Hypothesis

The mechanism of methane and dioxygen activation in the catalytic cycle of methane monooxygenase

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Abstract The binuclear structure of the active center of methane monooxygenase plays a determining role in dioxygen activation and in selectivity and specificity of alkane oxidation with this enzyme. A new mechanism is suggested for binding and activation of O_2, which involves side-on binding of O_2^{2-} to iron atoms followed by its conversion to the bis-μ-oxo complex considered as an alternative of ferryl in CH_4 activation. This mechanism results in the sequence of the cleavage of the O–O bond of peroxide O/O^{2-} instead of the opposite sequence O^{2-}/O, which takes place in the case of heme monooxygenase cytochrome *P*-450. Therefore, in this case there is no necessity of the charge relay system [N.B. Gerber and S.G. Sligar, J. Am. Chem. Soc. 114 (1992) 8742] for the transformation of O_2 to an active intermediate. The experiment for checking this hypothesis is suggested.

Key words: Methane monooxygenase; Alkane oxidation; Oxygen transfer catalysis; O_2 activation; CH_4 activation

1. Introduction

Monooxygenase oxidation processes play an important role in nature. Their high efficiency and selectivity are related to special mechanisms of O_2 activation and the oxygen transfer to a substrate involving biocatalyst monooxygenases.

$$S + O_2 \xrightarrow[\text{monooxygenase}]{2e^-,\ 2H^+} SO + H_2O \quad (S, \text{substrate})$$

These mechanisms make it possible to perform the oxygen transfer without free-radical chain processes due to the high degree of organization of active centers of natural catalysts. The existence of monooxygenase processes of alkane oxidation, especially of methane, which is the most inert alkane, is a serious challenge for chemists to create similar chemical systems that are capable of selective oxidation of these hydrocarbons under surrounding conditions, for example, $CH_4 + [O] \rightarrow CH_3OH$. The attempts to model biological methane oxidation have not yet been successful. To advance in this direction, it is very important to develop views about the ways of dioxygen and methane activation and about the nature of the active oxidant on the basis of new data on the structure and functioning of methane monooxygenase (MMO).

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2. Methane monooxygenase

Until recently, data on the structure of MMO have been based on spectral and magnetic studies of this enzyme [1]. It has been shown that the active center of MMO includes the binuclear μ-oxo-μ-carboxylate iron complex and is similar to the active centers of the oxygen-binding protein hemerythrin (Hr), a non-heme analog of hemoglobin, and to the redox enzyme ribonucleotide reductase (RNR), which participates in the synthesis of RNA. The X-ray structures of these centers are known [1,2] (Fig. 1). This conclusion has recently been confirmed by the first X-ray study [2,3] of soluble MMO from *Methylococcus capsulatus (Bath)*. As expected [4], the structures of MMO and RNR turned out to be sufficiently similar, involving the same NO_5-coordination of ligands around each iron atom (Fig. 1).

The establishment of the MMO structure gives a reliable ground for the discussion about the functioning of this enzyme and for a possibility of its adequate modelling. At the same time, the detailed study of hydroxylation mechanism allows the authors [5–7] to draw a conclusion that no unified mechanism can explain all of the data on MMO and several mechanisms are possible. In this work, an attempt is made to put forward a new concept for the mechanism of the MMO action, which provides a better explanation of some experimental data.

3. What can be an alternative for Fe = O in CH_4 activation?

It is accepted to consider that heme monooxygenase oxidation (cytochrome *P*-450 and its models) occurs involving ferryl complexes, which have the terminally bound O atom ($P^{+\bullet}M^{IV}=O$ or $PM^{V}=O$) [8]. It is suggested that non-heme monooxygenase oxidation also includes the mononuclear ($Fe^{V}=O$) or binuclear ($Fe^{IV}-O-Fe^{IV}=O$ for MMO) analogs of the heme complex [7,9]. However, it is difficult to realize a possibility of Fe = O formation in the MMO active center in the absence of cysteine thiolate co-action, which is determining in the case of cyt. *P*-450, since the sulfur to iron π-electron donation is necessary at the dioxygen cleavage stage and also, probably, at the final oxygen insertion stage [10].

In addition, there are some facts that cannot be explained on the basis of the common mechanism for cyt. *P*-450 and MMO.

First, different O donors, such as PhIO, $NaIO_4$, and t-BuOOH, which are active in the case of *P*-450 and its models, are inefficient in the case of MMO [7]. Although H_2O_2 can be used instead of O_2/NADH [7,9], the oxidation of *n*-alkanes in this case is low efficient and has different C–H selectivity [7].

Second, cyt. *P*-450 and MMO have different C–H selectivity

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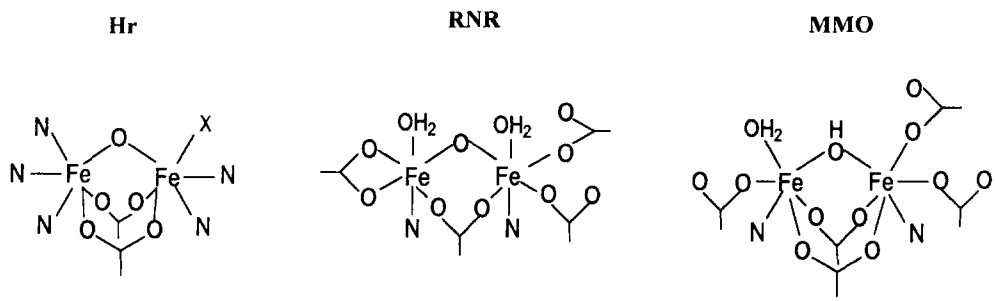

Fig. 1. Structures of active centers of binuclear iron proteins: hemerythrin (**Hr**), ribonucleotide reductase (**RNR**) and methane monooxygenase (N is nitrogen from imidasole of histidine, O\O is carboxylate of glutamic or aspartic acids).

and substrate specificity in alkane oxidation. Oxidation with MMO is rather specific for methane and low alkanes, while cyt. *P*-450 virtually does not oxidize these alkanes. C–H selectivity of cyt. *P*-450, i.e. relative rates of the attack at *prim* (1^o), *sec* (2^o) and *tert* (3^o) C–H bonds calculated per one bond, is in accordance with the C–H bond strength ($1^o < 2^o < 3^o$) and similar to that for Fe = O species, whereas alkane oxidation with MMO follows no simple regularity, which could be common for various alkanes [11,12]. Oxidation of lower alkanes is almost non-selective: $1^o = 2^o = 3^o$. For example, in the case of *iso*-pentane, $(CH_3)_2CHCH_2CH_3$, C–H selectivity $1^o:2^o:3^o$ is *1:25:150* for cyt. *P*-450, but *1:0.4:1.1* and *1:0.9:1.5* for MMO from *Ms. trichosporium* and *Mc. capsulatus*, respectively [12].

All these facts raise doubts about the possibility of the occurrence of ferryl as an active intermediate of MMO.

Thus, the question arises: does an alternative of ferryl exist for methane activation with MMO?

The studies [13] show that the peroxide precursor of ferryl FeOX containing the bridge O atom is sufficiently active to transfer this O to the C–H bond of alkanes. Such active intermediates seem much more preferable for functioning under physiological conditions than thermodynamically less favorable ferryl intermediates, especially in the case of non-heme systems [14,15].

Ferryl can be considered as the complex of the O atom with Fe^{II}, and perferryl is considered as that with Fe^{III}:

$$Fe^{II}:O: \leftrightarrow Fe^{III}-O^{\bullet} \leftrightarrow Fe^{IV}=O$$
$$Fe^{III}:O: \leftrightarrow Fe^{IV}-O^{\bullet} \leftrightarrow Fe^{V}=O$$

In the case of binuclear iron complexes, the O atom can be bound simultaneously with two Fe atoms in the structure of bis-μ-oxo complexes of Fe^{IV} (Fig. 2, complex **2**), which in this case is the real oxenoid reagent (Fig. 2B) similar to peroxides and peracids and can be considered as an alternative to ferryl. The tautomeric equilibrium between numerous possible canonical forms of **2**, some of which involve a lower oxidation state of iron (Fig. 2B), contributes to stabilization of **2**. Probably, there is some slight interaction between both O atoms in these forms, for example, of DA or CT types for the first one and magnetic coupling for the second one. It is likely that carboxylate must be the third bridge connecting two iron ions, and bis-μ-oxo Fe_2 fragment must be nonplanar. Relative stability of Fe_2O core at physiological pH favors the process of the oxygen transfer from **2**. Similar binuclear complexes of Mn^{IV} are strong oxidants that are capable of O_2 evolution from water or hydrogen peroxide and of alkane oxidation [16]. Such complexes for iron are yet unknown, probably, because of their high oxidation reactivity. Although **2** should be more thermodynamically stable than ferryl, especially in nonpolar media, its chemical reactivity can be even higher due to participation of two iron atoms in the transition state of the O atom transfer. In fact, it is shown in the case of analogs of molybdenum O-transferases [17] that the rate of the O transfer from $Mo^{IV}=O$ to the substrate increases in the case when the terminal O atom is bound to another Mo-atom and becomes the bridge atom in $Mo=O: \rightarrow Mo$. It is clear, because electrophilicity of O is increased by its bonding to two electrophylic centers.

4. A new mechanism of O_2 activation

The active intermediate **2** can be formed from molecular oxygen via the stage of μ-1,2-peroxide, Fe–O–O–Fe. However, the η_2,η_2-peroxide complex **1** (Fig. 2) is the most suitable its precursor and suggested as the first product of the reaction of the reduced MMO with O_2, and other authors [6] consider complex **1** as one of probable active intermediates. The hemocyanine oxygen complex [18] has a similar structure (Cu instead of Fe). It follows from the theoretical calculations [19] for the analogous manganese complex that binding O_2 to form this complex is energetically gained and, probably, irreversible. Mononuclear peroxide complexes of Fe^{III} often have side-on

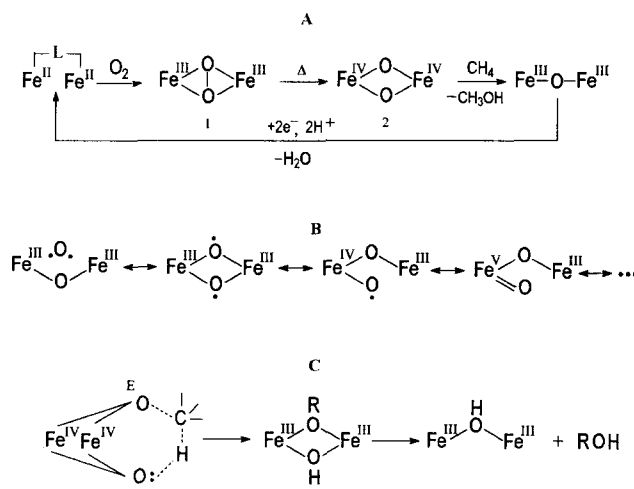

Fig. 2. New concept of the MMO catalytic cycle. (A) Mechanism of O_2 activation. (B) Some canonical forms of active intermediate **2**. (C) Mechanism of CH_4 activation.

binding of peroxide and there are no grounds to assume that similar structures are impossible for binuclear complexes.

Complex **1** is attractive as the first product of the reaction with O_2, because **2** can be obtained from **1** via a simple electron transfer with only slight rearrangement of nuclei. Thus, a principally new mechanism of O_2 activation by Fe^{II} can be suggested, which is possible only for binuclear complexes (Fig. 2A). In fact, in the case of iron porphyrin complexes, the peroxide intermediate must primarily react with the external electrophilic acceptor (H^+, CH_3CO^+) [15] to remove O^{2-} and form the active intermediate:

$$PFe^{III}-O-OH + H^+ \rightarrow P^{+\bullet}Fe^{IV} = O + H_2O.$$

In the case of binuclear complexes, two iron ions seem to be capable to accept of O^{2-} without involving an external electrophile as in the case of Ph_2SnO_2:$Ph_2SnO_2 + RH \rightarrow Ph_2SnO + ROH$ [15]. This accepted O^{2-} is removed from the binuclear reaction center in the form of water after ceasing the substrate oxidation at the subsequent stage of the reduction of Fe_2O complex or it is displaced by the O_2 molecule at the next stage of the catalytic cycle.

Thus, the sequence of detachment of the fragments of the activated oxygen molecule is another in the new mechanism: O^{2-}/O in the case of iron porphyrin complexes and O/O^{2-} in the case of binuclear iron complexes.

The existence of this type of O_2 activation can be checked by the performance of two cycles of MMO with labeled dioxygen, taking into account that exchange between the μ-oxo bridge and water is, probably, slow. In the result of the first cycle, the label must be equally distributed between the product (alcohol) and the μ-oxo bridge. Then the last label must go to water in the result of the second cycle. The similar experiment recently performed for RNR [20] has shown that dioxygen is the source of the μ-oxo bridge in the one cycle of the reaction of $Fe^{II}Fe^{II}$ and O_2. However, the O atom inserted in dihydroxyphenylalanine formed during Tyr-122 oxidation by $^{18}O_2$ in mutant RNR comes from H_2O and not from O_2. The authors of [20] suggest μ-1,1-peroxide and ferryl as intermediates. The structure of μ-1,1-peroxide was considered by us earlier as active species of the MMO catalytic cycle [14], but now we reject this assumption because of discrepancy with the recent data about transient intermediates of MMO (see below).

5. A putative mechanism of CH_4 activation

The hypothesis about bis-μ-oxo complex **2** as the active species of MMO catalytic cycle provides the explanation of unusual bond selectivity and substrate specificity of alkane oxidation with MMO.

The values of Michaelis constant K_m for methane and other low alkanes attest to their strong binding in the MMO active center [21]. The ratio V_{max}/K_m is characteristic of substrate affinity to the enzyme active center and its value for methane is about ten times higher than for other alkanes. This confirms that MMO is tuned very well for the methane oxidation.

We suppose that both O atoms of bis-μ-oxo diiron species **2** operate sinergetically in CH_4 activation, for example, one of the O atoms acts as an electron acceptor (E) and the other as a donor (N) in the heterolytic synchronous mechanism (Fig. 2C). It is likely that a similar situation takes place in methane binding. Such a conclusion follows from considering the selected canonical reactive forms for intermediate **2** (Fig. 2B).

The concerted O transfer to the C–H-bond can be performed via the electrophilic attack of one of the bridge atoms, according to the mechanism suggested previously [22] for solvated oxenoid. The process as a whole can be considered as the electrophilic attack to the C–H bond with the nucleophilic co-action via the multicentered cyclic transition state (Fig. 2C).

The explanation of the greatest reaction rate in the case of methane, as compared with other alkanes, can be given if the determining role of the nucleophilic co-action is accepted and/or steric hindrances are taken into account.

For the electrophylic attack to electrons of the C–H bond, the order of C–H selectivity is $1^O < 2^O < 3^O$ and the order of alkane reactivity $CH_4 < C_2H_6 < C_3H_8 <...$. The opposite is true for the nucleophylic attack to the H atom of the C–H bond, because this attack must be controlled by H-atom acidity, which is the highest for CH_4 compared to other alkanes.

The superposition of these two factors might result in observed C–H non-selectivity and almost the same reactivity of low alkanes in MMO oxidation: $CH_4 \approx C_2H_6 \approx C_3H_8$... and $1^O = 2^O = 3^O$. Another possible factor that operates in the opposite direction toward electrophylic reactivity is an enhancement of steric hindrances for approaching to the C–H bond as the number and the size of substituents at carbon atom increase.

The strong binding of lower alkanes in the MMO active center might be explained by the formation of the double bonded pre-reaction intermediate.

The known ability of the C–H bond to H bonding with the ether O atom [23] allows one to suggest that methane and other alkanes can be H-bonded to the μ-oxo bridge, which may demonstrate a noticeable basicity in a dry nonsolvating hydrophobic cavity of the active center of MMO. Apparently, stronger methane binding is explained by the formation of this H-bonded enzyme-substrate complex due to either of two μ-oxo bridges, because methane has the highest acidity of other alkanes.

On the other hand, the oxene O atom can form the σ-bond with the electron pair of the C–H bond. The intermediate of the $Fe-O-CH_4$ type with the pentacoordinated carbon atom has recently been proposed [24] for the new mechanism of the reaction of Fe = O with the alkane C–H bond instead of the rebound mechanism [8]. The last mechanism was invoked for the explanation of incomplete retention of the configuration at the carbon atom and the formation of the $R^\bullet$ radical in monooxygenase alkane oxidation and equally might be used in the case of bis-μ-oxo oxene intermediate **2** as well as in the case of Fe = O species. However, the authors [24] give arguments that there is no necessity for the implication of this mechanism and the known facts can be explained by the mechanism of concerted insertion, if the latter is added by the idea about the pentacoordinated carbon intermediate. Thus, incomplete retention of the configuration at the carbon atom and the possible detection of the $R^\bullet$ radical can be explained by the rearrangement of this intermediate and its reaction with a radical probe.

6. Some experimental support for the concept

Three intermediates **P**, **Q**, and **T** (Fig. 3) were observed by kinetic methods for fast reactions in one cycle of MMO from

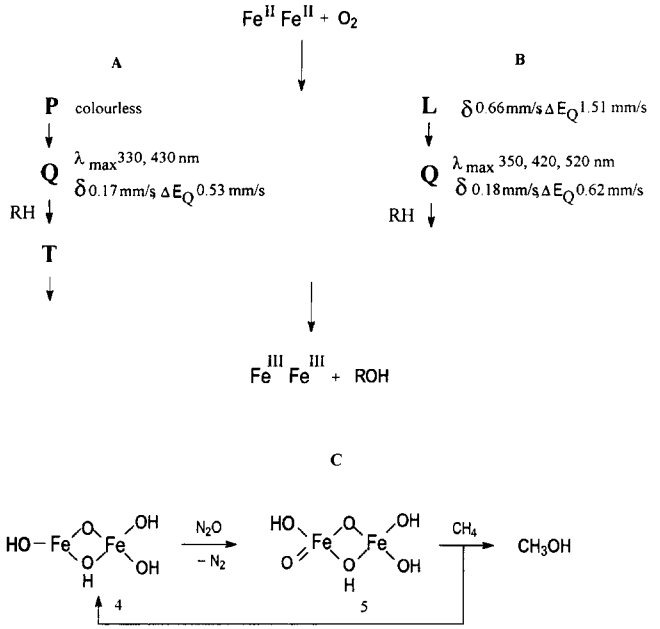

Fig. 3. Transient intermediates observed by stopped-flow spectrofotometry and rapid freeze-quench Moessbauer spectroscopy in the reaction of dioxygen with the reduced MMO hydroxylase from *Ms. trichosporium* [25,26] (A) and *Mc. capsulatus (Bath)* [28] (B). C. Methane oxidation by N_2O on α-centers of Fe-ZSM-5 zeolites [29,30].

M. trichosporium (**A**) [25,26]. The colorless intermediate **P** is formed immediately after mixing reduced MMO with O_2 and then slowly transformed to **Q**. The rate of the disappearance of **Q** depends on the nature and the concentration of the substrate and testifies that **Q** is an active intermediate. Finally, intermediate **T** formed in the reaction of **Q** with the substrate gives the product at the stage, which limits the rate of the whole process. According to Moessbauer spectra [26], compound **Q** is a diamagnetic binuclear complex containing two indiscernible atoms of Fe^{IV} (S = 2). It means that the active oxygen atom occupies the symmetric position in the cluster, and iron atoms are antiferromagnetically coupled. The value of the exchange interaction contstant $J > -60$ cm^{-1} ($H = JS_1 \times S_2$) corresponds to the μ-oxo bridge between the iron atoms and concords with structure **2** for intermediate **Q***. Structures **1** and **3** (Fig. 2) can be assigned to intermediates **P** and **T**. In fact, highly symmetric and weakly polarized complex 1 hardly has noticeable absorption in the visible spectral range, and the decomposition of complex **3** to the product is related to the serious rearrangement of the structure and, hence, is a relatively slow process.

These results were further develop and extended in [28] using the same methods for studying MMO from *Mc. capsulatus (Bath)* (Fig. 3, **B**). In this work, the intermediate similar to **Q** was characterized, which, however, have non-equivalent iron atoms and, as authors [28] note, the activated oxygen need not be bound symmetrically to the iron atoms. The authors [28] also note that the average isomeric shift δ in the Moessbauer spectrum of this intermediate, which characterizes the oxidation state of iron, is close but, nevertheless, differs from the values typical both of heme and non-heme Fe = O. The information about intermediate **L**, which reveals the symmetric quadrupole doublet in the Moessbauer spectrum, is of the most interest. It means that two iron atoms are in the identical coordinational surrounding. The Moessbauer parameters for **L** are very unusual for carboxylate bridge Fe_2 clusters. These parameters seem to be in agreement with structure **1** for **L**.

Stoichiometric oxidation of methane, CO, and benzene at room temperature observed [29] on the so-called α-centers of iron-containing zeolites ZSM-5, which, according to the theoretical calculations in [30], are surface hydroxide clusters of iron with structure **4** (Fig. 3C). Taking into account a possibility of H-bonding between adjacent O-atoms and tautomerism $O=Fe-O^- \leftrightarrow O^- - Fe=O$, real intermediate **5** can have the structure of the bis-μ-oxo Fe_2 complex. This seems to be the best functional model of MMO now.

The first $Fe_2(\mu\text{-OH})(\mu\text{-O})$ complex of iron has recently been synthesized [31]. This complex dehydrogenates 1-Me-1,4-cyclohexadiene to toluene and is capable of the O-atom transfer to give phospine oxide in the reaction with PPh_3. Evidently, there are no grounds to believe that the change in the coordinational surrounding and oxidation state of iron cannot make similar complex to be capable of the transfer of the μ-O atom to the C–H bond of alkanes.

The new concept of O_2 activation with the binuclear iron center of MMO provides some nishe for involving ferryl as an extremely transient intermediate (Fig. 2B). Besides, ferryl might be formed in H_2O_2-driven alkane oxidation via the substitution at the terminal water molecule and it would allow one to explain the observed difference in C–H selectivity. Finally, it is likely that some tautomerism is possible between terminal and bridged oxenes.

7. Conclusion and perspective

Thus, the concept of O_2 activation and CH_4 oxidation in the active center of MMO, which emphasizes an important role of the binuclear structure, is suggested and grounded. Although the bis-μ-oxo diiron complex and η^2,η^2-peroxide have already been considered as probable intermediates of the catalytic cycle of MMO [6,25,26,28], as far as we know, there were no attempts to explain the totality of the data on the basis of the united mechanism involving these intermediates. The bis-μ-oxo complex of iron is suggested to be an alternative to ferryl, which makes it possible to explain observed substrate specificity and C–H selectivity of oxidation of lower alkanes. This hypothesis assumes a new mechanism of binding and activation of O_2 involving side-on binding O_2^{2-} to iron atoms and the sequence of the cleavage of the O–O bond of peroxide O/O^{2-} instead of O^{2-}/O, which takes place in the catalytic cycle of cyt. *P*-450. The side-on coordination of O_2^{2-} must favor its further activation and cleavage to form an active intermediate because of the simultaneous action of two iron centers. The results of some recent works [26,28,31] seriously support the suggested hypothesis. The experiment for its checking is suggested.

This concept can stimulate the search of the methods for the synthesis of bis-μ-oxo complexes of iron and the studies of their reactivity in oxidation and oxygenation of different substrates, including alkanes. It is also of great interest to check the possibility of side-on O_2 binding with binuclear iron complexes and

*For the corresponding nonplanar Mn_2O_2 cluster, the *J* value is about −44 cm^{-1} [27], which tentatively correlates to the deflection of Mn^{IV} $(\mu\text{-O})_2Mn^{IV}$ ring from planarity due to the constraint exerted by the μ-acetato bridge.

to characterize the corresponding η^2,η^2-peroxides. On the other hand, the concept can stimulate the further identification of these intermediates in reactions of MMO and RNR.

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