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KINETICS OF OXIDATION WITH HYDROGEN PEROXIDE AND IRON(II) COMPLEX WITH A MACROCYCLIC BINUCLEATING LIGAND

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ABSTRACT

In the present study solutions of a complex of Fe(II) with a macrocyclic ligand were prepared and their oxidation kinetics with hydrogen peroxide examined . The kinetic studies of the oxidation processes lead to values of rate constant of two step which occur via first-order kinetics. The results are spected to result in a better knowledge of the mechanism of H_2O_2 activation in catalyzed oxidation of organic substrates.

RESUMO

No presente estudo soluções de um complexo de um ligante macrocíclico com Fe(II) foram preparadas e sua cinética de oxidação com peróxido de hidrogênio é examinada. O estudo cinético do processo de oxidação mostra os valores das constantes de velocidade para duas etapas que ocorrem através de cinéticas de primeira ordem. Espera-se que os resultados sirvam para melhor compreensão do mecanismo de ativação do H_2O_2 na catálise de oxidação de substratos orgânicos.

KEYWORDS: iron(II), macrocyclic binucleanting, oxidation kinetics

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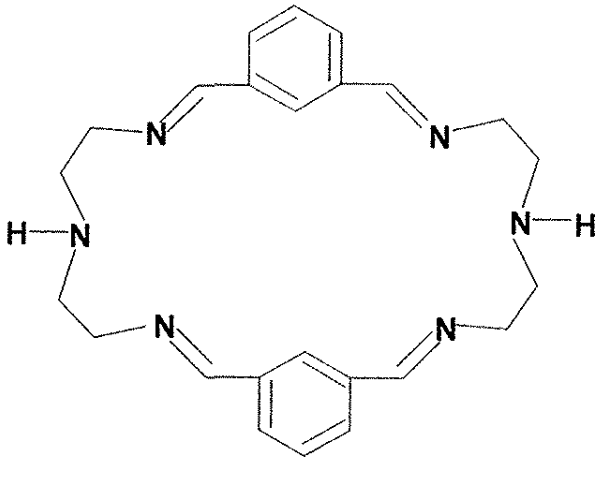
INTRODUCTION

The reduction of peroxides by transition metal complexes is important in many contexts because it is relevant for reactions that occur in biological systems and also for certain metal-catalyzed oxidations. The chemistry of non-heme iron centers has recently experienced a resurgence of interest as models for catalyzed oxidation. The incorporation of an oxygen atom into alkanes, alkenes, ethers and alicyclic, aromatic, and heterocyclic compound is very important and has practical applications in chemical industry as well as in sciences(1). One example of this applicability is the methane monooxygenase (MMO) that is found in methanotrophic bacteria which has one diiron active site and catalyzes the initial oxidation step in the conversion of methane to CO_2 , in which one atom of dioxygen is incorporated into the C–H bond of methane to yield methanol(2,3,4). Another structurally similar site is the dinuclear iron-oxo centers of hemerythrin(5,6).

EXPERIMENTAL

The $[Fe(CH_3CN)_6](BF_4)_2$ and (MX_2DIEN_2) [3,6,9,17,20,23hexaazatriciclo (23.3.1)triaconta1(29),2,9,11(30),12,14,16,23,25,27-decaeno] (1) were prepared according to the literature procedures(7,8). All manipulations were carried out under N_2 atmosphere using the standard Schlenck techniques. Reagents and solvents were obtained from Aldrich. Acetonitrile was distilled from P_4O_{10} and it was also deoxygenated immediately before use. All the experiments were carried out at 25°C and ionic strength 0,05 molar in Bu_4NBF_4.

Stock solutions of $[Fe(CH_3CN)_6](BF_4)_2$ and the ligand were prepared under N_2 and transferred with teflon tube to the syringes of the stopped flow or to a flow cell placed in the spectrophotometer. The kinetics of reactions were studied under pseudo first-order conditions using an excess of the oxidant.



1 - Hexaaza macrocyclic binucleating ligand

The kinetic information have been obtained in two different apparatus. For the slow reactions a Perkin-Elmer Lambda 3 spectrophotometer interfaced to PC-compatible computers was used and the rapid reactions were followed with an Applied-Photophysics stopped-flow DX17MV instrument interfaced to an Acorn 5000 computer. Absorbance versus time data were recorded and the data were analysed using the standard software of the instrument to obtain the pseudo-first order rate constants.

RESULTS AND DISCUSSION

Equilibrium mistures of $Fe(an)_6^{+2}$ (an= acetonitrile) and $L(MX_2DIEN_2)$ in 2:1 molar ratio in acetonitrile are stable under a N_2 atmosphere and show a band at 352 nm in the UV-Vis spectrum. These solutions contain the binuclear complex Fe_2L^{+4} in which two Fe(II) centers are coordinated to both N_3 subunits of the macrocycle and the remaining coordination site would be occupied by solvent molecules. When these solutions are mixed with solutions of water in acetonitrile, the spectral changes observed are very small and occur very rapidly (within the mixing time of the stopped-flow, about 2 ms). These small changes make impossible to determine the equilibrium constant for reaction of Fe_2L^{+4} with water and suggest that it is a fast process that leads to small amounts of substituted product. However, it seems unlikely that coordinated acetonitrile is not substantially substituted for water in the presence of a large water excess and so, an alternative explanation in that substitution of acetonitrile for water causes only minor changes it the spectrum of the complex.

Reaction of Fe_2L^{+4} with H_2O_2 in acetonitrile shows two kinetically distinguishable steps. The first step occurs in the stopped-flow time scale and it is characterized by an increase of absorbance at 480 nm (Figure 1). These kinetic traces in the presence of H_2O_2 excess can be easily analyzed by fitting to a single exponential to give the first order rate constant k_{1obs} included in Table 1. Figure 2 shows the dependence of k_{1obs} on the concentration of H_2O_2 and reveals a clear saturation behaviour. Actually, the reciprocal plot of Figure 3 illustrates the linear dependence of $1/k_{obs}$ on $1/[H_2O_2]$. A linear least-squares fitting of points in Figure 3 leads to Equation [1], which is easily converted to Equation [2], in which the saturation behavior is more evident. Because H_2O_2 solutions for kinetic work were prepared from 30% aqueous H_2O_2, this is the possibility that k_{1obs} corresponds to reaction of Fe_2L^{+4} with H_2O instead of H_2O_2. However this possibility can be ruled out because reaction with H_2O does not cause significant absorbance changes. Table 1 also includes kinetic data for the reaction with H_2O_2 . Moreover, the reproducibility of kinetic results in the presence of variable amounts of water indicates that free radicals (Fenton behaviour) are not involved in this reaction. On the contrary, kinetic experiments with t-BuOOH as oxidant showed small absorbance changes with unreproducible rate constant, which suggests that oxidation of Fe_2L^{+4} occurs in this case with formation of free radicals, i.e., the mechanism of the oxidation reaction is very dependent on the nature of the oxidant.

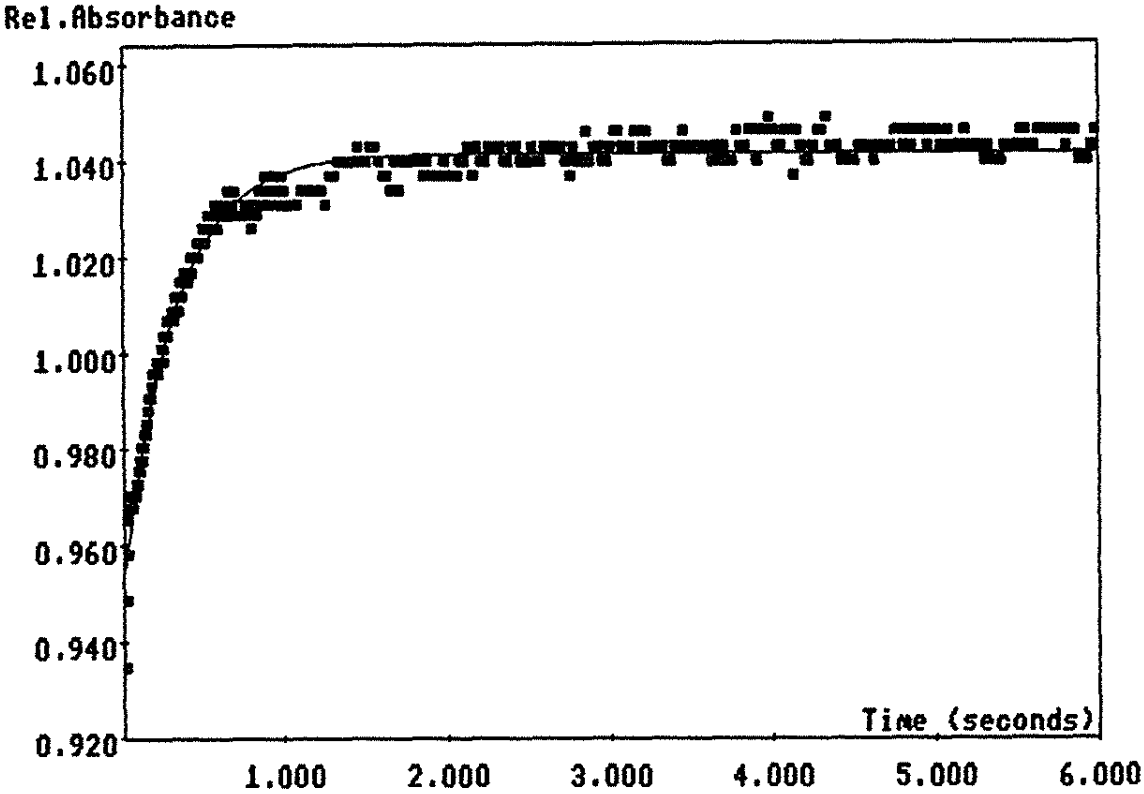


Figure 1: Absorbance versus time for the reaction of $[H_2O_2]$ 0,0960M and $\{Fe_2[(MX)_2(Dien)_2]\}^{+4}$ 5,0x10^{-4}M in acetonitrile. Time: 1,0-5,0 s. λ= 480 nm. T=25°C. μ=0,05M. Nitrogen atmosphere.

Table 1 . Kinetic data at 25°C for the fast step in the reaction of Fe_2L^{+4} with H_2O_2 (concentration of complex=2,5x10^{-3}M)

$[H_2O_2]$ (M)	k_{1obs} (s^{-1})	1/ $[H_2O_2]$ (M^{-1})	1/ k_{1obs} (s^{-1})
0.024	0.64	41.67	1.56
0.048	1.38	20.83	0.72
0.096	3.22	10.42	0.31
0.190	3.88	5.26	0.26
0.286	5.35	3.50	0.19
0.388	5.55	2.58	0.18
0.485	5.29	2.06	0.19
0.582	6.48	1.72	0.15
0.190[a]	3.59		
0.190[b]	3.78		
0.190[c]	3.47		

[a] 0.55 M additional water [b] 1.10 M additional water [c] 1.65 M additional water

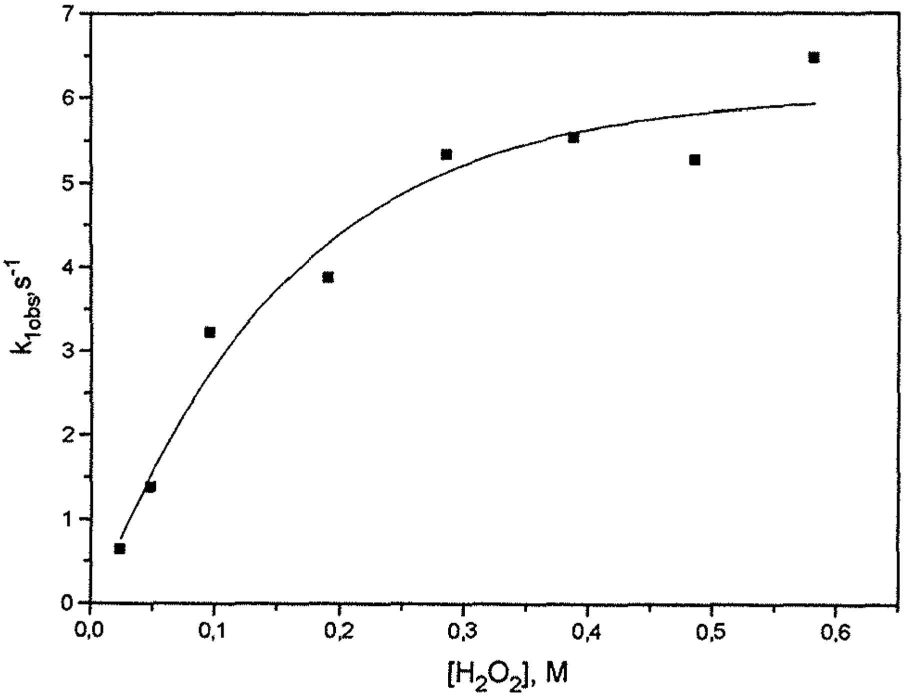


Figure 2: Plot of k_{1obs} versus $[H_2O_2]$ for the fast step in the reaction with H_2O_2

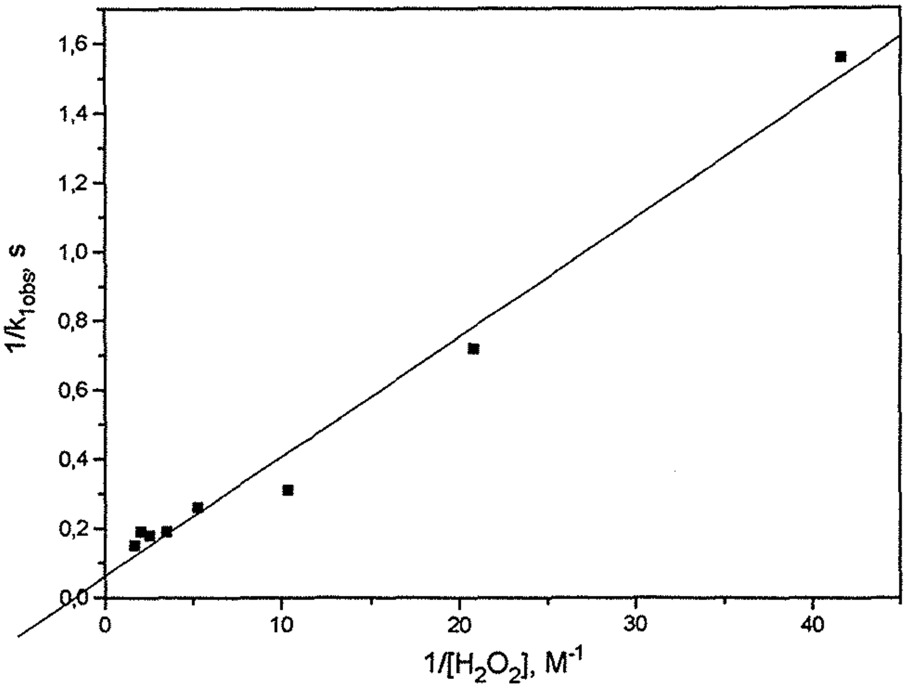


Figure 3: Reciprocal plot of kinetic data for the fast step in the reaction with H_2O_2

$$1/k_{1obs} = 0.064 + 0.035\ 1/[H_2O_2] \qquad [1]$$

$$k_{1obs} = 28.6\ [H_2O_2] / 1 + 1.8[H_2O_2] \qquad [2]$$

Kinetic results for the H_2O_2 reaction can be interpreted with the mechanism proposed in Equations [3] and [4], where Equation[3] represents a fast equilibrium to form an intermediate B which converts more slowly to C.

$$Fe_2L^{+4} + H_2O_2 \overset{K_1}{\rightleftharpoons} B \qquad [3]$$

$$B \xrightarrow{k_2} C \qquad [4]$$

$$k_{1obs} = k_2\ K_1\ [H_2O_2] / 1 + K_1\ [H_2O_2] \qquad [5]$$

The rate law for this mechanism is given by [5] and the comparison with [2] leads to K_1=1,8 M^{-1} and k_2=15,9 s^{-1}. According to this interpretation, reaction of Fe_2L^{+4} with H_2O_2 would lead initially to the formation of a substituted product with K_1=1,8 M^{-1} and then B would be converted to an oxidized complex C with k_2=15,9 s^{-1}.

In a slower reaction, complex C decomposes to give a misture of reaction products difficult to characterize. The kinetics of this reaction was studied by conventional spectrophotometry and the values of the observed rate constant k_{2obs} are given in Table 2. Figure 4 shows the linear dependence of k_{2obs} on the concentration of H_2O_2 and linear least-squares fit of the data leads to equation [6].

$$k_{2obs} = 0.95\times10^{-4} + 3.11\times10^{-4}\,[H_2O_2] \qquad [6]$$

This dependence and the formation of mixtures of products suggest that complex C decomposes through two parallel pathways with a different dependence on the concentration of oxidant. Moreover, the quality of the absorbance-time profiles and the dependence of k_{2obs} with $[H_2O_2]$ are not very well defined because of precipitation and probably also because of some contribution of free radical pathways.

Table 2 : Kinetic data for the slow step in the reaction of Fe_2L^{+4} with H_2O_2 (same conditions that data of Table 1)

$[H_2O_2]$ (M)	$10^4\ k_{2obs}$ (s^{-1})
0,048	1.21
0,096	1.02
0,190	1.70
0,380	2.10

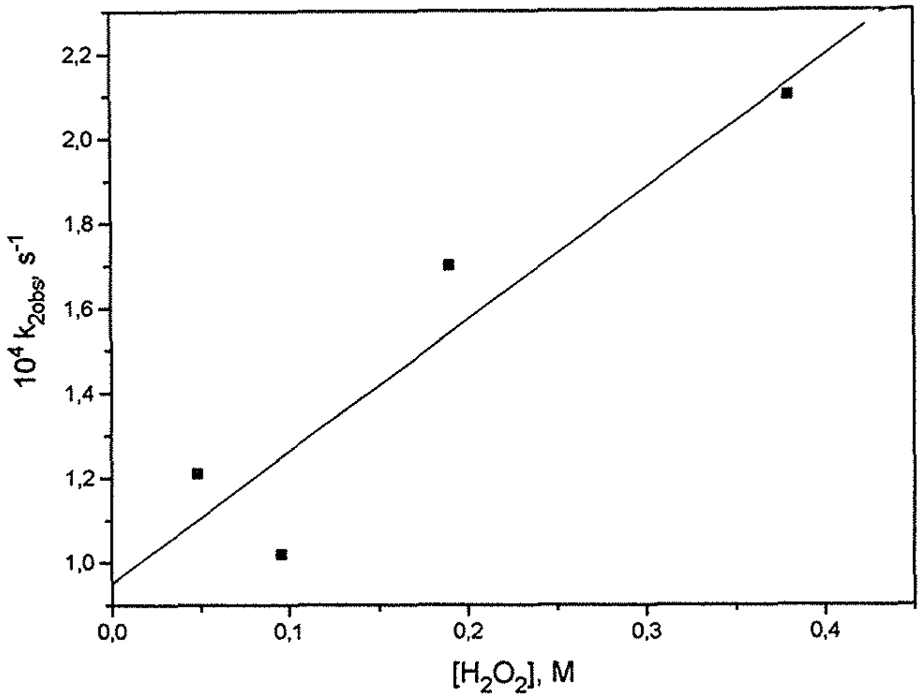
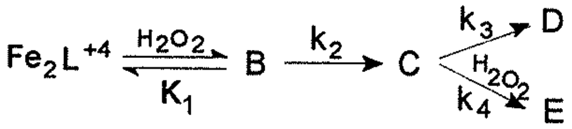


Figure 4: Dependence of k_{2obs} on the concentration of H_2O_2 for the slow step in the reaction with H_2O_2

Thus, kinetic results for the reaction of Fe_2L^{+4} with H_2O_2 in acetonitrile solution can be summarized with the following scheme:



The values derived for the constant are: K_1=1,8 M^{-1}, k_2=15,9 s^{-1}, k_3=0,95x10^{-4} s^{-1} and 3,11x10^{-4} $M^{-1}s^{-1}$. These data represent a full description of the reaction system as a function of time and can be used as a first approximation to the study of H_2O_2 oxidations catalyzed by the binuclear complex Fe_2L^{+4}. According to kinetic results, oxidation of organic substrate is most likely to occur through reaction with species C, because complex B is a substituted product and complexes D and E are decomposition products unable to react with more H_2O_2. Further work is in progress to the determine the nature of intermediate C and its role as active oxidant for different organic substrates.

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