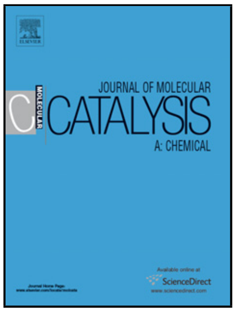

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Author: Evgeny V. Kudrik Alexander B. Sorokin

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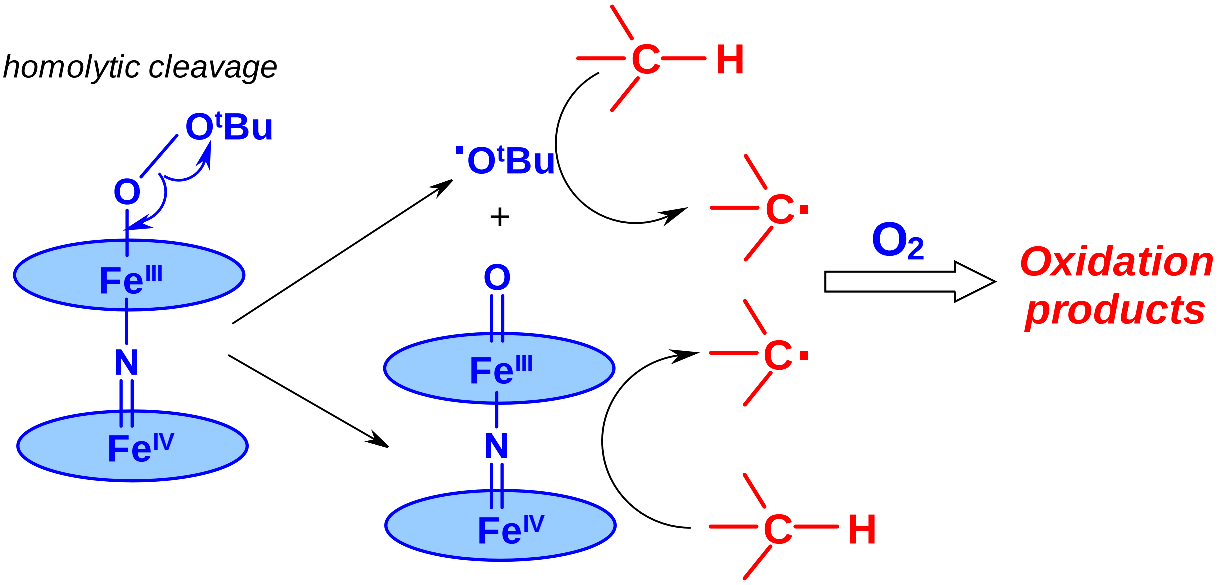
Oxidation of aliphatic and aromatic C-H bonds by *t*-BuOOH catalyzed by μ-nitrido diiron phthalocyanine

Evgeny V. Kudrik,[a,b] Alexander B. Sorokin[a*]

[a]Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), UMR 5256, CNRS-Université Lyon 1, 2, av. A. Einstein, 69626 Villeurbanne Cedex, France
[b] Institut of Macroheterocyclic Compounds, Ivanovo State University of Chemical Technology 7, av F. Engels; 153000 Ivanovo, Russia.
e-mail: alexander.sorokin@ircelyon.univ-lyon1.fr

The article is dedicated to Professor Georgii B. Shul'pin on the occasion of his 70th birthday.

Graphical Abstract



Highlights

- Formation of the diiron peroxo complex Fe(IV)=N–Fe(III)–OO^{t}Bu
- Homolytic cleavage of O–O bond leads to two active species reacting with C-H bonds
- Oxidation of cyclohexane, cyclohexene, toluene and benzene

Abstract

Low temperature selective transformation of alkanes to useful products continues to be an important challenge in chemistry and industry. µ-Nitrido diiron phthalocyanines in combination with H_2O_2 have been recently identified as powerful oxidation catalysts for these challenging reactions due to the formation of ultra-high valent diiron oxo species PcFe(IV)µNFe(IV)=O(Pc$^{+\cdot}$). This very strong *two-electron oxidizing* species is generated from peroxo complex PcFe(IV)µNFe(IV)-O-O-R(Pc) (R = H in the case of H_2O_2) via *heterolytic* O-O bond cleavage. Therein we show that the evolution of the peroxo diiron complex depends on the peroxide structure. Using ^{t}BuOOH we have demonstrated the formation of an *one-electron oxidizing* PcFe(IV)µNFe(IV)=O(Pc) and ^{t}BuO$^\cdot$ radical via *homolytic* O-O cleavage of the peroxocomplex. The reactivity of the µ-nitrido diiron tetra-t-butylphthalocyanine – ^{t}BuOOH catalytic system was investigated in the oxidation of different C-H bonds in alkanes, olefins, aromatic and alkylaromatic compounds. The main products of cyclohexane oxidation were cyclohexanone and cyclohexanol whereas bicyclohexyl was formed in minor amounts even in the presence of O2 and tBuOOH. Under optimal conditions, the turnover numbers of almost 5300 have been achieved.

Keywords: oxidation, catalysis, alkanes, cyclohexane, phthalocyanine, µ-nitrido dimer, hydroperoxides.

1. Introduction

Oxidation of aliphatic C-H bonds continues to attract a significant attention because selective transformation of alkanes to oxygenated products is a direct synthetic approach to a variety of valuable products and platform molecules. Since aliphatic C-H bonds are among the least reactive in organic chemistry, their selective oxidation still constitutes a fundamental academic and industrial challenge. This chemical transformation can be performed in a catalytic fashion using different catalysts involving transition metal sites [1-19]. Inorganic oxides are widely used for the activation of C-H bonds [5]. Noble metal species based on Pt, Pd, Au, Ag, Os, Ir, Rh [1,2] as well as transition metal complexes including vanadium, chromium, iron, manganese, cobalt and other sites [6-8] have been extensively studied for the C-H activation. Polynuclear copper complexes and coordination polymers were also applied for the oxidation of alkanes [15]. In the complimentary approach, bio-inspired catalytic systems [3,9,10] based on porphyrins [12-14], phthalocyanine [11] and non-heme complexes [15-18] have been developed for the efficient and selective oxidation of C-H bonds. For instance, aminopyridine iron [20] and manganese complexes [21] oxidize aliphatic C-H bonds with a high regio- and stereoselectivity.

Although a range of synthetic molecular catalysts for the alkane oxidation has been developed, there still remains much interest in systems that use abundant, inexpensive and environmentally compatible metals such as iron in combination with available and cheap ligands. In this context, phthalocyanine iron complexes are especially attractive because they are efficient catalysts for many reactions including various oxidations [11,22] and can be readily prepared on industrial scale. Catalytic studies of iron phthalocyanine complexes led to the discovery of the remarkable catalytic properties of µ-nitrido diiron phthalocyanine complexes $(FePc)_2N$ (Fig. 1), in which Fe(III) and Fe(IV) sites are connected by the bridging nitrogen atom to form a very stable delocalized Fe-N-Fe unit with equivalent iron sites in the +3.5 oxidation state [23].

These binuclear complexes are particularly efficient in challenging oxidation reactions including oxidation of methane [24-27], ethane [28] and even in the oxidative dehalogenation of C-F, C-Cl and C-Br bonds [29-31]. Such remarkable reactivity has been achieved using hydrogen peroxide as a terminal oxidant and can be associated with the formation of the ultra-high valent diiron oxo species (L)$Fe^{IV}NFe^{IV}$=O($L^{+\cdot}$) (L = macrocyclic ligand, phthalocyanine or porphyrin) showing the powerful oxidizing properties [23,32,33]. This short-lived species were prepared using H_2O_2 or *m*-chloroperbenzoic acid as oxygen donors and were spectroscopically characterized at very low temperatures [23]. Such ultra-high valent diiron oxo species are competent even for the oxidation of the strongest C-H bonds in methane.

It is of great interest to investigate the catalytic properties of μ-nitrido diiron complexes using other oxidants. Recently, we have shown that the μ-nitrido-bis(tetra-*tert*-butylphthalocyaninatoiron) complex $(FePc^tBu_4)_2N$ in combination with ^tBuOOH in inert atmosphere mediated the formation of C-C bonds in the hydroacylation of olefins by acetaldehyde to furnish methyl ketones [34]. Interestingly, the $(FePc^tBu_4)_2N$ – H_2O_2 system didn't show this reactivity suggesting different active species generated using H_2O_2 and ^tBuOOH. The ability of $(FePc)_2N$ – ^tBuOOH system to catalyze the C-C bond formation was explained by the involvement of one-electron oxidized (Pc)Fe^{IV}(μ-N)Fe^{IV}(Pc)=O species and $^tBuO^\cdot$ radical. Both species are capable of abstracting hydrogen atom from C-H bonds which initiate formation of the substrate radicals and their coupling under anaerobic conditions [34]. In the presence of air, this system should also exhibit oxidizing properties. In the present work, we have evaluated $(FePc^tBu_4)_2N$ in the aerobic oxidation of aliphatic C-H bonds using ^tBuOOH as the oxidant.

2. Experimental

2.1. Materials

Iron (II) 2,9(10),16(17),23(24)-tetra-*tert*-butylphthalocyanine was synthesized and purified according to a published protocol [35]. μ-Nitridobis(tetra-*tert*-butylphthalocyaninatoiron(III,IV) [24] was prepared as described previously. *tert*-Butyl hydroperoxide (70 % aqueous solution) was purchased from Sigma-Aldrich. All other chemicals were obtained from Alfa Aesar or Sigma-Aldrich and used as received. Adamantane-1,3-d_2 was prepared according to published procedure [36].

2.2. Instrumentation.

The reaction products were identified and quantified by GC-MS method (Hewlett Packard 5973/6890 system, electron impact ionization at 70 eV, He carrier gas, 30m x 0.25 mm HP-INNOWax capillary column, polyethylene glycol (0.25 μm coating) and by GC technique (Agilent 4890D chromatograph equipped with a flame ionization detector and a 30 m x 0.25 mm VF-5 MS capillary column) using chlorobenzene standard. The UV-vis spectra of phthalocyanine complexes were obtained with Agilent 8453 diode-array spectrophotometer. ^1H NMR spectra were recorded using a Bruker AM 250 spectrometer.

2.3. Catalytic procedures and product analysis

Oxidation of hydrocarbons substrates was performed in a 100 mL glass vessel under dioxygen or argon atmosphere. Typically, the reactor was charged with 1 or 2 mL either neat substrate or 0.1 M substrate solution in MeCN containing 0.1 mM $(FePc^tBu_4)_2N$. The reactions were initiated by addition of 70 % aqueous solution of tBuOOH. The reaction mixture was magnetically stirred at 25, 50 or 60°C for desired time. Reaction products were analyzed by GC-MS and GC directly or using Ph3P method introduced by Shul'pin [37]. Chlorobenzene standard was added as 0.1 M solution prior to analyses.

3. Results and Discussion

3.1. Oxidation of cyclohexane

Catalytic experiments were conducted in the presence of $(FePc^tBu_4)_2N$ and ^tBuOOH either in the neat substrates or in 0.1 M substrate solutions in MeCN. In the latter case 0.1 mol% catalyst loading was applied. The oxidation of neat cyclohexane at 25°C in the presence of 0.1 mM $(FePc^tBu_4)_2N$ and 0.2 M ^tBuOOH occurred with the turnover frequency of 3.9 min^{-1}. It should be noted that the corresponding monomeric complex $(FePc^tBu_4)Cl$ was much less efficient in the oxidation of cyclohexane providing cyclohexanol (Cy-OH) and cyclohexanone (Cy=O) in ~1:1 ratio with turnover number (TON) of 27. In addition, the $(FePc^tBu_4)Cl$ was decomposed after 20 min reaction.

The dependence of the initial rates of the cyclohexane oxidation expressed as total product concentration after 1 h reaction was examined as a function of the $(FePc^tBu_4)_2N$ concentration (Fig. 2).

This dependence indicates the first order reaction in $(FePc^tBu_4)_2N$. The rate of the cyclohexane oxidation didn't depend on the ^tBuOOH concentration between 0.05 M and 0.5 M in the presence of 0.05 mM $(FePc^tBu_4)_2N$ showing the zero order in ^tBuOOH. At lower oxidant concentration, $[^tBuOOH]$ significantly influenced the reaction rate.

Accumulation of the oxidation products with the reaction time is shown in Fig. 3.

Along with cyclohexanol (Cy-OH) and cyclohexanone (Cy=O) formed in the comparable amounts, the formation of bicyclohexyl (Cy-Cy) was observed even in the presence of dioxygen and high concentration of ^tBuOOH indicating the intermediate formation of cyclohexyl radicals. The treatment of the reaction mixture with Ph_3P according to Shul'pin method [37] didn't significantly change the product composition indicating that cyclohexyl hydroperoxide was not present in the reaction mixture in significant amounts. The product of coupling of cyclohexyl radicals represented 8.0 % of the reaction products while cyclohexanone and cyclohexanol accounted for 50.4 and 41.6 %, respectively. The total concentration of products attained 79.2 mM after 6 h and 98.4 mM after 24 h. The total turnover number reached 1063 cycles per catalyst molecule (bycyclohexyl originated from two cyclohexane molecules). The product yield on ^{t}BuOOH was 59 %.

The oxidation of cyclohexane was more efficient at 50°C and in the presence of 0.5 M ^{t}BuOOH resulting in 1877 turnovers after 14 h reaction. Cy-OH, Cy=O and Cy-Cy were obtained in 72.7, 103.0 and 12.0 mM concentrations, respectively (the product distribution: Cy-OH : Cy=O : Cy-Cy = 38.7 : 54.9 : 6.4). The product yield on ^{t}BuOOH was 67 %. Noteworthy, $(FePc^tBu_4)_2N$ was quite stable under reaction conditions. UV-vis analysis of the final reaction mixture was shown that only 10 % of the complex was decomposed.

In the next experiment, ^{t}BuOOH was added in three portions each introducing 0.25 M concentration at the reaction times of 0, 3 h and 6 h. The reaction was further performed for additional 17 h. The portion-wise addition of ^{t}BuOOH resulted in the higher yields and TON (Table 1).

The main oxidation product was Cy=O and the product distribution was rather constant during the reaction. The total TON progressively increased in the course of the reaction to achieve almost 5300 turnovers. Remarkably, the oxidation of neat cyclohexane resulted in 5.9 % conversion. The yields of the oxidation products based on BuOOH were 68, 81 and 94 % after 3, 6 and 9 h, respectively, attaining 114 % in the end of the reaction. This result indicates participation of O_2 in the oxidation.

The catalytic performance of $(FePc^tBu_4)_2N$ was also evaluated in the oxidation of 0.1 M cyclohexane solution in MeCN. When 2 equiv of ^{t}BuOOH was used, a 12 % Cy-H conversion was observed but the TON was moderate attaining 87 turnovers. Cy=O and Cy-OH were obtained in a 2.6 : 1 ratio.

3.2. Oxidation of toluene

The $(FePc^tBu_4)_2N$ – ^{t}BuOOH system mediated oxidation of neat toluene to benzyl alcohol, benzaldehyde and benzoic acid with 10, 52 and 38 % selectivity, respectively. The total TON achieved 1216. The trace amounts of *ortho-* and *para*-cresols, 2-methylbenzoquinone and $PhCH_2$–OO^tBu coupling product were also formed. Thus, this catalytic system shows a clear preference for aliphatic C-H oxidation over the oxidation of aromatic C-H bonds. It should be noted that the oxidation of 0.1 M toluene solution in MeCN was less efficient: benzaldehyde and benzoic acid were obtained with turnover numbers of 23 and 3, respectively. Taking into account that the oxidation of benzyl alcohol (0.1 M solution in MeCN) provided benzaldehyde with a 28 % yield at 36 % conversion and total TON of 360, one can suggest that the initial cleavage of the benzylic C-H bond is the limiting step.

3.3. Oxidation of adamantane. Determination of intramolecular k_H/k_D

Kinetics of the oxidation of 0.1 M adamantane solution in MeCN in the presence of 0.1 mM $(FePc^tBu_4)_2N$ and 0.25 M ^tBuOOH (catalyst:substrate:oxidant = 1:1000:2500) at 50°C is shown in Fig. 4.

Adamantane conversion of 67 % was achieved after 6 h. The oxidation occurred mostly at tertiary C-H bond with 3°/2° parameter of 17 after correction on the number of C-H bonds. Total TON attained 670 and 1-adamantanol, 2-adamantanone and 2-adamantanol were obtained with 57, 8 and 2 % yields, respectively.

In order to probe the mechanism of the alkane oxidation, we have investigated the kinetic isotope effect (k_H/k_D) on the oxidation of adamantane-1,3-d_2. This useful probe contains equivalent tertiary C-H and C-D bonds and enables determination of *intra*-molecular k_H/k_D [36]. The analysis of the isotopic composition of the adamantanol-1 provides a relatively high k_H/k_D value of 3.67 ± 0.11 which didn't change during 3 h of the reaction (Fig. 5).

3.4. Oxidation of cyclohexene

The oxidation of neat cyclohexene was studied in the presence of 0.2 mM $(FePc^tBu_4)_2N$ and 0.25 M ^tBuOOH at 60°C. The main oxidation products were 2-cyclohexen-1-ol, 2-cyclohexen-1-one, 3-*tert*-butylperoxocyclohexene and 3,3'-bicyclohexenyl while the epoxide was obtained only in minor amount. The yields of the products and the product composition were strongly affected by the presence or absence of dioxygen (Fig. 6).

When the reaction was performed under Ar, the total concentration of the products decreased down to 198.9 mM compared with 535.6 mM obtained under air. Under air, allylic alcohol (23.3 %) and ketone (68.7 %) were the major oxidation products whereas 3-*tert*-butylperoxocyclohexene and 3,3'-bicyclohexenyl accounted for 6.8 and 1.2 %. Under inert atmosphere, the main reaction product was allylic peroxide (53.9 %) and the content of allylic alcohol and ketone decreased to 11.1 and 19.2 %, respectively. Remarkably, the concentration of 2-cyclohexen-1-one dropped from 368 mM under air down to 38.2 mM under Ar. The significant amount of 3,3'-bicyclohexenyl (15.8 %) arising from coupling of cyclohexenyl radicals was formed. The total TON dropped from 2709 under air down to 1152 under Ar. The yield of the oxidation products based on the ^tBuOOH amount was 361 %. All these results indicate the involvement of dioxygen in the oxidation of cyclohexene.

3.5. Oxidation of benzene

The catalytic activity of the $(FePc^tBu_4)_2N$ - ^tBuOOH system toward aromatic C-H bonds was lower than that of $(FePc^tBu_4)_2N – H_2O_2$. The $(FePc^tBu_4)_2N – H_2O_2$ system oxidized benzene to phenol with the TON of 66 [38]. The oxidation of neat benzene in the presence of 0.5 mM $(FePc^tBu_4)_2N$ and 0.35 M ^tBuOOH at 60°C for 24 h resulted in the formation of 14.5 mM of biphenyl and less than 1.5 mM of phenol. The combined TON achieved 32 turnovers. The oxidation of a 1 : 1 C_6H_6 / C_6D_6 mixture provided biphenol with following isotopic composition: 47.7 % C_6H_5-C_6H_5, 45.0 % C_6H_5-C_6D_5 and 7.3 % of C_6D_5-C_6D_5 after 3 h. This isotopic composition didn't change after 24 h reaction. Thus, k_H/k_D in the oxidation of benzene was calculated to be 2.36. Noteworthy, k_H/k_D in the oxidation of the C_6H_6 / C_6D_6 mixture by the $(FePc^tBu_4)_2N$ - H_2O_2 system at 60°C was determined to be 1.16 [38].

3.5. Mechanistic considerations

The present study shows that the $(FePc^tBu_4)_2N$ – ^tBuOOH system efficiently oxidizes C-H bonds of alkanes, olefins, alkyl aromatic and aromatic compounds in the presence of dioxygen. Under anaerobic conditions, the same system was particularly efficient in the addition of CH_3CHO to a range of olefins whereas the conventional oxidation products were obtained in very minor amounts [34]. Importantly, the $(FePc^tBu_4)_2N – H_2O_2$ system didn't exhibit such a reactivity. Several lines of evidence point out on the difference between these systems. Both oxidants are activated via initial formation of negatively charged diiron peroxo complexes Fe-N-Fe–OOH (A) and Fe-N-Fe–OO^{t}Bu (B) which were detected by ESI-MS technique [29,33] (Fig. 7).

To rationalize this different catalytic behaviour of $(FePc)_2N – H_2O_2$ (strong oxidizing properties) and $(FePc)_2N$ – ^tBuOOH (strong C-C forming ability in aerobic conditions) systems, we have proposed the different evolution of the corresponding μ-nitrido diiron peroxo species (Fig. 7). $(Pc)Fe^{IV}(\mu\text{-}N)Fe^{III}(Pc)\text{-}O\text{-}OH$ undergoes the heterolytic cleavage resulting in $(Pc)Fe^{IV}(\mu\text{-}N)Fe^{IV}(Pc^{+\cdot})=O$ transient complex having two redox equivalents above initial Fe(+3.5)Fe(+3.5) state. This species is a strong two-electron oxidant. Thus, the high reactivity of μ-nitrido diiron macrocyclic complex – H_2O_2 system toward strong C-H bonds of the light alkanes was associated with their ability to form high-valent diiron oxo complex $(L)Fe^{IV}(\mu\text{-}N)Fe^{IV}=O(L^{+\cdot})$, L = phthalocyanine or porphyrin [24,26]. These highly active oxidizing species obtained using H_2O_2 or *m*-chloroperbenzoic acid as oxygen donors have been characterized at low temperatures by several spectroscopic techniques and isotopic labeling [23]. DFT calculations have also indicated particularly strong oxidizing properties of the $(L)Fe^{IV}(\mu\text{-}N)Fe^{IV}=O(L^{+\cdot})$ species and their high reactivity in the oxidation of methane [23,27,39,40]. We have experimentally evidenced that (L)Fe^{IV}(μ-N)Fe^{IV}=O(L$^{+\cdot}$) is competent for methane oxidation and its reactivity is different from that of hydroxyl radical [24-26].

Contrary to the peroxo complex derived from H_2O_2, (Pc)Fe^{IV}(μ-N)Fe^{III}(Pc)-O-O^{t}Bu was proposed to undergo the homolytic O-O cleavage producing *one-electron oxidized* (Pc)Fe^{IV}(μ-N)Fe^{IV}(Pc)=O and ^{t}BuO$^\cdot$ radical. Under inert atmosphere $(FePc)_2N$ – ^{t}BuOOH system exhibited a strong tendency for the formation of C-C bonds due to the involvement of Fe^{IV}(μ-N)Fe^{IV}=O and ^{t}BuO$^\cdot$ species which attract the hydrogen atom from C-H bonds of the substrates to generate radicals which then recombine forming coupling products. In the presence of dioxygen, these radicals are intercepted by O_2 forming peroxo radicals which initiate radical oxidation reaction. The particular feature of this system is the simultaneous generation of two active species capable of reacting with C-H bonds. This increases the efficiency of the process. The proposed reaction mechanism is shown in Fig. 8.

Cyclohexenyl hydroperoxyde CyOOH is an important product of this radical oxidation. In turn, it can be activated by μ-nitrido diiron complex to form (Pc)Fe^{IV}(μ-N)Fe^{III}(Pc)-O-O^{t}Cy followed by the formation of (Pc)Fe^{IV}(μ-N)Fe^{IV}(Pc)=O and CyO$^\cdot$ radical which initiate further oxidation. Thus, the (FePc^{t}Bu$_4$)$_2$N - ^{t}BuOOH system operates via one-electron oxidation pathways involving free radicals. Following observations are in agreement with this mechanism:

(i) Formation of 3,3’-bicyclohexenyl in notable amounts even in the presence of dioxygen and high concentration of ^{t}BuOOH. Homolytic O-O cleavage generates two active species, (Pc)Fe^{IV}(μ-N)Fe^{IV}=O(Pc) and ^{t}BuO$^\cdot$ radical which rapidly react with surrounding cyclohexane molecules to form two cyclohexyl radicals in close proximity to each other. This can explain the formation of Cy-Cy even in the presence of high concentrations of O_2 and ^{t}BuOOH oxidants. These radicals can recombine to give rise a coupling product Cy-Cy or diffuse out the cage to be trapped by dioxygen to form Cy-O-O$^\cdot$ radical. The Cy$^\cdot$ radicals can also react with other oxidizing species.

(ii) Formation of Cy-OH and Cy=O in comparable amounts are usually observed when Cy-O-O$^\cdot$ radicals are involved. Two Cy-O-O$^\cdot$ molecules interact according to Russell termination mechanism to form Cy-O-O-O-O-Cy intermediate which generates Cy-OH, Cy=O and O_2 upon degradation.

(iii) A 114 % product yield based on ^{t}BuOOH obtained in the cyclohexane oxidation with portion-wise addition of ^{t}BuOOH suggests the involvement of O_2.

(iv) When 0.1 M cyclohexane solution was used, the Cy-Cy coupling product was absent and Cy=O accounted for 72 % of products despite a moderate TON (87 turnovers). The predominant formation of Cy-OH could be expected under these conditions. This result can be explained by the fact that parallel formation of two adjacent radicals is disfavoured by the lower substrate concentration. Instead, Cy-H molecule reacts with either $(Pc)Fe^{IV}(\mu\text{-}N)Fe^{IV}{=}O(Pc)$ or $^{t}BuO^{\cdot}$ radical to form Cy radical which then trapped by adjacent active species to form oxidation product (Fig. 8).

(v) It is believed that low values of 3°/2° parameter (3°/2° < 6) in adamantane oxidation are indicative of a free-radical mechanism [41] although $^{t}BuO^{\cdot}$-initiated reactions show the high values (3°/2° ~ 10) [42]. The 3°/2° values greater than 13-15 are usually associated with a metal-based mechanism [43]. Cytochrome P450 and heme complexes exhibit the 3°/2° adamantane regioselectivity as high as 48:1 [44]. Thus, the 3°/2° value of 17 obtained in the oxidation of adamantane by the $(FePc^{t}Bu_4)_2N$ - $^{t}BuOOH$ system is compatible with simultaneous involvement of both $(Pc)Fe^{IV}(\mu\text{-}N)Fe^{IV}{=}O(Pc)$ and $^{t}BuO^{\cdot}$ species.

(vi) Significant kinetic isotope effect of 3.67 observed in the oxidation of adamantane-*d₂* is compatible with participation of both $(Pc)Fe^{IV}(\mu\text{-}N)Fe^{IV}{=}O(Pc)$ and $^{t}BuO^{\cdot}$ species. The values of k_H/k_D in the oxidation of p-xylene and toluene by high-valent iron oxo species of cytochrome P-450 and by $^{t}BuO^{\cdot}$ were nearly identical: 6.4 vs 6.3 and 5.9 vs 6.0, respectively [45].

(vii) Composition of the products of cyclohexene oxidation including allylic oxidation products and 3,3'-bicyclohexenyl strongly suggests the involvement of radicals and one-electron oxidants.

(viii) Strong dependence of the yield and composition of the products of cyclohexene oxidation on the presence of O_2 (Fig. 6) indicates the participation of O_2 in the reaction. A sharp decrease of 2-cyclohexen-1-ol and 2-cyclohexen-1-one amounts observed in anaerobic conditions, from 125.2 mM and 368 mM down to 22 mM and 38.2 mM, respectively, indicates that these products should be formed through the reaction pathways involving O_2. In turn, a strong increase of 3-tert-butylperoxocyclohexene and 3,3'-bicyclohexenyl contents under Ar points out that the concurrent recombination of cyclohexenyl and $^{t}BuO^{\cdot}$ radicals becomes a predominate pathway in the absence of O_2.

(ix) While phenol was the principal product of benzene oxidation by the $(FePc^{t}Bu_4)_2N$ – H_2O_2 system operating via two-electron mechanism with the intermediate formation of benzene epoxide [38], biphenyl was obtained with a 91 % selectivity using the $(FePc^{t}Bu_4)_2N$ - $^{t}BuOOH$ system. Kinetic isotope effects in the oxidation of benzene by $^{t}BuOOH$ and H_2O_2 catalyzed by $(FePc^{t}Bu_4)_2N$ are also different: 2.36 and 1.16, respectively. The $^{t}BuO^{\cdot}$ radical was published to be incompetent in the oxidation of benzene [46]. Decomposition of $^{t}BuOOH$ in benzene in the presence of $^{t}BuOO^{t}Bu$ initiator produced acetone, $^{t}BuOH$, CO, CO_2 and small amount of O_2 without products of benzene oxidation. Consequently, formation of the benzene oxidation products by the $(FePc^{t}Bu_4)_2N$ - $^{t}BuOOH$ system is compatible with the proposed mechanism and in particular, with the participation of $(Pc)Fe^{IV}(\mu\text{-}N)Fe^{IV}{=}O(Pc)$ in the oxidation by abstracting of hydrogen atom from benzene. Phenyl radicals recombine to form biphenyl since their recombination with alkoxyl radicals is slow.

4. Conclusions

The results of the current study confirm that the structure of the oxidant determines the mechanism of its activation by µ-nitrido diiron phthalocyanine resulting in different active species. Using H_2O_2, a very strong *two-electron oxidizing* species PcFe(IV)µNFe(IV)=O($Pc^{+\cdot}$) is generated from the peroxo complex PcFe(IV)µNFe(IV)-OOH(Pc) via *heterolytic* O-O bond cleavage. In contrast, PcFe(IV)µNFe(IV)-OO^{t}Bu(Pc) generated from ^{t}BuOOH undergoes a *homolytic* O-O cleavage to form an *one-electron oxidizing* PcFe(IV)µNFe(IV)=O(Pc) and $^tBuO^\cdot$ radical showing a different reactivity. The $(FePc^tBu_4)_2N$ - ^{t}BuOOH catalytic system is efficient in the oxidation of C-H bonds of alkanes, olefins, alkylaromatic and aromatic compounds furnishing oxidation products with high turnover numbers within several hours at low catalyst loading. The efficiency of this system can be explained by generation from one peroxide molecule two active species able to react with different C-H bonds thus opening interesting possibilities for catalytic oxidation.

In addition, the catalytic system consisting of accessible, earth abundant and non-toxic iron-based catalyst and industrial environmentally compatible oxidant would be of great practical interest. *N*-Bridged diiron phthalocyanine complexes are non-expensive and non-toxic, and can be available on a large scale. They can be readily immobilized onto different supports. For all these reasons we believe that this novel approach might be useful for the development of novel oxidation processes. Radical reactions catalyzed by transition metal catalysts gain in importance in modern catalysis [47-49]. The further development of this approach might results in useful synthetic transformations in mild and environmentally benign conditions.

5. Acknowledgements

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6. References

[1] A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2879-2932.

[2] A.E. Shilov, G.B. Shul'pin, Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes.Kluwer Academic Publishers, Dordrecht/Boston/London, 2000, 548 pp.

[3] A. Company, J. Lloret, L. Gómez, M. Costas, in Alkane C-H Activation by Single-Site Metal Catalysis, ed. P.J. Pérez, Springer, Heidelberg, v. 38, pp. 143-228.

[4] J.F. Hartwig, J. Am. Chem. Soc. 138 (2016) 2-24.

[5] C. Copéret, Chem. Rev. 110 (2010) 656-680.

[6] G.B. Shulpin, Org. Biol. Chem. 8 (2010) 4217-4228.

[7] G.B. Shul'pin, Dalton Trans. 42 (2013) 12794-12818.

[8] M.M. Vinogradov, Y.N. Kozlov, D.S. Nesterov, L.S. Shul'pina, A.J.L. Pombeiro, G.B. Shul'pin, Cat. Sci. Technol. 4 (2014) 3214-3226.

[9] A.C. Lindhorst, S. Haslinger, F.E. Kühn, Chem. Commun. 51 (2015) 17193-17212.

[10] A.A. Shteinman, Russ. Chem. Rev. 77 (2008) 945-966.

[11] A.B. Sorokin, Chem. Rev. 113 (2013) 8152-8191

[12] M. Costas, Coord. Chem. Rev. 255 (2011) 2912-2932.

[13] H. Li, X.P. Zhang, Chem. Soc. Rev. 40 (2011) 1899-1899.

[14] C.-M. Che, J.-S. Huang, Chem. Commun. (2009) 3996-4015.

[15] E.P. Talsi, K.P. Bryliakov, Coord. Chem. Rev. 256 (2012) 1418-1434.

[16] A.M. Kirillov, M.V. Kirillova, A.J.L. Pombeiro, Coord. Chem. Rev. 256 (2016) 2741-2759.

[17] W. Nam, Y.-M. Lee, S. Fukuzumi, Acc. Chem. Res. 47 (2014) 1146-1154.

[18] X. Engelmann, I. Monte-Pérez, K. Ray, Angew. Chem. Int. Ed. 55 (2016) 7632-7649.

[19] A.E. Shilov, A.A. Shteinman, Russ. Chem. Rev. 81 (2012) 291-316.

[20] J. Serrano-Plana, W.N. Oloo, L. Acosta-Rueda, K.K. Meier, B. Verdejo, E. Garcia-Espana, M.G. Basallote, E. Münck, L. Que, Jr., A. Company, M. Costas, J. Am. Chem. Soc. 137 (2015) 15833-15842.

[21] R.V. Otenbacher, D.G. Samsonenko, E.P. Talsi, K.P. Bryliakov, Org. Lett. 14 (2012) 4310-4313.

[22] A.B. Sorokin, E.V. Kudrik, Catal. Today 159 (2011) 37-46.

[23] P. Afanasiev, A.B. Sorokin, Acc. Chem. Res. 49 (2016) 583-593.

[24] A.B. Sorokin, E.V. Kudrik, D. Bouchu, Chem. Commun. (2008) 2562-2564.

[25] A.B. Sorokin, E.V. Kudrik, L.X. Alvarez, P. Afanasiev, J.M.M. Millet, D. Bouchu, Catal. Today 157 (2010) 149-154.

[26] E.V. Kudrik, P. Afanasiev, L.X. Alvarez, P. Dubourdeaux, M. Clémancey, J.-M. Latour, G. Blondin, D. Bouchu, F. Albrieux, S.E. Nefedov, A.B. Sorokin, Nature Chem. 4 (2012) 1024-1029.

[27] Ü. Işci, A.S. Faponle, P. Afanasiev, F. Albrieux, V. Briois, V. Ahsen, F. Dumoulin, A.B. Sorokin, S.P. de Visser, Chem. Sci. 6 (2015) 5063-5075.

[28] L.X. Alvarez, A.B. Sorokin, J. Organomet. Chem. 793 (2015) 139-144.

[29] P. Afanasiev, D. Bouchu, E.V. Kudrik, J.M.M. Millet, A.B. Sorokin, Dalton Trans. (2009) 9828-9836.

[30] C. Colomban, E.V. Kudrik, P. Afanasiev, A.B. Sorokin, J. Am. Chem. Soc. 136 (2014) 11321-11330.

[31] C. Colomban, E.V. Kudrik, P. Afanasiev, A.B. Sorokin, Catal. Today 235 (2014) 14-19.

[32] C. Colomban, E.V. Kudrik, V. Briois, J.C. Shwarbrick, A.B. Sorokin, P. Afanasiev, Inorg. Chem. 53 (2014) 11517-11530.

[33] P. Afanasiev, E.V. Kudrik, J.M.M. Millet, D. Bouchu, A.B. Sorokin, Dalton Trans. 40 (2011) 701-710.

[34] L.X. Alvarez, E.V. Kudrik, A.B. Sorokin, Chem. Eur. J. 17 (2011) 9298-9301.

[35] J. Metz, O. Schneider, M. Hanack, Inorg. Chem. 23 (1984) 1065-1071.

[36] A. Sorokin, A. Robert, B. Meunier, J. Am. Chem. Soc. 115 (1993) 7293-7299.

[37] G.B. Shul’pin, J. Mol. Catal. A : Chem. 189 (2002) 39-66.

[38] E.V. Kudrik, A.B. Sorokin, Chem. Eur. J. 14 (2008) 7123-7126.

[39] R. Silaghi-Dimitresku, S.V. Makarov, M.-M. Uta, I.A. Dereven’kov, P.A. Stuzhin, New J. Chem. 35 (2011) 1140-1145.

[40] M.G. Quesne, D. Senthilnathan, D. Singh, D. Kumar, P. Maldivi, A.B. Sorokin, S.P. de Visser, ACS Catal. 6 (2016) 2230-2243.

[41] G. Olivo, O. Lanzalunga, S. Di Stefano, Adv. Synth. Catal. 358 (2016) 843-863.

[42] D.H.R. Barton, A.H. Beck, D.K. Taylor, Tetrahedron 51 (1995) 5245-5254.

[43] M. Costas, K. Chen, L. Que, Jr., Coord. Chem. Rev. 200-202 (2000) 517-544.

[44] J.T. Groves, T.E. Nemo, J. Am. Chem. Soc. 105 (1983) 6243-6248.

[45] J.I. Manchester, J.P. Dinnocenzo, L.A. Higgins, J.P. Jones, J. Am. Chem. Soc. 119 (1997) 5069-5070.

[46] R.R. Hiatt, T. Mill, J.K. Casteman, J. Org. Chem. 33 (1968) 1421-1428.

[47] M.V. Kirillova,Y.N. Kozlov, L.S. Shul’pina, O.Y. Lyakin, A.M. Kirillov, E.P. Talsi, A.J.L. Pombeiro, G.B. Shul’pin, J. Catal. 268 (2009) 26-38.

[48] M. Sutradhar, M.V. Kirillova, M.F.C. Guedes da Silva, L.M.D.R.S. Martins, A.J.L. Pombeiro, Inorg. Chem. 51 (2012) 11229-11231.

[49] M.V. Kirillova, A.M. Kirillov, A.J.L. Pombeiro, Chem. Eur. J. 16 (2010) 9485-9493.

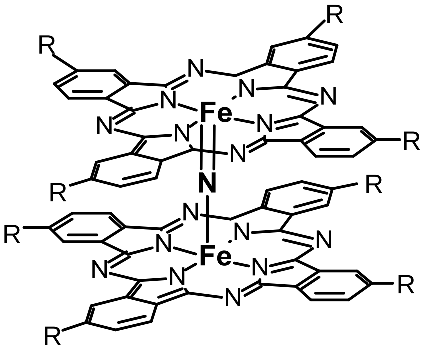

Fig. 1. General structure of µ-nitrido diiron phthalocyanine complexes. The complex with R = ^{t}Bu was used in this study.

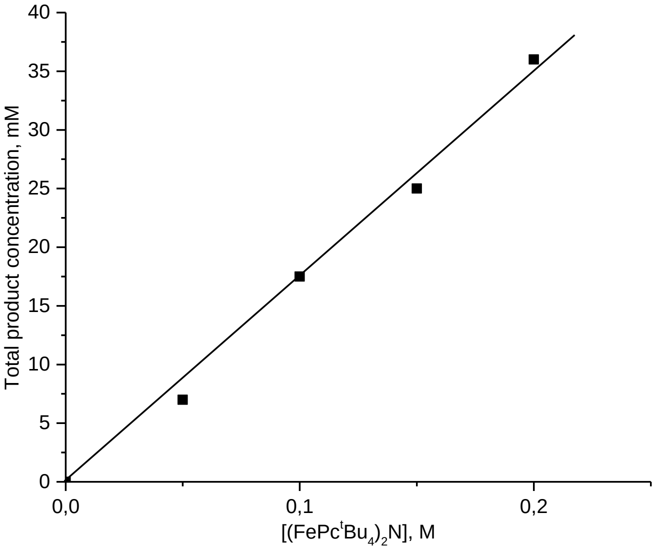

Fig. 2. Dependence of the total product yield of cyclohexane oxidation after 1 h on (FePc^{t}Bu$_4$)$_2$N concentration. Experimental conditions: 1mL cyclohexane (9.26 M), [^{t}BuOOH] = 0.2 M, 25°C.

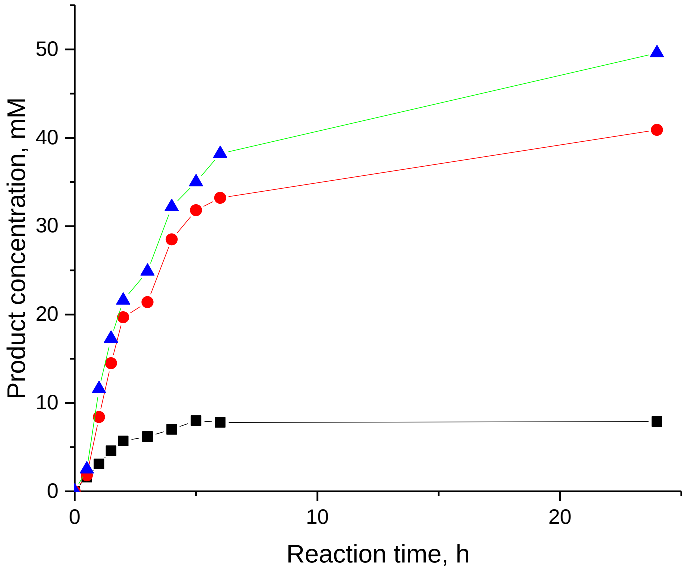

Fig. 3. Accumulation of cyclohexanone (▲), cyclohexanol (●) and bicyclohexyl (■) during oxidation of neat cyclohexane. Experimental conditions : 1mL cyclohexane (9.26 M), [(FePctBu4)2N] = 0.1 mM, [tBuOOH] = 0.25 M, 25°C.

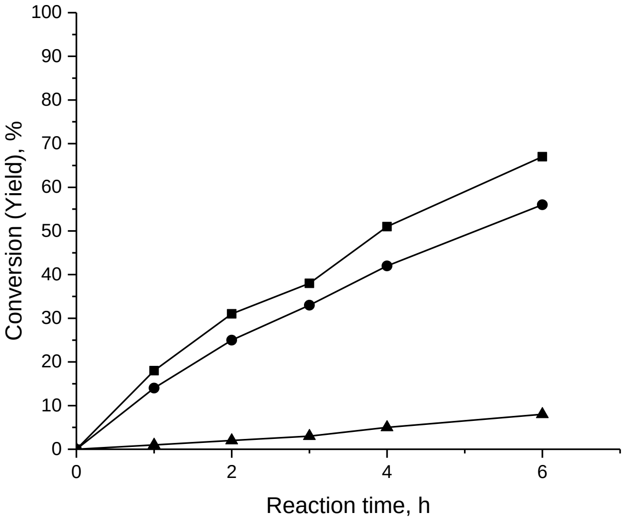

Fig. 4. Oxidation of adamantane catalyzed by $(FePc^tBu_4)_2N$ - ^tBuOOH system in MeCN at 50°C. Adamantane : $(FePc^tBu_4)_2N$: ^tBuOOH = 0.1 M : 0.1 mM : 0.25 M. ■ - conversion of adamantane, ● – 1-adamantanol yield, ▲ – 2-adamantanone yield.

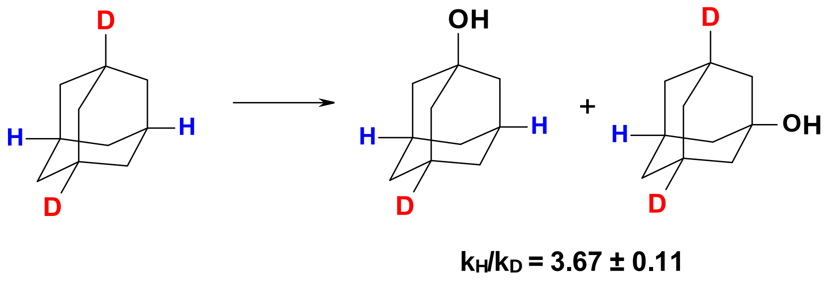

Fig. 5. Determination of the intramolecular isotope effect using adamantane-1,3-*d*$_2$.

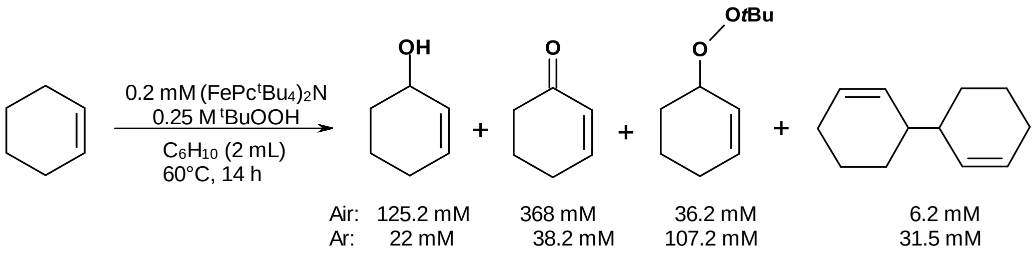

Fig 6. Oxidation of neat cyclohexene (2mL, 9.87 M) by (FePc^{t}Bu$_4$)$_2$N - ^{t}BuOOH system under air and under inert atmosphere.

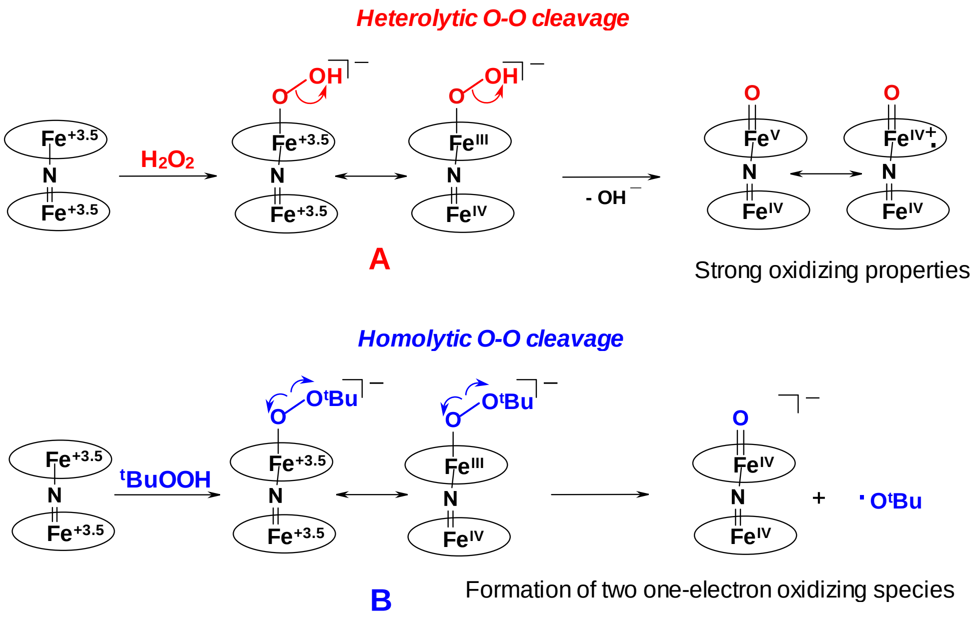

Fig. 7. Formation of diiron peroxo complexes in the presence of H_2O_2 and ${}^tBuOOH$ and their transformation to different diiron oxo species via heterolytic and homolytic O-O bond cleavage, respectively.

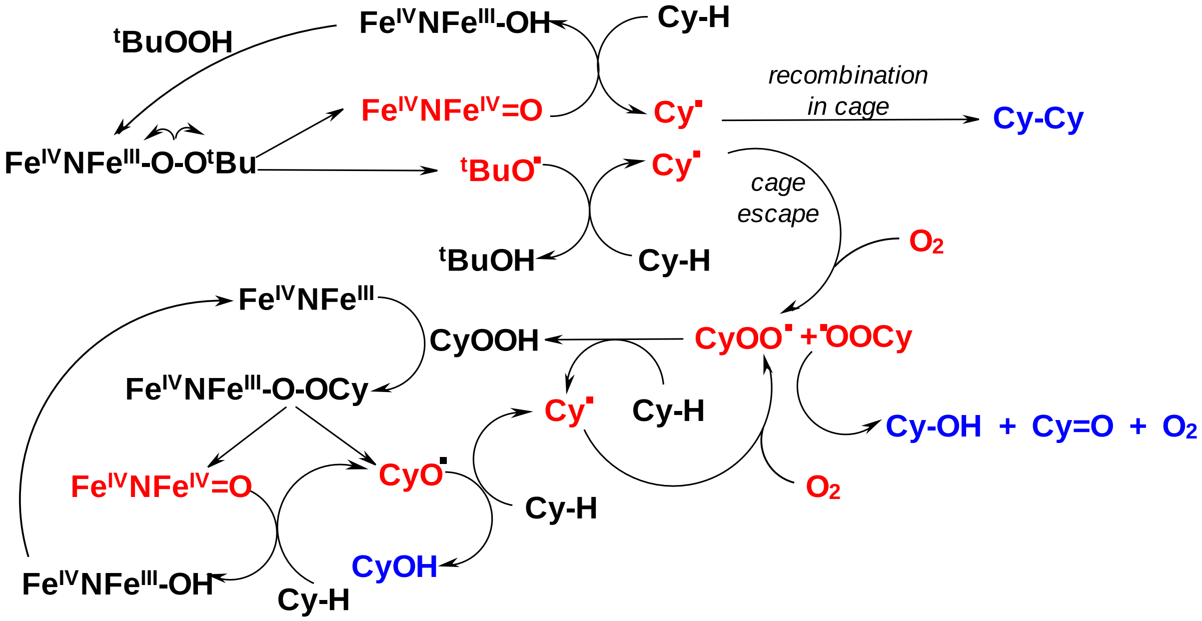

Fig. 8. Proposed mechanism of the oxidation of cyclohexane by $(FePc^tBu_4)_2N$ – ${}^tBuOOH$ system. Phthalocyanine ligands are omitted for clarity. Species reacting with C-H bonds are depicted in red and principal products are in blue.

Table 1. Oxidation of neat cyclohexane by (FePc^{t}Bu$_4$)$_2$N - ^{t}BuOOH system.

Reaction time, h	Concentration, mM			Distribution, % Cy-OH:Cy=O:Cy-Cy	Yield on ^{t}BuOOH, %^{b}	Total TON
	Cy-OH	Cy=O	Cy-Cy			
3	48.3	59.4	2.2	44 : 54 : 2	68	1099
6	117.8	141.9	5.0	44 : 54 : 2	81	2647
9	195.5	246.5	14.0	43 : 55 : 2	94	4560
23	191.2	323.7	14.7	36 : 61 : 3	114	5296

a Conditions: 2 mL of cyclohexane (9.26 M), [(FePctBu4)2N] = 0.1 mM, tBuOOH was added in three portions at 0, 3 and 6 h, total [tBuOOH] = 0.75 M, 50°C. b Yield was based on the amount of the oxidant tBuOOH added before analysis taking into account that two oxidant equivalents are consumed to produce Cy=O. The yield of 114 % (last line) is due to the involvement of O2 in the oxidation reaction.