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Kinetics of reaction of the Fe^{II}–cyclam complex with H_2O_2 in acetonitrile and the mechanism of catalyzed epoxidation of cyclohexene

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Abstract—The Fe^{II} complex with macrocycle cyclam (1,4,8,11-tetraazacyclotetradecane) reacts with H_2O_2 in acetonitrile to give a mixture of products which result from oxidation both at the metal center and the ligand. At 25°C in the presence of 0.05 M Bu_4NBF_4 the reaction occurs with three kinetically distinguishable steps. The first two steps are first order with respect to both H_2O_2 and the metal complex. The values of the second order rate constants are $k_1 = 3.7$ M^{-1} s^{-1} and $k_2 = 0.83$ M^{-1} s^{-1}. EPR spectra suggest that intermediates formed in these two steps are low spin Fe^{III} complexes. The kinetics of the third step is more complicated, with a dependence on the concentration of H_2O_2 of the form $k_3[H_2O_2]+k_4$, with $k_3 = 2.72\times10^{-3}$ M^{-1} s^{-1} and $k_4 = 2.18\times10^{-4}$ s^{-1}. This rate law is interpreted in terms of two parallel pathways leading to Fe^{III} and extensively dehydrogenated cyclam. NMR experiments suggest that the active catalyst in the iron-cyclam catalyzed epoxidation of cyclohexene is the intermediate formed in the first step. However, this intermediate is not able to transfer an oxygen atom directly to the substrate and requires the participation of additional H_2O_2, in a mechanism very different to that proposed for porphyrin complexes. © 1997 Elsevier Science Ltd

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Metal complexes able to catalyze the selective oxidation of organic substrates under mild conditions are very attractive for many industrial processes [1]. An approach for the development of useful catalysts is to prepare systems that mimic the behaviour of oxigenases [2] and so, metal porphyrins are perhaps the best studied homogeneous oxidation catalysts. The active species for iron–porphyrin catalyzed oxidations is a ferryl intermediate [3] able to transfer an oxygen atom to the substrate. There are also many reports of oxidation processes catalyzed by non-porphyrin metal complexes but less is known in these cases about the nature of the active catalyst [4].

The synthesis of Fe^{II}–cyclam complexes in acetonitrile was reported many years ago [5], but it was only recently that Valentine and coworkers [6–8] demonstrated its ability to catalyze the selective epoxidation of cyclohexene by 30% aqueous H_2O_2. The formation of very small amounts of allylic products suggests that free radicals are not involved in the catalytic process. On the contrary, when H_2O_2 is replaced by *t*-BuOOH oxidation leads to 2-cyclohexen-1-one, 2-cyclohexen-1-ol and traces of the epoxide. These results show clearly that the catalytic behaviour of Fe^{II}–cyclam depends on the oxidant used and different active intermediates are probably involved in these oxidations. Possible structures for these intermediates have been discussed on the basis of results obtained for catalyzed oxidations under a wide variety of conditions, although direct evidence on the formation of these intermediates was not obtained. It is also interesting to note that oxidation of the Fe^{II}–cyclam complex with O_2 in acetonitrile leads [9] to a dimeric Fe^{II} complex containing a binucleating ligand derived from oxidative coupling of two oxidized cyclam moieties. Several iron and nickel complexes of this type have been prepared and their properties are currently under study [10] but the role of these binuclear species in catalytic oxidation cycles has not been explored.

In this paper, we report a kinetic study of the reaction of Fe^{II}–cyclam with H_2O_2 in acetonitrile and dis-

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cuss the nature of the intermediates formed in the oxidation process and their role in catalytic epoxidation of cyclohexene. The results also lead to a better understanding of the kinetic pathways leading to unwanted degradation of the catalyst.

EXPERIMENTAL

$[Fe(MeCN)_6](BF_4)_2$ was prepared by a literature procedure [11]. The iron–cyclam complex was obtained using the method described by Busch and coworkers [5] for $[FeL(MeCN)_2](PF_6)_2$, except that PF_6^- was substituted for BF_4^-. All other reagents were obtained from Aldrich and used without further purification. Acetonitrile was obtained from SDS and dried by distillation from P_4O_{10}. It was also deoxygenated by bubbling argon immediately before use. All manipulations were carried out under argon atmosphere using standard Schlenck and syringe techniques.

Samples for infrared spectra were prepared as KBr pellets or Nujol mulls and the spectra were obtained with a Mattson 5020 instrument. Elemental analyses were carried out at the Serveis Cientifico-Tecnics of the Universidad de Barcelona. EPR spectra were recorded at the X-band frequency with a Bruker 200D spectrometer.

NMR spectra were recorded with a Varian Unity 400 instrument. The solvent used was CD_3CN for the iron complex and reaction intermediates or $CDCl_3$ for solids obtained by concentration of $CHCl_3$ extracts. For experiments of cyclohexene epoxidation, a small amount (*ca* 5 mg) of the iron complex or one of its reaction intermediates was dissolved in 0.5 ml of a concentrated solution of cyclohexene in CD_3CN (*ca* 1 M). Under these conditions, the carbon spectra only show the signals of cyclohexene. 0.1 ml of 30% aqueous H_2O_2 was then added to the NMR tube and reaction was allowed to proceed for 30 min before recording a new spectrum. All the carbon spectra were obtained with 4096 transients using an acquisition time of 1 s. In this way, the signal to noise ratio is high enough to see clearly the signals of products resulting from oxidation of cyclohexene.

Kinetic measurements

Stopped-flow experiments were carried out with an Applied-Photophysics SX17MV instrument. The kinetics of slow reactions was studied with a Perkin–Elmer Lambda 3B spectrophotometer interfaced to a PC computer. All experiments were carried out at 25°C under an argon atmosphere in acetonitrile solutions containing 0.05 M Bu_4NBF_4.

Solutions of the iron–cyclam complex (FeL^{2+} for simplification) were prepared either from $[FeL(MeCN)_2](BF_4)_2$ or from mixtures of $[Fe(MeCN)_6](BF_4)_2$ and L (cyclam) which were previously allowed to react for 2 h. No differences in the kinetic behaviour were detected using both procedures. Most kinetic experiments were carried out using an excess of H_2O_2 and the values obtained for the rate constants are independent of the concentration of FeL^{2+}, showing that the reaction order with respect to the iron complex is one for all kinetic steps. Additional experiments in the absence of cyclam showed that absorbance changes for oxidation of $[Fe(MeCN)_6]^+$ are very small and slower than reaction of FeL^{2+} and so, possible interferences caused by reactions of $[Fe(MeCN)_6]^{2+}$ were ignored in the analysis of the data.

Analysis of kinetic data

Reaction of FeL^{2+} with H_2O_2 shows a polyphasic kinetics with two steps in the stopped-flow time scale and a slower one which lasts for thousands of seconds. Data for the fast steps were initially obtained at multiple wavelength and analyzed using program GLOBAL [12]. This program leads to values of the rate constants for both steps and calculates the spectra of the absorbing species. Although both steps may occur in reverse order, this possibility was ruled out because a change in the order of the two rate constants leads to unsatisfactory spectra for the species involved. The order of the two steps was also confirmed in some experiments with an excess of FeL^{2+} over H_2O_2, which showed a single kinetic step with a rate constant similar to that proposed to be the first one in the experiments with H_2O_2 excess. Because the acquisition of data at multiple wavelength requires both a larger amount of sample and longer experiments, most kinetic data were obtained from absorbance-time profiles at 540 and 630 nm. The rate constants derived from non-linear least-squares fit of these curves to two consecutive exponentials are in satisfactory agreement with those obtained with GLOBAL analysis and so they are used through the paper. Reported values of these constants are the average of 5–10 determinations with a standard deviation lower than 5%.

Rate constants for the slow step in the reaction of FeL^{2+} with H_2O_2 were obtained by conventional linear least-squares analysis of kinetic traces at 630 nm during two half-lives. In some cases, a reliable value for the final absorbance could not be obtained because precipitation occurs before the end of the experiment. In these cases the rate constant was obtained by non-linear fit to a single exponential of the first part of the curve.

RESULTS AND DISCUSSION

Kinetics of reaction with H_2O_2

Solutions of FeL^{2+} in acetonitrile prepared under argon and containing 0.05 M Bu_4NBF_4 show a band at 540 nm ($\varepsilon = 70\ M^{-1}\ cm^{-1}$) that agrees well with previous report [5] ($\lambda_{max} = 540$ nm, $\varepsilon = 65\ M^{-1}\ cm^{-1}$). Addition of an excess of 30% aqueous H_2O_2 changes the colour of the solution from pale purple to intense blue in a few seconds. The reaction continued for 1–2 h to give a brown precipitate and a weakly coloured blue solution.

The kinetics of the initial change of colour was studied using the stopped-flow instrument. The absorbance changes in the first 100–200 s are very complicated and reveal the existence of more than one kinetic step (Fig. 1). Some experiments were carried out using the spectral scanning facilities of the instrument and the data were analyzed with the program GLOBAL [12]. A satisfactory fit was obtained using a model with two consecutive exponentials that lead to formation of intermediates B and C, whose spectra are shown in Fig. 2. The observed rate constants are independent of the concentration of FeL^{2+} showing that formation of both intermediates is first order in the iron–cyclam complex. The values of k_{1obs} and k_{2obs} for different concentrations of H_2O_2 are included in Table 1 and show in both cases a linear dependence with the concentration of H_2O_2 (Fig. 3). The values derived for the second order rate constants are $k_1 = (3.7 \pm 0.2)\ M^{-1}\ s^{-1}$ and $k_2 = (0.83 \pm 0.04)\ M^{-1}\ s^{-1}$.

The slow conversion of intermediate C to the final products was studied using a conventional spectrophotometer and the rate constants (k_{3obs}) are also included in Table 1. The dependence with the concentration of H_2O_2 is given in this case by eq. (1), with $k_3 = (2.72 \pm 0.05)\ 10^{-3}\ M^{-1}\ s^{-1}$ and $k_4 = (2.18 \pm 0.09)\ 10^{-4}\ s^{-1}$ (see Fig. 4).

$$k_{3obs} = k_3[H_2O_2]+k_4 \qquad (1)$$

Equation (1) suggests the existence of two parallel reaction pathways that may lead to the same compound or to different products. At higher concentrations of H_2O_2, the second order pathway becomes more important and the amount of pre-

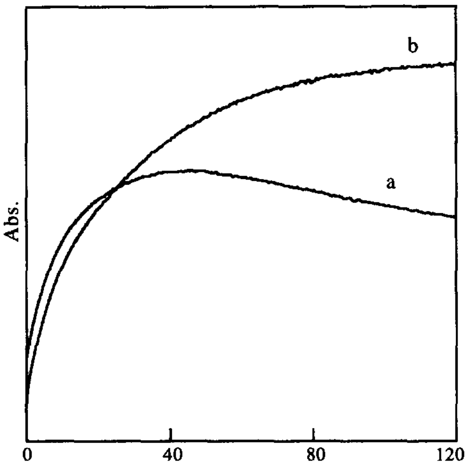

Fig. 1. Absorbance–time traces for the reaction of FeL^{2+} with H_2O_2 showing two separate kinetic steps. Curve (a) was obtained at 540 nm and (b) at 630 nm.

Table 1. Observed rate constants for the reaction of FeL^{2+} (5.0×10^{-4} M) with H_2O_2 in acetonitrile at 25°C and 0.05 M Bu_4NBF_4

$[H_2O_2]$ (M)	k_{1obs} (s^{-1})	k_{2obs} (s^{-1})	$10^4\ k_{3obs}$ (s^{-1})
0.012	0.034	0.010	—
0.024	0.066	0.017	—
0.048	0.129	0.043	3.44
0.095	0.355	0.069	4.85
0.141	0.424	0.106	5.93
0.186	0.700	0.165	7.34
0.231	0.840	0.187	8.42

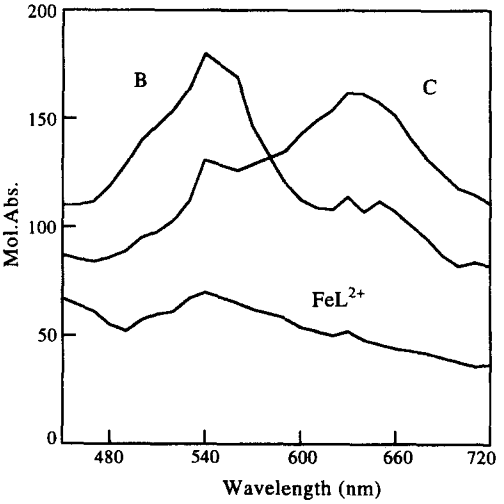

Fig. 2. Spectra of FeL^{2+} and intermediates B and C in the reaction with H_2O_2. These spectra were calculated by fitting experimental spectral changes to two consecutive first order processes.

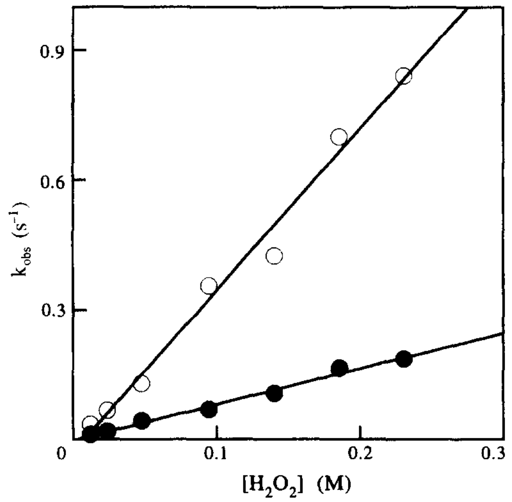

Fig. 3. Dependence of observed rate constants k_{1obs} (hollow) and k_{2obs} (filled) on the concentration of H_2O_2.

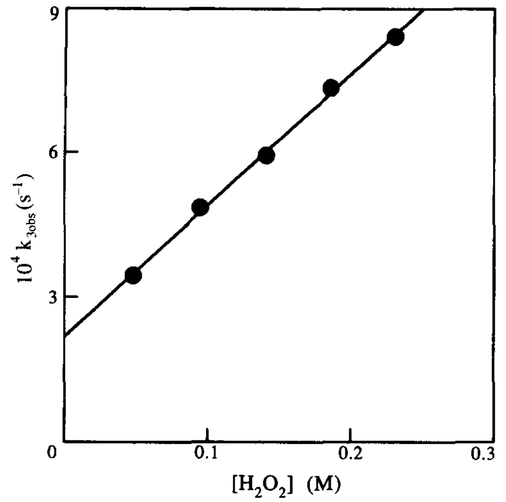

Fig. 4. Dependence of k_{3obs} on the concentration of H_2O_2.

cipitate increases, which suggests that k_3 corresponds to formation of the insoluble product. On the contrary, no precipitate is observed at low $[H_2O_2]$ and reaction occurs then mainly through the first order pathway k_4. All kinetic data for the reaction of FeL^{2+} with H_2O_2 in acetonitrile can be rationalized with the mechanism shown in eqs (2)–(5), where B and C represent reaction intermediates and D and E the final reaction products.

$$FeL^{2+} + H_2O_2 \xrightarrow{k_1} B \quad (2)$$

$$B + H_2O_2 \xrightarrow{k_2} C \quad (3)$$

$$C + H_2O_2 \xrightarrow{k_3} D \quad (4)$$

$$C \xrightarrow{k_4} E \quad (5)$$

Independent experiments with H_2O in the absence of H_2O_2 did not show any significant spectral change, which suggests that FeL^{2+} does not react to an appreciable extent with H_2O. However, as the H_2O_2 solutions used in kinetic work were prepared from 30% aqueous H_2O_2, there is the possibility that some of the kinetic steps observed for the oxidation process correspond to reaction with H_2O. To analyze this possibility, some experiments were carried out at fixed $[H_2O_2]$ and different concentrations of water. The results are included in Table 2 and show that the rate constants k_{1obs}, k_{2obs} and k_{3obs} do not change with $[H_2O]$, in agreement with the mechanism proposed in eqs (2)–(5). However, the participation of H_2O in some of the kinetic steps can not be completely ruled out because the absence of $[H_2O]$ in the kinetic equations can result from simplification of more complicated rate equations under the experimental conditions used (large excess of H_2O).

According to the previous interpretation, for experiments carried out using an excess of FeL^{2+} over H_2O_2, a single step leading to formation of intermediate B is expected. Kinetic traces under these conditions can be fitted to a single exponential and results in Table 3 lead to $k_1 = 2.6 \pm 0.3\ M^{-1}\ s^{-1}$, in good agreement with the value obtained from experiments with H_2O_2 excess.

Table 2. The effect of added water on the observed rate constants for the reaction of FeL^{2+} with H_2O_2 (other experimental conditions similar to those of Table 1)

$[H_2O_2]$ (M)	$[H_2O]$ (M)	k_{1obs} (s^{-1})	k_{2obs} (s^{-1})	k_{3obs} (s^{-1})
0.186	1.56	0.700	0.165	7.34
0.186	2.11	0.694	0.201	
0.186	3.78	0.703	0.172	
0.186	7.11	0.682	0.183	
0.141	1.28	0.424	0.106	5.93
0.141	1.71			6.94
0.141	3.38			5.93

The nature of reaction intermediates and final oxidation products

Results in previous sections give a complete picture of the kinetics of reaction and the number of species formed in the FeL^{2+}–H_2O_2 system but nothing can be deduced about the nature of these species. Unfortunately, addition of an H_2O_2 excess to acetonitrile solutions of FeL^{2+} results in rapid formation of paramagnetic species which can not be studied by NMR. So, it seems reasonable to conclude that species B, C, D and E are paramagnetic.

To obtain some information about intermediates B and C, a solution of H_2O_2 was added dropwise under N_2 to an acetonitrile solution of FeL^{2+}. Addition was continued until the colour changes to that corresponding to one of the reaction intermediates. An excess of toluene was then added to precipitate the iron complexes in solution. These experiments lead to solids with UV–vis spectra very similar to those in Fig. 2 for intermediates B and C but all attempts

Table 3. Observed rate constants for the reaction of FeL^{2+} with H_2O_2. The concentration of H_2O_2 is 3.5×10^{-4} M and other conditions are similar to those in Table 1

10^3 $[FeL^{2+}]$ (M)	10^3 k_{1obs} (s^{-1})
0.75	1.78
1.14	2.98
1.33	3.90

to obtain crystalline solids were unsuccessful. EPR spectra of these samples strongly suggest that intermediates B and C contain low spin Fe^{III} in an orthorhombic environment. Thus, samples corresponding to both intermediates show broad signals at g values close to 2 (2.011 for B and 2.020 for C) in the powder spectra at room temperature. Frozen acetonitrile solutions at 77 K show spectra with signals at $g = 2.328$, 2.424 and 2.967 (intermediate B) and $g = 2.016$ and 2.330 (C). Most spectra also show a weaker signal close to $g = 4.3$. The absence of this signal in some of the spectra leads us to think that it corresponds to a different Fe^{III} complex formed during the handling of the samples. Thus, although EPR data do not lead to an unequivocal structural proposal for both reaction intermediates they show that conversion of FeL^{2+} to B involves oxidation of the metal centre to Fe^{III}. The second kinetic step probably involves ligand oxidation to form a complex containing partially dehydrogenated cyclam. Actually, Fe^{III} complexes with tetraazamacrocycles containing two amine and two imine donor groups are low spin and show EPR spectra with three signals close to $g = 2.0$ [13]. An alternative interpretation is that conversion of B to C is not an oxidation process and C results from a substitution process to form a hydroperoxocomplex. In any case, no evidence has been obtained for the formation of a high valent iron–oxo species similar to that proposed for the case of porphyrin complexes.

In some other experiments, oxidation was quenched at different reaction times by rapid addition of sodium sulfite. A large excess of EDTA (aqueous solution at pH = 10) was then added to complex the metal ion. Under these conditions, cyclam and any other ligand formed in the oxidation process will be uncoordinated and can be extracted with chloroform. NMR spectra of these extracts are very complicated but show clearly that the oxidation process causes important transformations at the ligand. Although several experiments were carried out under slightly different conditions, noone of the spectra showed the signals of cyclam. On the contrary, the proton spectra showed signals at 5.4 ppm and many overlapping multiplets between 1.7 and 3.5 pm. The multiple couplings between these signals suggest the formation of a mixture of species derived from oxidative dehydrogenation at different positions of the cyclam module. On the other hand, although one of the final products in the oxidation of FeL^{2+} precipitates in acetonitrile solution (species D), its nature could not be established because elemental analyses revealed a very low C, H, N content that suggests it is an inorganic salt of Fe^{III}. All these results show that the oxidations sequence in eqs (2)–(5) leads to Fe^{III} complexes of ligands resulting from oxidative dehydrogenation of cyclam. Both metal-centred and ligand-centred oxidations are well illustrated for complexes of cyclam and other polyamines [14].

It is interesting to note that binuclear Fe^{II} complexes are not formed in the reaction of FeL^{2+} with H_2O_2. Oxidation of FeL^{2+} with O_2 in acetonitrile is much slower than reaction with H_2O_2. Following initial spectral changes during the first 500–1000 s, a very intense band at 870 nm is formed in a slow process. This band is typical of binuclear Fe^{II} complexes with a macrocycle formed by oxidative coupling of two partially oxidized cyclam molecules [9,10]. Formation of the binuclear complex takes several hours at 25°C and occurs with unreproducible kinetics, as expected for a free radical mechanism similar to that proposed for oxidative dehydrogenation of complexes with cyclam [10a] and other saturated polyazamacrocycles [14]. The very different kinetics for the oxidation of FeL^{2+} with H_2O_2 and O_2 and the absence of binuclear species in the H_2O_2 reaction show that these species do not participate in FeL^{2+}-catalyzed epoxidation of cyclohexene.

Catalyzed epoxidation of cyclohexene

Because of the many possibilities that exist for the interaction between metal centre, oxidant and substrate, the determination of reaction mechanisms for oxidations catalyzed by metal complexes is a difficult problem. However, the knowledge of reaction pathways for oxidation of the metal complex in the absence of substrate simplifies the problem and leads to a better understanding of the mechanism of the catalyzed reaction.

For the case of the Fe^{II}–cyclam complex, Valentine and coworkers showed [6–8] that FeL^{2+} catalyzes the selective oxidation with H_2O_2 of cyclohexene to its epoxide but oxidation with *t*-BuOOH only leads to small amounts of allylic products and traces of the epoxide. Similar conclusions have been obtained in this work from ^{13}C NMR experiments. Thus, addition of *t*-BuOOH to a CD_3CN solution of FeL^{2+} containing an excess of cyclohexene causes small changes in the spectra and signals for oxidation products are too weak to allow a reasonable assignment. On the contrary, addition of H_2O_2 results in formation of detectable amounts of cyclohexene oxide (signals at 20.2, 25.1 and 53.2 ppm), although the major oxidation product is *trans*-1,2-cyclohexanediol (signals at 25.3, 34.5 and 75.6 ppm), which can be formed by hydrolysis of the epoxide. Independent experiments using an authentic sample of cyclohexene oxide were carried out to confirm the previous assignments of signals and to show that addition of HNO_3 converts the epoxide to the *trans*-diol.

The complex oxidation behaviour of FeL^{2+} with H_2O_2 allows many possibilities for the mechanisms of catalysis, but the problem can be simplified by assuming two general types of mechanism. The first type would consist of sequential reaction with cyclohexene (CH) and H_2O_2:

$$X \xrightarrow{CH} X.CH \xrightarrow{H_2O_2} CHO + H_2O + X \qquad (6)$$

where CHO represents cyclohexene oxide and X is one of the species resulting from oxidation of FeL^{2+} (B, C, etc.). The second type of mechanism would involve two of the species in eqs (2)–(5). One of them would act as an oxygen donor to form the epoxide and the earlier intermediate in the oxidation of FeL^{2+}, for example:

$$B + CH \xrightarrow{k_{cat}} CHO + FeL^{2+} \qquad (7)$$

To discriminate between these possibilities, FeL^{2+} was substituted for B, C and D in the NMR experiments described above. The second type of mechanism is rule out because in the absence of H_2O_2 none of these species converts cyclohexene to the epoxide. In the presence of added H_2O_2, cyclohexene oxide was detected in experiments using FeL^{2+} and intermediate B but not for the case of C and D. Independent NMR and stopped-flow experiments showed that FeL^{2+} does not react with cyclohexene during the time required for oxidation of the iron complex with H_2O_2. All these results suggest that intermediate B is the active catalyst and epoxidation occurs through its sequential interaction with CH and H_2O_2. The whole process can be represented by adding eqs (8) and (9) to the oxidation sequence in eqs (2)–(5).

$$B + CH \rightarrow B.CH \qquad (8)$$

$$B.CH + H_2O_2 \rightarrow B + CHO + H_2O \qquad (9)$$

Reaction of FeL^{2+} with H_2O_2 generates the active catalyst B, able to epoxidize cyclohexene but which decomposes through direct reaction with H_2O_2. The structure of B has not been determined but it must be a low spin Fe^{III} complex able to interact with cyclohexene and activate it towards epoxidation. In any case, a high valent iron-oxo species does not seem to be involved in the FeL^{2+}–cyclohexene–H_2O_2 system and the catalyzed oxidation occurs through a mechanism very different to that proposed for porphyrin complexes.

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