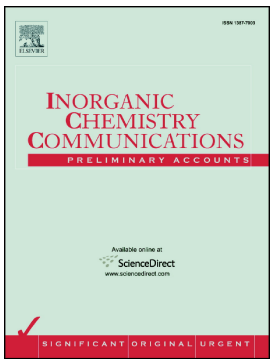


Catalytic and stoichiometric C-H oxidation of benzylalcohols and hydrocarbons mediated by nonheme oxoiron(IV) complex with chiral tetrapyridyl ligand

Dóra Lakk-Bogáth, Balázs Kripli, Bashdar I. Meena, Gábor Speier, József Kaizer

PII: S1387-7003(19)30217-5
DOI: https://doi.org/10.1016/j.inoche.2019.04.008
Reference: INOCHE 7352

To appear in: *Inorganic Chemistry Communications*

Received date: 4 March 2019
Revised date: 1 April 2019
Accepted date: 7 April 2019

Please cite this article as: D. Lakk-Bogáth, B. Kripli, B.I. Meena, et al., Catalytic and stoichiometric C-H oxidation of benzylalcohols and hydrocarbons mediated by nonheme oxoiron(IV) complex with chiral tetrapyridyl ligand, Inorganic Chemistry Communications, https://doi.org/10.1016/j.inoche.2019.04.008

Catalytic and stoichiometric C-H oxidation of benzylalcohols and hydrocarbons mediated by nonheme oxoiron(IV) complex with chiral tetrapyridyl ligand

Dóra Lakk-Bogáth, Balázs Kripli, Bashdar I. Meena, Gábor Speier and József Kaizer*

[a]*Department of Chemistry, Universtiy of Pannonia, 8201 Veszprém, Hungary*

Abstract

Bioinspired chiral iron(II) complex $[((R)\text{-}(-)\text{-N4Py*})Fe^{II}(CH_3CN)]^{2+}$ (**1**) (N4Py* = *N*,*N*-bis(2-pyridylmethyl)-1,2-di(2-pyridyl)ethylamine) has been shown to efficiently catalyze the benzylic C-H oxidation of ethylbenzene with *tert*-butyl hydroperoxide (TBHP), H_2O_2, and *meta*-chloroperoxybenzoic acid (mCPBA) resulting in enantiomerically enriched 1-phenylethanol up to 12.5% *ee* and the corresponding acetophenone, where the $[Fe^{IV}(N4Py*)(O)]^{2+}$ (**2**) intermediate has been detected by UV/Vis spectrometry. The stoichiometric oxidation of benzyl alcohol and various hydrocarbon derivatives including the asymmetric hydroxylation of ethylbenzene with **2** has also been investigated. Detailed kinetic, and mechanistic studies (kinetic isotop effect (*KIE*) of 31 and 38, and Hammett correlation with ρ = -0.32 and -0.98 for $PhCH_2OH$ and $PhCH_3$, respectively, and the linear correlation between the normalized bimolecular reaction rates and bond dissociation energies (BDE_{CH})) lead to the conclusion that the rate-determining step in these reactions above involves hydrogen-atom transfer between the substrate and the Fe(IV)-oxo species. The stoichiometric **2**-mediated hydroxylation of ethylbenzene affords 1-phenylethanol in up to 33% *ee*, suggesting clear evidence for the involvement of the oxoiron(IV) species in the enantioselective step. The moderate enantioselectivity may be explained by the epimerization of the long-lived substrate radical before the rebound step (non-rebound mechanism, where $k_{ep}>k_{reb}$). The kinetic resolution of the resulting chiral alcohol due to its metal-based overoxidation process into acetophenone in the catalytic metal-based ethylbenzene oxidation can be excluded.

Keywords: Biomimetic oxidation, C-H activation, Asymmetric hydroxylation, Chiral iron complex, Kinetics.

*Corresponding author. Tel.: +36 88 62 4720; Fax: + 36 88 62 4469.
E-mail address: kaizer@almos.uni-pannon.hu.

Biological oxidation reactions are amongst the most frequent reactions that occur in nature, where they are catalyzed by metalloenzymes belonging to the oxidoreductases. The majority of these metalloproteins exploit the oxidative power of dioxygen to catalyze a broad spectrum of crucial metabolizing reactions, which have medical, pharmaceutical, agricultural or commercial significance [1-7]. The synthesis of enantiopure compounds for the production of drugs, agricultural or other specialty fine chemicals is one of the most active fields in organic chemistry, but the asymmetric functionalization of sp^3 C-H bonds, including the asymmetric hydroxylation of alkanes still remains a challenge [8-11]. Nonheme iron enzymes [12-16], and their corresponding biomimetic complexes, including the formation and reactivity of high-valent oxoiron species, have been extensively studied [17- 21]. These systems are responsible for a broad range of oxidative transformations. Fe(II)/α-ketoglutarate-dependent taurine dioxygenase, that catalyzes the hydroxylation of taurine yielding sulfite and aminoacetaldehyde, is one of the nonheme iron enzymes that is capable of carrying out stereospecific and enantoselective C-H oxidation, where the formation of O_2-derived high-valent $Fe^{IV}O$ was proposed as iron-based oxidant [15]. We have recently been successful in obtaining well characterized synthetic analogues of high-valent non-heme iron species with chiral ligands, $[Fe^{IV}(N4Py^*)(O)]^{2+}$ (**2**) (N4Py* = *N*,*N*-bis(2-pyridylmethyl)-1,2-di(2-pyridyl)ethylamine), which serve as synthetic models for non-heme iron-dependent oxygenases [22]. These chiral complexes have been studied in enantioselective oxidations such as sulfoxidation [22], Baeyer-Villiger oxidation [23], and epoxidation [24]. Recently, Sun and co-workers reported a chiral enantiopure L-prolin derived aminopyridine ligand, and the corresponding oxoiron(IV) species could perform asymmetric C-H hydroxylation with 14% ee [25]. We now want to describe herein the kinetics and mechanism of the oxidative C-H activation processes of substituted benzyl alcohols, and various hydrocarbons mediated by chiral nonheme oxoiron(IV) complex (Fig.1), compared to previously studied Fe(IV)O intermediates with N4Py-type pentadentate ligands (N4Py = *N*,*N*'-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine [26, 27]; N3PyBim = [*N*-(1-methyl-2-benzimidazolyl)methyl-*N*-(2-pyridyl)methyl-*N*-(bis-2-pyridylmethyl)amine] [28]; N2Py2Bim = [*N*-bis(1-methyl-2-benzimidazolyl)methyl-*N*-(bis-2-pyridylmethyl)amine]) [28], furthermore the enantioselective hydroxylation of ethylbenzene under catalytic and stoichiometric conditions.

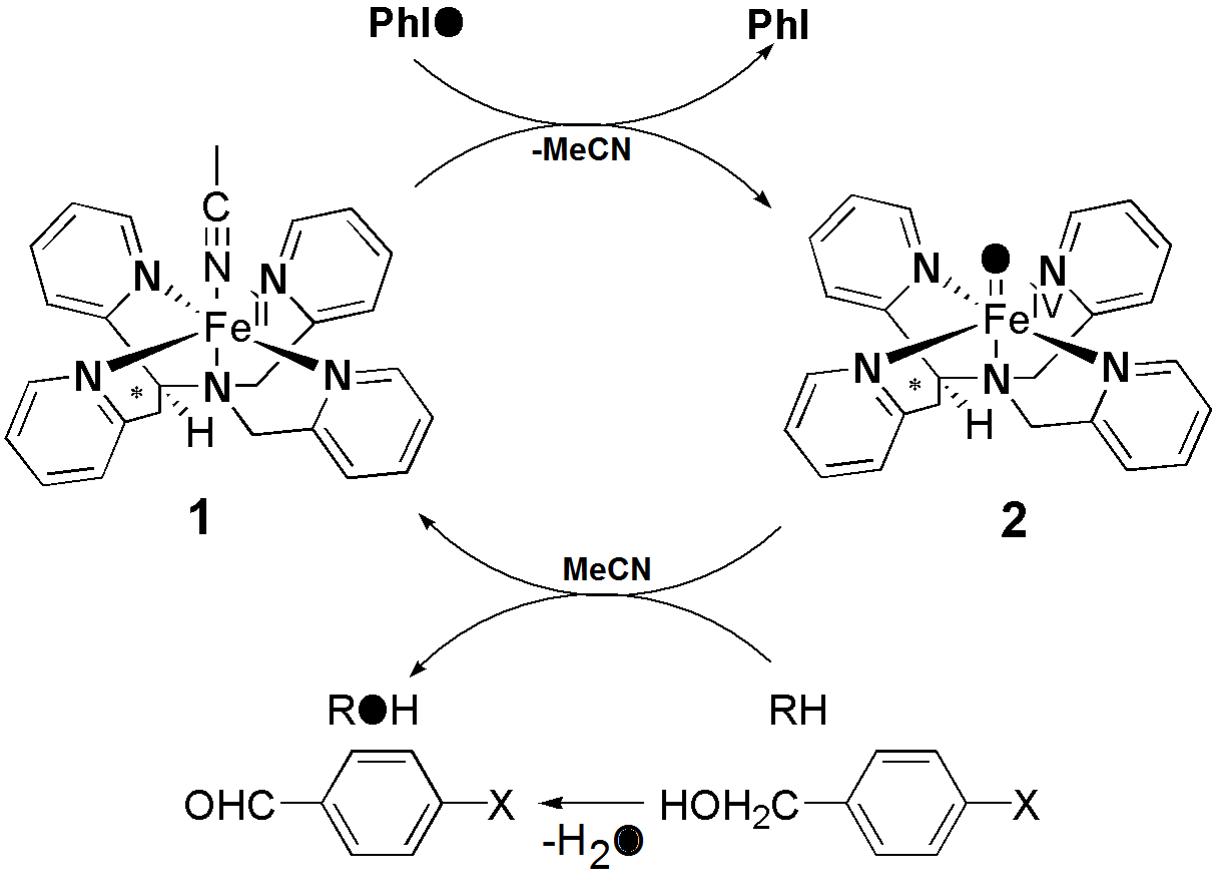


Fig. 1. Oxoiron(IV) mediated C-H oxidation in this study.

We have shown earlier that Fe(II) complexes with chiral pentadentate aminopyridine ligands can form relatively stable high valent oxoiron(IV) species with various oxidants such as H_2O_2, *tert*-butyl hydroperoxide (TBHP), PhIO and *meta*-chloroperoxybenzoic acid (mCPBA), which are possible candidates for stereoselective C-H oxidation reactions [22]. The catalytic activity including the enantioselective behaviour of enantiopure ligand-containning $[Fe^{II}(N4Py^*)(CH_3CN]^{2+}$ ((*R*)-(-)-**1**) was studied in the oxidation of ethylbenzene, utilizing TBHP, H_2O_2 and mCPBA as co-oxidants. No oxidation products were obtained when the reactions were carried out without any metal catalyst. Using an identical concentration of precursor/substrate/co-oxidant (**1**/ethylbenzene/co-oxidant = 1/100/25), Table 1 shows that there is an increase of the yield when the co-oxidants employed are mCPBA, H_2O_2 and TBHP (from 4.6 to 21%), furthermore, moderate enantioselective hydroxylation could be obtained in all cases. The reaction afforded a mixture of the 1-phenylethanol and its overoxidized product, acetophenone. It can be seen that, with three different co-oxidants mCPBA, H_2O_2 and TBHP, the enantiomeric excess values are similar according to a probably same optically active intermediate. A decrease of the [**1**]/[TBHP]

ratio decreases significantly the K/A ratio but increases slightly the *ee* from 7.5 to 14.4% (Fig. 2). Similar results have been observed for electron-rich iron porphyrin/H_2O_2 (yield 5%; 15 % ee in MeOH/H_2O) [29], and μ-oxo diferric/H_2O_2 systems (15 % ee) [30, 31]. The moderate enantioselectivity may be explained by the parallel enantioselective metal-based and non-selective Fenton-type radical processes [32], furthermore, by the epimerization of the long-lived substrate radical before the rebound step (non-rebound mechanism, where $k_{ep}>k_{reb}$) [33]. Complex **1** with mCPBA (50 equiv.) oxidizes the 1-phenylethanol in CH_3CN at 0°C, and a TON of 17.8 for acetophenone was observed with an overall yield of 35.6 % (based on oxidant) and without any enantioselectivity. Based on this result the kinetic resolution of the resulting chiral alcohol due to its metal-based overoxidation process (the selective overoxidation of one of the isomer) into acetophenone in the catalytic metal-based ethylbenzene oxidation can be excluded.

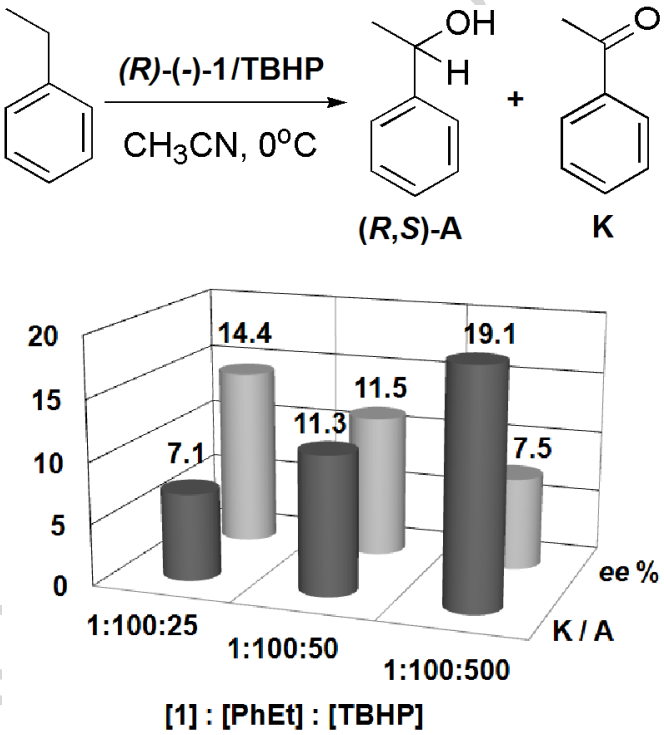


Fig. 2. Dependence of the K/A ratio and the enantiomeric excess (ee %) on the oxidant concentrations for ethylbenzene oxidation in CH_3CN at 0°C.

Table 1

Catalytic oxidation of ethylbenzene carried out by (*R*)-(-)-**1** with various co-oxidants[a].

[**1**] : [PhEt] : [Co-oxidant]	TON (A[b])	TON (K[c])	Yield (%)[d]	K/A	ee (%)
1 . 100 :25 (mCPBA)	0.58	0.57	5	0.98	13.4 (*R*)
1 . 100 :25 (H_2O_2)	1.40	2.08	12	1.5	12.1 (*R*)
1 . 100 :25 (TBHP)	0.63	4.46	20	7.1	14.4 (*R*)
1 . 100 :50 (TBHP)	0.84	9.47	21	11.3	11.5 (*R*)
1 : 100 : 500 (TBHP)	1.2	22.9	24[e]	19.1	7.5 (*R*)

[a]Reaction conditions: see Experimental section. [b]1-Phenylethanol. [c]Acetophenone. [d]Based on oxidant. [e]Based on substrate.

Spectral investigations on the catalytic system above have confirmed the formation of oxoiron(IV) species **2** (705 nm (ε = 400 M^{-1} cm^{-1})) (Fig. 3A) [22], that undergoes a monotonic decay, which is affected by the addition of 100 equivalent of ethylbenzene (Fig. 3B). These results, including the observed enantioselectivity, may suggest that a high-valent oxoiron(IV) species is able to control the stereochemistry of the reaction. However, nonselective hydroxylation reactions involving free radicals such as HO$^{\bullet}$, *tert*-BuO$^{\bullet}$ and dioxygen are competing with the above process [34].

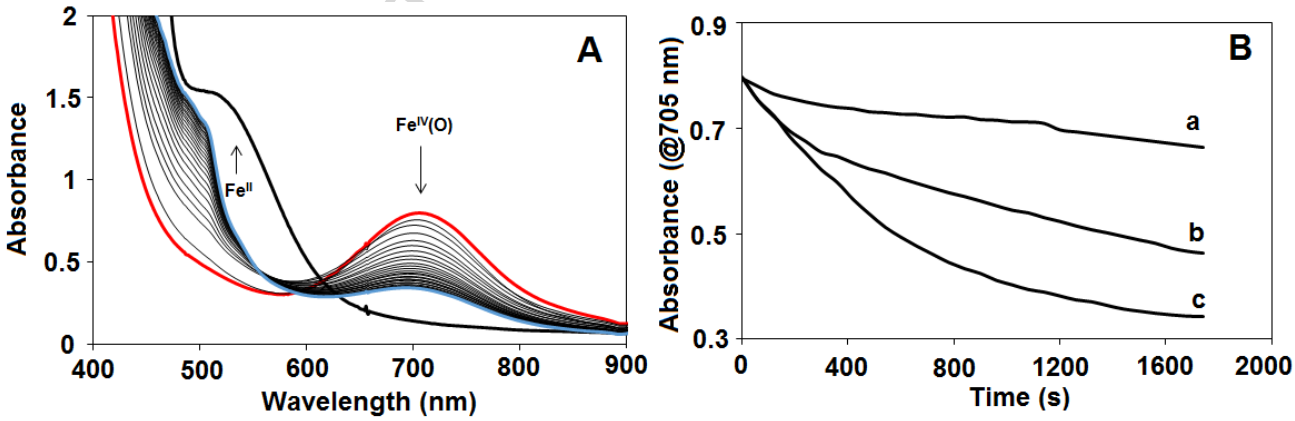
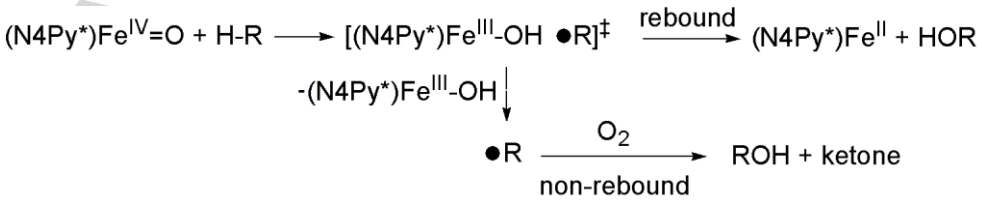


Fig. 3. The UV-Vis spectral change of **2** upon addition of TBHP to **1** in the presence of ethylbenzene in CH_3CN at room temperature (**A**), and time courses of the decay of **2** in the absence and in the presence of ethylbenzene: [1]:[PhEt]:[TBHP] = 1:-:500 (**a**); 1:100:50 (**b**); 1:100:500 (**c**) in CH_3CN at 25°C (**B**).

Oxygenation, or oxygen atom transfer from an oxygen source to a metal center and eventually to an organic substrate is a matter of great interest in organic synthesis and transition metal catalysis. To get direct evidence for the involvement of the oxoiron(IV) species in the C─H activation processes, the reactions of **2** with various substrates, such as benzyl alcohol, 9,10-dihydroanthracene, fluorene, triphenylmethane, cumene, ethylbenzene, toluene and cyclohexane were investigated (Table S1). The identities of the products (anthracene, fluorenone, triphenylmethanol, benzaldehyde, ethylmethylketone (1-phenylethanol), cyclohexanone (cyclohexanol), respectively) were confirmed by comparison with authentic samples and GC-MS. The oxoiron(IV) complex was generated by in situ reaction of **1** with 2 equivalent of PhIO (Fig. 4a), and its reaction with benzyl alcohol and toluene was measured as a function of the concentration of added substrates (Fig. 4b). It was found that the complex **2** is able to oxidize the benzyl alcohol (BA) to benzaldehyde (yields ~75 % based on **2**), and the toluene (T) to benzyl alcohol and benzaldehyde (yields ~50 %) at 298 K, and the oxoiron(IV) species reverted back to the precursor complex **1** showing pseudo-first-order decays (Fig. 4a). Kinetic experiments revealed 1st-order dependence on both the oxoiron(IV) and the substrate concentration with k_2 (BA) = 1.10 × 10^{-2} M^{-1} s^{-1}, $\Delta H^{\neq}$ = 60 kJ mol^{-1} and $\Delta S^{\neq}$ = -123 J mol^{-1} K for benzyl alcohol, and k_2 (T) = 2.10 × 10^{-5} M^{-1} s^{-1}, $\Delta H^{\neq}$ = 41 kJ mol^{-1} and $\Delta S^{\neq}$ = -84 J mol^{-1} K for toluene in MeCN at 298 K (Table 2). Reaction rates obtained for the oxidation of benzyl alcohol and toluene are smaller by one order of magnitude than those observed for oxoiron(IV) complex with N4Py ligand (k_2 = 9.9 × 10^{-2} M^{-1} s^{-1} [35], and 1.50×10^{-4} M^{-1} s^{-1} [24], respectively), and smaller by two and three order of magnitude than those observed for $Fe^{IV}O$/toluene system based on modified N4Py type ligands, N3PyBim (1.30×10^{-3} M^{-1} s^{-1}), and N2Py2Bim (1.20×10^{-2} M^{-1} s^{-1}), respectively [28]. The activation enthalpy of 60 kJ mol^{-1} is relatively higher than those obtained in the oxidation of benzyl alcohol by $[Fe^{IV}(N4Py)(O)]^{2+}$ (32 kJ mol^{-1}) [35], and in the oxidation of benzaldehyde by $[Fe^{IV}(N4Py)(O)]^{2+}$ (32 kJ mol^{-1}) [20]. The relatively large negative entropies are typical of associative processes (Fig. 4g). The substrate $C_6H_5CH_2OH/C_6D_5CD_2OH$ and $C_6H_5CH_3/C_6D_5CD_3$ kinetic isotop effects (*KIE*) were also investigated. The involvement of the benzylic C-H bond in the rate-determining step in both cases is indicated by the magnitude of the k_{CH}/k_{CD} kinetic isotope effects of 31 for benzyl alcohol (Fig. 4c), and 38 for toluene (Fig. 4d). These values are larger than „classical" *KIE* values (*KIE* ~ 7), and comparable to those measured in the oxidation of benzyl alcohol, benzaldehyde and toluene by polypyridyl oxoiron(IV) complexes (KIE_{TPA} = 58 and KIE_{N4Py} = 48 for benzyl alcohol [35]; KIE_{N4Py} =

26.5 and KIE_{N4Py*} = 37 for benzaldehyde [20]; KIE_{N4Py} = 20 for toluene [26]), indicating that the oxoiron(IV) intermediate activates the benzyl alcohol, benzaldehyde and toluene in the same manner by an H-atom abstraction from the benzylic position (HAT). Upon using *para*-benzyl alcohols with electron donating groups the rate of the decay processes were increased remarkably (Table 2, Fig. 4e). Relative rates determined from these plots showed a good linear correlation (r = 0.99, n = 5) with the Hammett substituent parameters. The reaction constant, ρ, is negative (ρ = -0.32). It is 5-fold larger than those obtained for the $[Fe^{IV}(N4Py)(O)]^{2+}$/$PhCH_2OH$ (ρ = -0.07) and $[Fe^{IV}(TPA)(O)]^{2+}$/$PhCH_2OH$ (ρ = -0.06) systems, but comparable to that measured in the oxoiron(IV)porphyrin radical cation)/$PhCH_2OH$ (ρ = -0.43) system [35], where α-C-H hydrogen atom abstraction and concomitant electron transfer was proposed. The relatively small ρ value suggests that the metal-based oxidant is electrophilic, but there is only a small development of positive charge on the substrate in the transition state. Competitive reactions were also performed with *para*-substituted toluene derivatives, and the Hammett correlation (r = 0.98, n = 5, ρ = -0.98) demonstrates that the rate constant for the oxidation of toluene by **2** is much more sensitive to changes in the electronic properties of the toluene compared to the **2**/$PhCH_2OH$ system mentioned above. The magnitude of the ρ value in both cases is in a good agreement with a hydrogen-atom-transfer (HAT) model [18]. A good linear correlation has been found between logk_2' (Fig 4h, k_2' is the second-order rate constant divided by the number of equivalent C-H bonds in the substrate) and C-H BDE for several hydrocarbons with a slope of -0.3, which is comparable to those obtained in C-H bond oxidations by mononuclear nonheme oxoiron(IV) species including rate-determining HAT process, following by rebound and/or non-rebound mechanism (Scheme 1) [33].



Scheme 1. Schematic illustration of possible reaction pathways for oxoiron(IV)-mediated oxidation of alkanes.

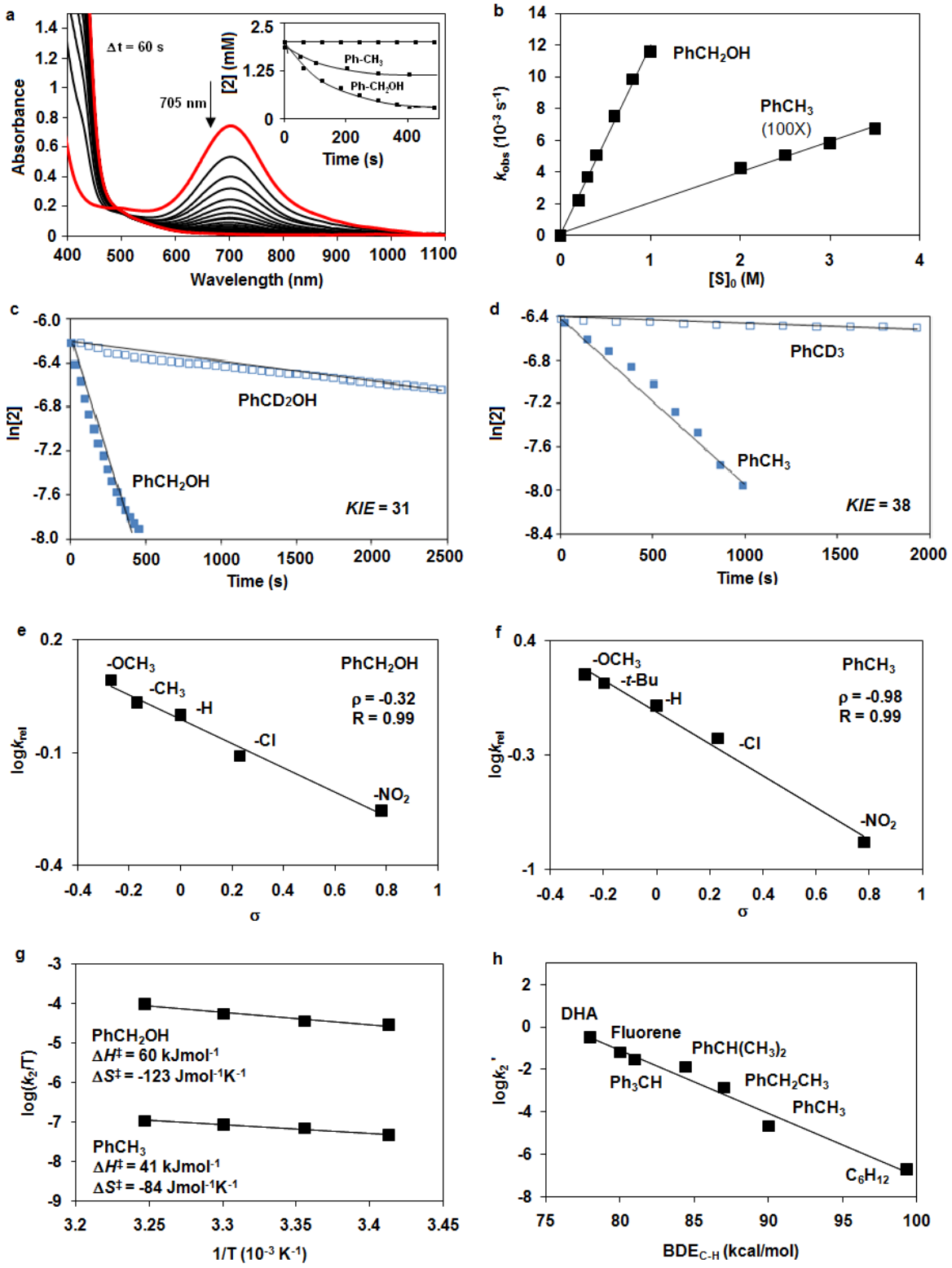


Fig. 4. Reactions of [Fe^{IV}(N4Py*)(O)] (**2**) with benzyl alcohols and hydrocarbons in CH_3CN (Table S1). (a) UV-vis spectral change of **2** upon addition of 100 equiv. benzyl alcohol at 298 K. Inset shows time course of the decay of **2** monitored at 705 nm with toluene and benzyl alcohol ($[\mathbf{2}]_0$ = 2 mM, $[PhCH_2OH]_0$= 0.2 M, $[PhCH_3]_0$ = 2.0 M). (b) Plot of k_{obs} versus [substrate] for reactions of **2** (2mM) with benzyl alcohol and toluene. (c) Plots of ln[**2**] versus

time for reactions of **2** (2 mM) with 100 equiv. benzyl alcohol and d_7-benzyl alcohol. (d) Plots of ln[**2**] versus time for reactions of **2** (2 mM) with 1000 equivToluene and d_8-toluene. (e) Hammett plot of log k_{rel} against the σ_p of *para*-substituted benzyl alcohols. (f) Hammett plot of log k_{rel} against the σ_p of *para*-substituted toluenes. (g) Eyring plots of logk/T versus 1/T for benzyl alcohol and toluene ([**2**]$_0$ = 2 mM, [$PhCH_2OH$]$_0$= 0.2 M, [$PhCH_3$]$_0$ = 2.0 M). (h) The logk_2' (second-order rate constant divided by the number of equivalent C-H bonds in the substrate) versus BDE_{C-H} plots.

Table 2

Kinetic parameters determined in the oxidation of benzyl alcohol and different alkane substrates by oxoiron(IV) complexes in acetonitrile at 25°C.

complex	substrate	k_2 ($M^{-1}s^{-1}$)	ρ	*KIE*	$\Delta H^{\neq}$ ($kJmol^{-1}$)	$\Delta S^{\neq}$ ($Jmol^{-1}K^{-1}$)	$\Delta G^{\neq}$ ($Jmol^{-1}K^{-1}$)	Refs.
N4Py	$PhCH_2OH$	9.90×10^{-2}	-0.07	48	32	-184	82	[32]
N4Py*	$PhCH_2OH$	1.10×10^{-2}	-0.32	31	60	-123	97	this work
N4Py*	$PhCH_3$	2.10×10^{-5}	-0.98	38	41	-84	66	this work
N4Py	$PhCH_3$	1.50×10^{-4}		20	n.a.	n.a.	n.a.	[26]
N3PyBim	$PhCH_3$	1.30×10^{-3}		14	n.a.	n.a.	n.a.	[28]
N2Py2Bim	$PhCH_3$	1.20×10^{-2}		11	n.a.	n.a.	n.a.	[28]

Stoichiometric oxidation of ethylbenzene by [Fe^{IV}((*R*)-(-)-N4Py*)(O)] ((*R*)-(-)-**2**) in CH_3CN at 0°C gave 33% enantiomeric excess (ee) of 1-phenylethanol after 90 minutes, and 25% ee after 180 minutes under Ar (Fig. S1). Since the oxoiron(IV) species was generated by PhIO, the presence of hydroxyl and *tert*-butoxyl radicals and their non-selective reaction with the substrate in the stoichiometric reaction can be excluded. Based on that, the moderate enantioselectivity and the decrease on the ee value during the reaction can be explained by the epimerization of the long-lived substrate radical (rotation process through C-C bond of the radical species) before the rebound step (non-rebound mechanism, where $k_{ep}>k_{reb}$) [33]. Much lower value (14% ee) was observed in the oxidation of methyl 1-tetralone-2-carboxylate [25].

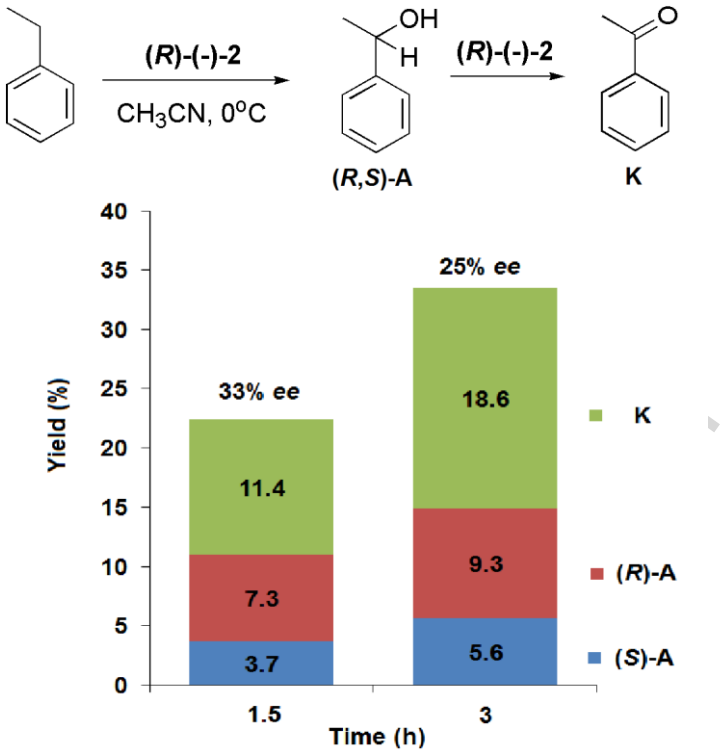


Fig. 5. Time dependence on the K/A ratio and the enantiomeric excess (ee %) for the stoichiometric oxidation of ethylbenzene with (*R*)-(-)-**2** in CH_3CN at 0°C

Efforts have been made to develop a highly efficient asymmetric catalyzed oxidation of various alkanes by introducing the chiral moiety to ligands as well as their detailed mechanistic aspects. In summary, we have reported one of the first example of enantioselective C-H oxidation mediated by chiral oxoiron(IV) intermediate. Based on detailed mechanistic studies on stoichiometric benzyl alcohol (*KIE* of 31, r = -0.32) and hydrocarbon (*KIE* of 38, r = -0.98) oxidation that have been investigated with in situ generated high-valent oxoiron(IV) complex, a plausible mechanisms have been proposed for both systems, in which the oxidation of alcohols and hydrocarbons occurs in the same manner by HAT in the rate-determining step. In this study we have also demonstrated that the enantioselectivity depends on the nature of the following step (rebound versus non-rebound mechanisms). Moderate yields and poor ee values can be expected for substrates with stronger C-H bonds, where the radical dissociation pathway can become prominent. The oxidation of ethylbenzene by the chiral oxoiron(IV) intermediate attains moderate enantioselectivities up to 33% ee, which can be explained by the epimerization of the long-lived substrate radical before the rebound step (non-rebound mechanism, where $k_{ep}>k_{reb}$). Much lower ee values (up to 14%) have been observed for the catalytic oxidation of ethylbenzene, which can be

explained by the parallel enantioselective metal-based, oxoiron(IV)-mediated and non-selective Fenton-type radical processes [34].

Supplementary material

Supplementary data for this article can be found, in the online version, at…

Acknowledgements

Financial support of the Hungarian National Research Fund (OTKA K108489), and GINOP-2.3.2-15-2016-00049 are gratefully acknowledged.

References

[1] A.C. Rozenweig, S.J. Lippard, Acc. Chem. Res. 27 (1994) 229.

[2] J.B. Wallar, J.D. Lipscomb, in: Chem. Rev. (1996) 2625.

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

[4] M. Costas, M.P. Mehn, M.P. Jensen, L. Que, Jr., Chem. Rev. 104 (2004) 939.

[5] S.V. Kryatov, E.V. Rybak-Akimova, S. Schindler, Chem. Rev. 105 (2005) 2175.

[6] E.G. Kovaleva and J.D. Lipscomb, Nat. Chem. Biol. 4 (2008) 186.

[7] M.M. Abu-Omar, A. Loaiza and N. Hontzeas, Chem. Rev. 105 (2005) 2227.

[8] C. Zheng, S.L. You, RSC Adv. 4 (2014) 6173.

[9] W. Zhang, F. Wang, S.D. McCann, D. Wang, P. Chen, S.S. Stahl, G. Liu, Science 353 (2016) 1014.

[10] Q. Lu, F. Glorius, Angew. Chem. Int. Ed. 56 (2017) 49.

[11] H.J. Lu, X.P. Zhang, Chem. Soc. Rev. 40 (2011) 1899.

[12] O.A. Andersen, A.J. Stokka, T. Flatmark and E. Hough, J. Mol. Biol. 333 (2003) 747.

[13] K.E. Goodwill, C. Sabatier and R.C. Stevens, Biochemistry 37 (1998) 13437.

[14] J.C. Price, E.W. Barr, B. Tirupati, J.M. Bollinger, C. Krebs, Biochemistry 42 (2003) 7497.

[15] S. Sinnecker, N. Svensen, E.W. Barr, S.Ye, J.M. Bollinger, F. Neese, C. Krebs, J. Am. Chem. Soc. 129 (2007) 6168.

[16] D.A. Proshlyakov, T.F. Henshaw, G.R. Monterosso, M.J. Ryle, R.P. Hausinger, J. Am. Chem. Soc. 126 (2004) 1022.

[17] A.R. McDonald and L. Que, Jr., Coord. Chem. Rev. 257 (2013) 4357.

[18] L. Que, Jr., Acc. Chem. Res. 40 (2007) 493.

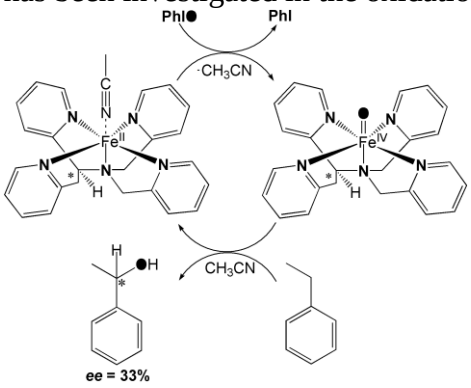
[19] W. Nam, Acc. Chem. Res. 40 (2007) 465.

[20] R. Turcas, D. Lakk-Bogáth, G. Speier, J. Kaizer, Dalton. Trans. 47 (2018) 3248.
[21] R. Turcas, B. Kripli, A.A.A. Attia, D. Lakk-Bogáth, G. Speier, M. Giorgi, R. Silaghi-Dumitrescu, J. Kaizer, Dalton. Trans. 47 (2018) 14416.
[22] D. Lakk-Bogáth, R. Csonka, G. Speier, M. Reglier, A.J. Simaan, J.V. Naubron, M. Giorgi, K. Lazar, J. Kaizer, Inorg. Chem. 55 (2016) 10090.
[23] R. Turcas, D. Lakk-Bogáth, G. Speier, J. Kaizer, Inorg. Chem. Commun. 92 (2018) 141.
[24] B.I. Meena, D. Lakk-Bogáth, B. Kripli, G. Speier, J. Kaier, Polyhedron 151 (2018) 141.
[25] J. Du, J. Zhang, J. Zhu, C. Xia, W. Sun, New J. Chem. 42 (2018) 8315.
[26] J. Kaizer, E.J. Klinker, N.Y. Oh, J.U. Rohde, W.J. Song, A. Stubna, J. Kim, E. Munck, W. Nam and L. Que Jr., J. Am. Chem. Soc. 126 (2004) 472.
[27] E.J. Klinker, J. Kaizer, W.W. Brennessel, N.L. Woodrum, C.J. Cramer and L. Que Jr., Angew. Chem. Int. Ed. 44 (2005) 3690.
[28] M. Mitra, H. Nimir, S. Demeshko, S.S. Bhat, S.O. Malinkin, M. Haukka, J. Lloret-Fillol, G.C. Lisensky, F. Meyer, A.A. Shteinman, W.R. Browne, D.A. Hrovat, M.G. Richmond, M. Costas and E. Nordlander, Inorg. Chem. 54 (2015) 7152.
[29] P.L. Maux, H.F. Srour, G. Simonneaux, Tetrahedron 68 (2012) 5824.
[30] H. Srour, P.L. Maux, S. Chevance, G. Simonneaux, Coord. Chem. Rev. 257 (2013) 3030.
[31] Y. Mekmouche, C. Duboc-Toia, S. Menage, C. Lambeaux, M. Fontecave, J. Mol.Catal. A: Chem. 156 (2000) 85.
[32] M. Costas, K. Chen, L. Que, Jr., Coord. Chem. Rev. 200-202 (2000) 517.
[33] K.-B. Cho, H. Hirao, S. Shaik, W. Nam, Chem. Soc. Rev. 45 (2016) 1197.
[34] M. Mitra, H. Nimir, D.A. Hrovat, A.A. Shteinman, M.G. Richmond, M. Costas, E. Nordlander, J. Mol. Catal. A. Chem. 426 (2017) 350.
[35] Y. Morimoto, J. Park, T. Suenobu, Y.-M. Lee, W. Nam, S. Fukuzumi, Inorg. Chem., 51 (2012) 10025.

Catalytic and stoichiometric C-H oxidation of benzylalcohols and hydrocarbons mediated by nonheme oxoiron(IV) complex with chiral tetrapyridyl ligand

Dóra Lakk-Bogáth, Balázs Kripli, Bashdar I. Meena, Gábor Speier and József Kaizer*

The reactivity of oxoiron(IV) complex, $[Fe^{IV}(asN4Py)(O)]^{2+}$ with chiral pentadentate ligand, has been investigated in the oxidation of various hydrocarbons and alcohols.



Graphical abstract

*Corresponding author. Tel.: +36 88 62 4720; Fax: + 36 88 62 4469.
E-mail address: kaizer@almos.uni-pannon.hu.

Highlights

- Catalytic ethylbenzene oxidation with chiral Fe(II)-polypyridyl complex.
- Evidence for the formation of oxoiron(IV) intermediate (oxidant).
- Oxoiron(IV)-mediated C-H activation of benzyl alcohols and hydrocarbons.
- Reaction kinetics with UV-Vis spectroscopy.
- Oxoiron(IV)-mediated enantioselective oxidation.