Journal of Molecular Catalysis A: Chemical 426 (2017) 499–505

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Editor's choice paper

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

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ARTICLE INFO

Article history:
Received 1 August 2016
Received in revised form 11 August 2016
Accepted 12 August 2016
Available online 12 August 2016

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

Keywords:
Oxidation
Catalysis
Alkanes
Cyclohexane
Phthalocyanine
μ-Nitrido dimer
Hydroperoxides

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($Pc^{+\bullet}$). This very strong *two-electron oxidizing* species is generated from peroxo complex PcFe(IV)μNFe(III)—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$^\bullet$ 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 O_2 and ^{t}BuOOH. Under optimal conditions, the turnover numbers of almost 5300 have been achieved.

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],

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http://dx.doi.org/10.1016/j.molcata.2016.08.013
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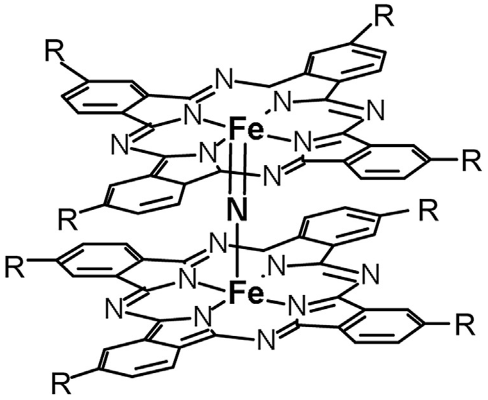

Fig. 1. General structure of μ-nitrido diiron phthalocyanine complexes. The complex with R=^{t}Bu was used in this study.

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 $(L)Fe^{IV}NFe^{IV}{=}O(L^{+\bullet})$ (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 ^{t}BuOOH 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 ^{t}BuOOH. The ability of $(FePc)_2N{-}^tBuOOH$ system to catalyze the C—C bond formation was explained by the involvement of one-electron oxidized $(Pc)Fe^{IV}(\mu\text{-}N)Fe^{IV}(Pc){=}O$ species and $^tBuO^\bullet$ 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 ^{t}BuOOH 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, 30 m × 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 × 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. ^{1}H NMR spectra were recorded using a Bruker AM 250 spectrometer.

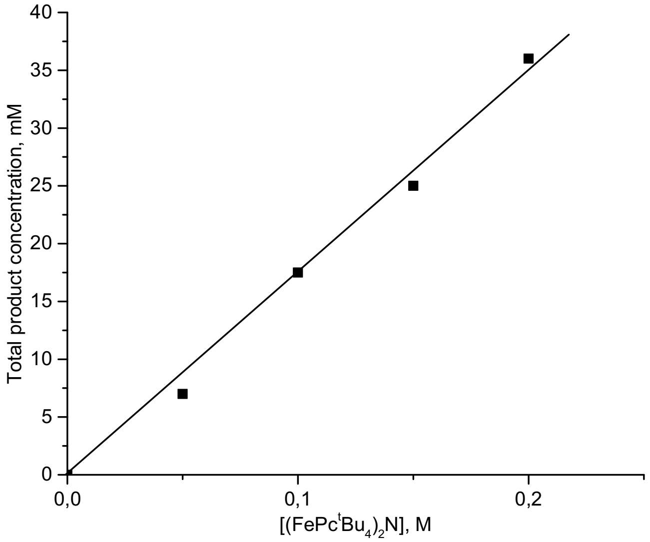

Fig. 2. Dependence of the total product yield of cyclohexane oxidation after 1 h on $(FePc^tBu_4)_2N$ concentration. Experimental conditions: 1 mL cyclohexane (9.26 M), [^{t}BuOOH] = 0.2 M, 25 °C.

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 Ph_3P 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 ^{t}BuOOH 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 ^{t}BuOOH 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