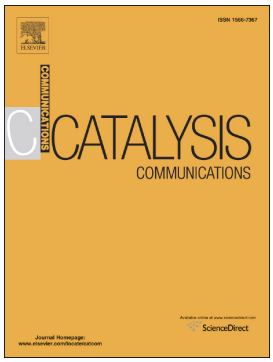

Direct reactivity studies of non-heme iron-oxo intermediates toward alkane oxidation

Alexandra M. Zima, Oleg Y. Lyakin, Konstantin P. Bryliakov, Evgenii P. Talsi

PII: S1566-7367(18)30048-7
DOI: doi:10.1016/j.catcom.2018.01.034
Reference: CATCOM 5313

To appear in: *Catalysis Communications*

Received date: 6 December 2017
Revised date: 17 January 2018
Accepted date: 31 January 2018

Please cite this article as: Alexandra M. Zima, Oleg Y. Lyakin, Konstantin P. Bryliakov, Evgenii P. Talsi , Direct reactivity studies of non-heme iron-oxo intermediates toward alkane oxidation. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Catcom(2017), doi:10.1016/j.catcom.2018.01.034

Direct Reactivity Studies of Non-Heme Iron-Oxo Intermediates toward Alkane Oxidation

Alexandra M. Zima[a,b], Oleg Y. Lyakin[a,b], Konstantin P. Bryliakov[a,b], Evgenii P. Talsi[a,b,*]

[a] *Novosibirsk State University, Pirogova 2, Novosibirsk 630090, Russian Federation*

[b] *Boreskov Institute of Catalysis, Pr. Lavrentieva 5, Novosibirsk 630090, Russian Federation*

* Corresponding Author. *E-mail address:* talsi@catalysis.ru (E.P. Talsi).

Abstract

Iron complexes [((*S*,*S*)-PDP*)Fe^{III}(μ-OH)$_2$$Fe^{III}$((*S*,*S*)-PDP*)](OTf)$_4$ (**6**), (*S*,*S*)-PDP* = *N*,*N*′-bis(3,5-dimethyl-4-methoxypyridyl-2-methyl)-(*S*,*S*)-2,2′-bipyrrolidine, and [(TPA*)Fe^{III}(μ-OH)$_2$$Fe^{III}$(TPA*)](OTf)$_4$ (**7**), TPA* = tris(3,5-dimethyl-4-methoxypyridyl-2-methyl)amine, catalyze the selective hydroxylation of alkanes with H_2O_2 and peroxycarboxylic acids. Using in situ EPR spectroscopy, direct kinetic data on the reactivity of the iron-oxo intermediates formed in the catalyst systems **6**,**7**/oxidant/RCOOH (RCOOH = acetic acid (AA) or 2-ethylhexanoic acid (EHA)) toward cyclohexane have been obtained for the first time, thus corroborating their key role in the selective C–H oxidation. Intermediates $\mathbf{6a^{AA}}$, $\mathbf{6a^{EHA}}$ and $\mathbf{7a_2^{EHA}}$ with proposed structures [((*S*,*S*)-PDP*)Fe^{V}=O(OC(O)CH_3)]$^{2+}$, [((*S*,*S*)-PDP*)Fe^{V}=O(OC(O)R)]$^{2+}$ and [(TPA*)Fe^{V}=O(OC(O)R)]$^{2+}$ (RCOOH = EHA) display similar EPR spectra (g_1 = 2.07, g_2 = 2.01, g_3 = 1.96) and have close reactivities toward cyclohexane at −70 °C (k_2 = 2–3 × 10^{-3} $M^{-1}s^{-1}$).

Keywords

C–H oxidation, enzyme models, EPR spectroscopy, iron, reaction mechanisms