistributed through the orbitals of O<sub>2</sub> and Fe(Por), the total population of the O<sub>2</sub> orbitals and 3d orbitals of Fe remaining practically unchanged. Such a redistribution of electrons among the orbitals is characteristic for chemical bonding of organic molecules with transition-element atoms, and it is reflected in the well-known model of Dewar, Chatt, and Duncanson [23].

Our hypothesis, that singlet oxygen coordinated on [TMPPMn] behaves (toward olefins with donor substituents) the same as a free molecule O<sub>2</sub>(<sup>1</sup>Δ), leads to the conclusion that interaction of the complex [TMPPMnO<sub>2</sub>] with an olefin begins with an attack of the bound oxygen on that one of the two C atoms of the olefin carrying the groups with greatest electron-donor properties (CH<sub>3</sub>, etc.). This explains the high regioselectivity of the olefin oxida-

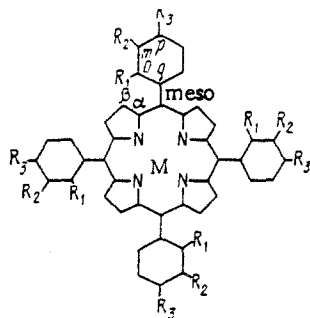
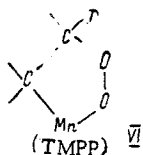


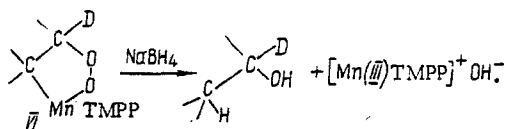
Fig. 2. Structure of meso-substituted metalloporphyrin [MTArylP]. Double bonds are not indicated; phenyl substituents are practically perpendicular to porphyrinato plane. Carbon atom notation the same as in [25]. When  $R_1 = R_2 = R_3 = H$ , the product is [MTPP]. The nature of the substituent depends on the selection of  $R_1$ ,  $R_2$ , and  $R_3$ ; when the carbon atom in the p-position is replaced by nitrogen, with  $R_3$  absent and with  $R_1 = R_2 = H$ , porphyrin No. 6 from Table 2 is obtained, etc.

tion process that we are considering. In this reaction, cholesterol behaves like an olefin, since the oxygen reacts with the solitary double bond  $C=C$  located on the periphery of the molecule. This position of the double bond in cholesterol sterically permits the complexes described below, which are formed upon coordination through the double bond.

The intermediate complex can be represented in the form



and its decomposition under the influence of the reducing agent, according to our hypothesis, is described by the following overall scheme:



On the basis of this analysis, the lack of any catalytic activity in this process in the case of porphyrin complexes of cobalt is explained on the basis that, in these complexes, the coordinated oxygen is not in a reactive singlet state. Promotion of the  $O_2$  molecule to the state  $^1\Delta$  can be accomplished only under the influence of a complex in which the metal is in the appropriate electronic state. It has been established experimentally that for the metals we have examined, the state with  $5/2$  spin is active. In [MP] complexes, the relative weight of the high-spin state ( $S = 5/2$ ) for complexes with  $M = Mn^{2+}$  or  $Fe^{3+}$  will depend on the meso-substituents and the axial ligands [24, 25]. Therefore, by changing the substituent in the meso-position of the porphyrin, the catalytic activity of complexes can be regulated.

Rate constants for the oxidation of cholesterol catalyzed by various manganese(II) porphyrins are listed in Table 2. In order to explain the dependence of the rate constant on the nature of the meso-substituent in compounds 1-8 (Table 2), we will examine, within the framework of the concepts set forth above, the mechanism through which influence is transmitted from a phenyl (or pyridyl) ring positioned nearly perpendicular to the porphyrinato ring (Fig. 2) to the transition-metal atom. It is known that an electronegative hetero atom in an alternant hydrocarbon molecule takes on a negative charge. When this happens, the electron density on the neighboring atom is reduced (an additional charge  $\delta_1^+ > 0$  appears), on

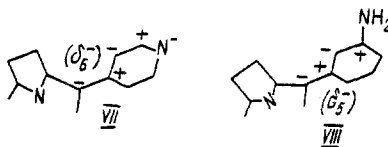
TABLE 2. Specific Effective Rate Constant  $k$  for Oxidation of Cholesterol ( $10^{-1}$  M) by Molecular Oxygen (0.2 M) in the Presence of Manganese Porphyrinates ( $6 \cdot 10^{-3}$  M)\*

No.	Porphyrin	$k$ , liter/mole·sec
1	Tetraphenylporphinatomanganese acetate	0.48
2	Tetra(p-methoxyphenyl)porphinatomanganese chloride	0.55
3	Tetra(p-aminophenyl)porphinatomanganese acetate	0.76
4	Tetra(o-aminophenyl)porphinatomanganese acetate	0.67
5	Tetra(m-aminophenyl)porphinatomanganese acetate	0.78
6	Tetra(p-pyridyl)porphinatomanganese acetate	1.03
7	Tetra(p-natriosulfonatophenyl)porphinatomanganese acetate	0.38
8	Tetra(p-N-iodopyridyl)porphinatomanganese acetate	0.51

\*In ethyl alcohol at room temperature.

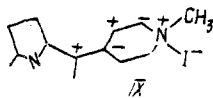
the next atom in line an additional charge  $\delta_2^- < 0$  appears, and so on, such that we can speak of the appearance of a wave of charge density. In the case of an electropositive hetero atom, this wave has the reverse sign.

A hetero atom in an aryl meso-substituent of the porphyrin creates a wave of charge density such that either a positive or negative charge will appear on the atoms of the pyrrole rings. The change in charge influences the spin state of the metal atom and hence affects the rate of the process catalyzed by the particular metal complex. Let us examine a fragment of porphyrin No. 6 from Table 2; we will compare the charge distribution on the atoms with the corresponding distribution in porphyrin No. 1, and we will direct our attention to the sign and magnitude of the expected addition to the charge on the  $C_{\text{meso}}$  atom:

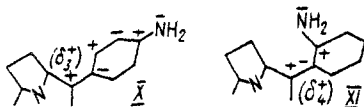


As can be seen from scheme VII, on  $C_{\text{meso}}$  we expect an addition to the charge  $\delta_6^- < 0$ . In porphyrin No. 5 (scheme VIII), we likewise find that a negative addition to the charge  $\delta_5^- < 0$ . The corresponding rate constants  $k_6$  and  $k_5$  are both greater than for the unsubstituted phenyl porphyrin 1. Thus, a negative addition to the charge on  $C_{\text{meso}}$  increases the rate constant  $k$  in the reaction under consideration.

In porphyrin No. 8, a  $\text{CH}_3$  group and an electronegative I atom are attached to the pyridine nitrogen atom) therefore, in comparison with porphyrin 6, a positive addition appears on the pyridine nitrogen atom and on  $C_{\text{meso}}$ :

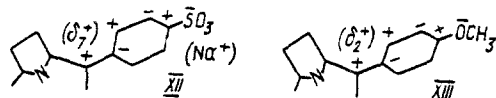


In this case, the relationship  $k_8 < k_6$  should be fulfilled, and this is in agreement with experiment. In para- and ortho-aminosubstituted porphyrins (Nos. 3 and 4 in Table 2), a positive additional charge appears on  $C_{\text{meso}}$  in comparison with porphyrin 1;  $\delta_3^+ > 0$  and  $\delta_4^+ > 0$ :



According to the rule that has been found, the oxidation rate constants should be lower for these porphyrins, but this is contradictory to experiment:  $k_3 > k_4 > k_1$ .

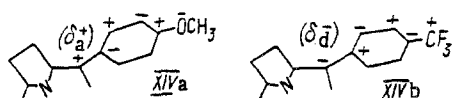
In the case of porphyrin 7 (scheme XII), the  $\text{SO}_3\text{Na}$  groups dissociate completely in solution, forming  $\text{SO}_3^-$ :



Therefore, on the sulfur atom in porphyrin 7, a negative charge appears, and on  $C_{\text{meso}}$  an additional positive charge  $\delta_7^+ > 0$ . This should lead to a decrease in the constant  $k$  in comparison with porphyrin 1, and this is supported by experiments:  $k_7 < k_1$ . In the case of  $\text{SO}_3\text{H}$  the electron density on the sulfur, in comparison with porphyrin 7, would be lower, and the rate constant ranking would be reversed. Finally, in porphyrin 2 (scheme XIII), an additional positive charge  $\delta_2^+ > 0$  appears on  $C_{\text{meso}}$ , such that we should find  $k_2 < k_1$ . Experiment indicates that  $k_2 > k_1$  (Table 2), so we have one more deviation from the established rule.

The correlation that we have found between the observed rate constant  $k$  and the type of substituent in the phenyl radical of tetrasubstituted porphyrins can be formulated in terms commonly used in the chemistry of benzene derivatives, as follows: The observed oxidation rate constant  $k$  will be higher to the degree that the  $q$ -position of the aryl radical of the tetra-meso-substituted porphyrin is more strongly deactivated with respect to electrophilic substitution in the aromatic series.

Propagation of a wave of additional charges through six or seven bonds in the system, with breakdown of continuous conjugation, is supported by experimental data [25] on measurements of  $^{13}\text{C}$  NMR chemical shifts on atoms of a chain of bonds between the hetero atom of a meso-substituent and  $C_{\text{meso}}$ . In [25], a study was made of porphyrin complexes  $[\text{TAr}1\text{PFe}(\text{III})]\text{ClO}_4$ ; in the notation of Fig. 2,  $M = \text{Fe}$ ,  $R_1 = R_2 = \text{H}$ ; and  $R_3$  is either (a)  $\text{OCH}_3$ , (b)  $\text{H}$ , (c)  $\text{Cl}$ , or (d)  $\text{CF}_3$ . In that study it was found that the influence of substituents in this series leads to a change in the spin state of the  $\text{Fe}(\text{III})$  complex, increasing the contribution of the state with spin  $S = 5/2$  (in a mixed state with spins  $S = 3/2$  and  $S = 5/2$ ). In the two extreme cases, the "waves of additional charges" are depicted by the schemes



The change to the high-spin state corresponds to a change from a positive ( $\delta_a^+ > 0$ ) to a negative ( $\delta_d^- < 0$ ) addition to the charge on  $C_{\text{meso}}$ ; for the Mn porphyrins examined above, this corresponds to an increase in the rate constant  $k$  in the oxidation of cholesterol (olefin).

Let us examine the chemical shifts on the carbon atoms of the  $\text{Fe}(\text{III})$  porphyrins in the series a-d [25]; we will estimate the general trend of change in chemical shift, using for this purpose the difference  $\Delta = \delta_d - \delta_a$  (in ppm), where  $\delta_a$  and  $\delta_d$  are the chemical shifts on the corresponding carbon atoms in XIVa and XIVd, the extreme members in the series a-d:

Carbon atom (see Fig. 2)	<i>p</i>	<i>m</i>	<i>o</i>	<i>q</i>	<i>meso</i>	$\alpha$	$\beta$
$\Delta$ , ppm . . . . .	-30	+16	~0	+13	-17	+300	+210
Additional charge (in XIVd) . . . . .	$\delta^-$	$\delta^+$	$\delta^-$	$\delta^+$	$\delta^-$	-	-

These data indicate that the introduction of stronger and stronger deactivators in the series a-d leads to additional chemical shifts, alternating along the chain of carbon atoms. This confirms the scheme of alternation of additional charges, since a correlation has been established in many examples [26] between the additional  $^{13}\text{C}$  NMR chemical shifts ( $\Delta_i$ ) and the ad-

ditional charge ( $\delta_i$ ) on the same carbon atom  $C_i$ , the correlation taking the form  $\Delta_i = \text{const} \cdot \delta_i$ . The anomalously large additional chemical shifts on the pyrrole carbon atoms are not related to large additional charges on these atoms, rather being determined by interaction of the transition metal with the paramagnetic ion. The large energies of these additional chemical shifts indicate a change in spin state of the paramagnetic center.

Within the framework of the proposed approach, the spin state of the transition-metal ion determines the catalytic activity of the complex. Therefore, the influence of meso-substituents in the porphinato ring on the spin state of the ion explains the change in catalytic activity of the complexes. Here we have not considered other effects due to replacement of meso-substituents. It is possible that the deviations we have noted from the established correlation are due specifically to such unaccounted effects such as interaction of meso-substituents with cholesterol and the influence of a polar solvent.

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ANALYSIS OF INFLUENCE OF SPIN RELAXATION ON FORM OF NUCLEAR  
MAGNETIC RESONANCE SPECTRA IN LIQUIDS WITH RADIOFREQUENCY PUMPING

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For a model system of two nonequivalent nuclei with spin 1/2, the NMR spectrum of one of the nuclei has been calculated under conditions of pumping of the second spin, and a study has been made of the spectral transformation upon changing the times of transverse and longitudinal relaxation of both spins. It has been established that the form of the spectrum undergoes qualitative changes. An increase in the rate of transverse relaxation not only broadens the observed lines, but simultaneously changes the character of motion of the spins in the pumping field: With increasing relaxation rate, the motion is converted from coherent motion (nutations) to incoherent motion (transitions between levels, saturation effect). Transformations of the spectrum are related specifically to these changes.

The theory of the form of NMR spectra when pumping is present is quite well developed; see for example [1-3]. The clearest manifestations of radiofrequency pumping are a merging of all components of the multiplet into one line (spin-decoupling) or splitting of NMR spectral lines with nonresonance pumping (tickling effect). The form of the NMR spectra observed in these experiments depends substantially on the rates of magnetic relaxation of the spins, playing a dual role. On the one hand, relaxation tends to disrupt the coherence of motion of nuclear spins in the pumping field, which is responsible for spin-decoupling and tickling. On the other hand, random turnovers of nuclear spins in the process of spin-lattice relaxation modulate the *jj*-interaction between nuclei. As a result, with a sufficiently high rate *w* of relaxation turnovers, such that *w* is greater than the constant of *jj*-interaction (*w* > *J*), the phenomenon of exchange narrowing appears: All components of the multiplet merge into a single narrow line.

Thus, the merging of lines of a multiplet into a single line may be achieved by modulating *jj*-interaction of spins, both by radiofrequency agitation (spin-decoupling) and by re-

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