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## From DNA to Catalysis: Thymine-acetate ligated non-heme iron(III) catalyst for oxidative activation of aliphatic C-H bonds

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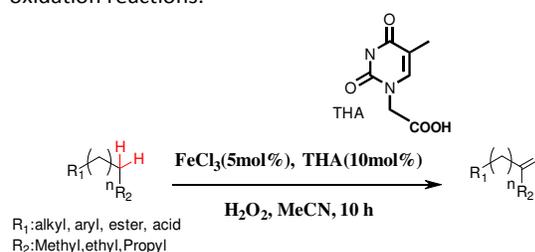
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**Abstract** A non-heme, iron(III)/THA(thymine-1-acetate) catalyst together with H<sub>2</sub>O<sub>2</sub> as an oxidant is efficient in oxidative C-H activation of alkanes. Although having a higher preference for tertiary C-H bonds the catalyst oxidizes also aliphatic secondary C-H bonds into carbonyl compounds with good to excellent conversions. Based on the site selectivity of the catalyst and our mechanistic studies the reaction proceeds via a Fe-oxo species without long lived carbon centered radicals.

C-H activation is a fundamental chemical transformation and highly valuable in the functionalization of alkanes and aliphatic hydrocarbons.<sup>[1,2]</sup> Although extensively studied, the topic remains one of the significant challenges in modern chemistry; inactivated sp<sup>3</sup> C-H bonds have high dissociation energy (90–100 kcal/mol) and low acidity (pK<sub>a</sub> = 45–60).<sup>[3]</sup> To be practical in synthesis, a catalyst has to sustain a very high reactivity combined with predictable site selectivity. Necessity of a catalytic system which comprises these two conflicting demands into one species, keeps the challenge high and alive. The majority of recent studies is devoted to routes using biologically inspired iron catalysts and hydrogen peroxide as an oxidant.<sup>[4–5]</sup> Fe-based catalytic methods are also particularly appealing due to the availability, lack of toxicity of this element and because iron-based reagents are very reactive, capable to hydroxylate not only 3° C–H groups, but also 2° alkyl sites, thus complementing existing oxidizing methodologies without the implication of free-diffused radicals are attempting.<sup>[6–8]</sup> In general, the catalysts have promising hydroxylation reactivity with unactivated tertiary C–H bonds.<sup>[7]</sup> The challenge remains to develop facile and high reactive catalytic systems for secondary C–H bonds, which are less reactive than the tertiary C–H bonds. Fortunately, some of these unique catalysts were very recently demonstrated as a powerful synthetic tool in C-H

oxidation reactions.<sup>[7]</sup>



Scheme 1. Oxidative activation of aliphatic C-H bonds by the thymine-acetate ligated non-heme iron(III) catalyst.

We reported recently in-situ prepared Fe(III)/thymine-1-acetate catalyst for the oxidation of primary and secondary aliphatic alcohols and diols into corresponding carbonyl compounds. Characteristic for the Fe(III)/THA catalyst is high reactivity.<sup>[9]</sup> During the reaction optimization for alcohol oxidation, an oxidation of a some solvent residue (hexane) was also observed. This observation prompted us further studies along the oxidative activation of aliphatic C-H bonds. Herein we report the novel highly active iron based system Fe(III)/THA with predictable selectivity among aliphatic secondary C-H bonds when H<sub>2</sub>O<sub>2</sub> is used as a terminal oxidant (Scheme 1). After optimizing reaction conditions, we investigated the substrate scope under similar reaction conditions using H<sub>2</sub>O<sub>2</sub> as a terminal oxidant. A variety of cyclic alkanes are oxidized with good to excellent yields to ketones (Table 1, entries 1 and 2). Oxidation of *trans*-decalin shows preferential oxidation at the secondary site than sterically and more protected tertiary (Table 1, entry 3). Further on, π-activated C-H bonds, both tertiary and secondary ones, were also oxidized with good to excellent conversions and with excellent selectivity (Table 1, entries 4 - 9). The low yield of 2-benzylpyridine presumably due to coordination of pyridine to the iron center (Table 1, entry 10). Next we examined the effect of electron-withdrawing groups on the site selectivity of oxidation using simple substrates (Table 1, entries 11 and 12). The carboxylate group on the substrate such as 4-methylvaleric acid directed the C-H

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oxidation site towards the remote site (up to four carbons away from carboxylic group). A five-membered lactone ring formed in 53% yield, whereas a terminal ester group formed a ketoester at C<sub>4</sub> as the major product. Surprisingly the absence of directing groups, aliphatic hydrocarbons such as *n*-octane and *n*-decane were oxidized into ketones in a normalized 8:5:1 C<sub>3</sub>:C<sub>2</sub>:C<sub>4</sub> mixture and remarkable 62-68% combined yields. This shows that C<sub>2</sub> and C<sub>3</sub> are more reactive, under these conditions, than C<sub>4</sub>. However, a slight preference towards the oxidation of C<sub>4</sub> carbon was observed (Table 1, entries 13 and 14). Very limited examples with similar selectivity are found in literature.<sup>[10,11]</sup> The results above highlight the substantial scope for Fe(III)/THA catalyzed oxidation of alkanes.

Although the main product in these reactions is ketone, which formally indicates the involvement of freely diffusing carbon-centered radicals, low alcohol amounts are likely due to over-oxidation of alcohol intermediates. In fact, monitoring the oxidation of ethyl benzene under limited oxidant and at room temperature shows a rise of alcohols via GC-MS. Noteworthy, peroxides tend to decompose in oxidation which complicate mechanistic interpretations. Therefore, the Ph<sub>3</sub>P treatment of the reaction samples prior GC indicated that the product distribution was unchanged.<sup>[12]</sup>

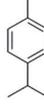
We further investigated the oxidation of substituted cycloalkanes with different 2° and 3° C-H bonds to assist the selectivity of our iron-based catalyst (Table 2). Various mono and substituted cyclohexane derivatives were employed in this study. The reactivity of 1,1-dimethylcyclohexane and *tert*-butylcyclohexane were investigated using the same condition (Table 2 entries 15 and 16). With *tert*-butylcyclohexane, oxidation is observed at the C<sub>4</sub> carbons with a 3:1 ratio to the C<sub>2</sub> carbons. With 1,1-dimethylcyclohexane, the oxidation occurs mainly at C<sub>4</sub> and C<sub>2</sub> carbons with a 2:1 ratio. Noteworthy, oxidation of the primary carbon is not noted in any of those substrates. Furthermore, the catalyst shows a preferential oxidation to the more accessible secondary site when tertiary C-H bonds are sterically hindered. Nevertheless, a good preference for tertiary C-H bonds over secondary ones was observed with adamantane (Table 2 entry 17).<sup>[10]</sup> A high ratio of tertiary/secondary C-H bond activation (~9:1) indicates the involvement of highly selective metal centered oxidant.<sup>[10]</sup>

Interestingly, when we tested 3 mol% of the catalyst for the oxidation of terpenoid (-)-ambroxide, which contains two tertiary C-H sites and 14 methylenic sites, the activated methylenic C-H bond adjacent to the ether moiety was preferentially oxidized affording sclareolide in 30% yield (Table 2, entry 19). The catalyst was also applied to oxidize cyclic alkenes such as cyclooctene and cyclohexene, were both found to undergo formation of carbonyl compounds together with small amount of epoxidation (Table 2, entries 20, 21).

For mechanistic studies, the pre-made complex powder was analyzed using electrospray ionization mass spectra (ESI-MS), IR spectroscopy and elemental analysis and all analysis data confirm Fe<sup>III</sup>(THA)<sub>2</sub>Cl as a structure of the complex (see supporting information). In the ESI-MS spectrum the major peak at *m/z*=457.99 corresponds to the protonated complex,

[Fe(THA)<sub>2</sub>Cl]H<sup>+</sup>. The catalyst can also be prepared *in situ* using Fe:THA ratio 1:2.

**Table 1. Oxidation of substituted aliphatic alkanes<sup>a</sup>**

Run	Substrate	Main product	Time (h)	Total yield [%] <sup>b</sup>	selectivity (%): (Isolated Yield) <sup>c</sup>
1 <sup>d</sup>			10	86	68:(65)
2			10	83	83
3 <sup>d,g</sup>			10	46	90
4			6	68	98:(61)
5 <sup>f</sup>			10	67	99
6 <sup>f</sup>			8	80	80:(70)
7			12	85	99:85
8			7	95	95:(91)
9			8	89	99:88
10			6	91	90:(88)
11			10	60 <sup>g</sup>	90
12 <sup>h</sup>			10	72	59
13 <sup>f,g</sup>			12	60	37
14 <sup>f,g</sup>			12	52	35

<sup>a</sup> Reaction conditions: substrate 2.0 mmol, iron(III) chloride 5 mol%, THA 10mol%, H<sub>2</sub>O<sub>2</sub> 6.5 mmol (30% in water), MeCN 1 mL and 60 °C.

<sup>b</sup>The results were based on substrate conversion collected with <sup>1</sup>H NMR using dichlorobenzene as an internal standard and GC-MS (all experiments were repeated at least 3 times) and all products were based on and identified by comparison of their analytical data with those of previous reports or commercial materials. <sup>c</sup>Selectivity toward the main product, isolated yield after purification in a column chromatography. <sup>d</sup>Other products entry 1: 1,2-cyclooctanedione(20%) and 1,2-cyclooctanediol(13%); entry3: 1-decalone:15%, 5%[octahydronaphthalenol and decahydro-2-naphthol] <sup>e</sup> Other products we found 10% lactone. <sup>f</sup>The normalized C<sub>2</sub>/C<sub>3</sub>/C<sub>4</sub> selectivity ratio (5:8:1). <sup>g</sup> Other products 4% 3-keto-4-methyl pentanoic acid and 4-methyl-3-ene-pentanoic acid <sup>h</sup> H<sub>2</sub>O<sub>2</sub> 6.5 mmol (30% solution in water) was used as oxidant at 80°C, Cat:H<sub>2</sub>O<sub>2</sub>:Substrate 5:360:100.

The yellow *in-situ* prepared catalyst shows no free ligand in ESI-MS studies, but a prominent ion peak at *m/z*=457.99

assigned above. A second prominent peak appears at  $m/z=493.96$  and according to isotope analysis, it is  $[\text{Fe}(\text{THA})_2(\text{Cl})_2]^+$  where THA coordinates as a neutral ligand to the iron center (Figure 6-7 in SI.). Furthermore, UV-vis analysis of the complex solution shows dominant maximum at 364 nm which is characteristic for  $\text{Fe}^{(\text{III})}$  complexes and magnetic studies using the Evans' NMR method<sup>[11]</sup> show that in the solution the iron complexes are in a low-spin state with  $S=1/2$  (effective magnetic moment  $\mu_{\text{eff}}=1.65$  B.M.). Despite of our efforts, unfortunately all attempts to obtain single crystals of the complex for X-ray analysis failed.

The characterized complex solution was monitored after addition of  $\text{H}_2\text{O}_2$  and *n*-hexane (as a substrate). ESI-MS studies in the MeCN/ $\text{H}_2\text{O}$  show disappearance of the above described Fe complexes and the appearance of new iron species. A peak at  $m/z=298.06$  is worth to note, as the peak is assigned to dicationic  $[\text{Fe}^{\text{IV}}(\text{THA})_2(\text{C}_6\text{H}_{11}\text{O})(\text{OOH})\text{H}]^{2+}$  complex, where the oxidized substrate has coordinated to a high valent iron peroxo center (Figures 10-12 in SI). Additional complementary evidence for these species is obtained by in-situ IR spectroscopy studies of the complex containing solution as a new band representing the stretching vibration of Fe–O bond gradually accumulates with time at  $837\text{ cm}^{-1}$  (Figure 1).<sup>[13]</sup> The UV-vis analysis of the solution shows two new, distinct absorption maxima at 436 nm and 591 nm which corresponds to  $\text{Fe}^{(\text{IV})}$  (Figure 13 in SI). Furthermore, Evans' method gave magnetic moment  $\mu_{\text{eff}} 6.25$  B.M, which has previously been assigned for a binuclear  $\text{Fe}^{(\text{IV})}\text{-Fe}^{(\text{V})}$  high-spin state complex.<sup>[7,8]</sup> The Evans' method confirms the UV-vis and ESI-MS results concerning the presence of high valent iron species but the lack of a  $m/z$  feature corresponding to the  $\text{Fe}^{(\text{IV})}\text{-Fe}^{(\text{V})}$  dimer should not be considered infallible proof of its absence and responsibility for catalytic activity via O–O bond homolysis mechanism (see below).

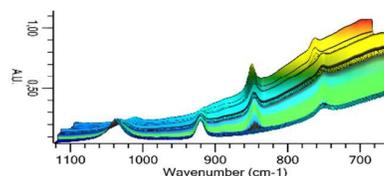
$^{18}\text{O}$  labeling experiments were used for deducing whether the peroxide O–O bond cleavage occurs prior to the attack of substrates by establishing the source of oxygen atoms incorporated into the products.<sup>[10]</sup> By carrying out isotopic labeling experiments using cyclohexane as a model substrate. First the oxidation reaction was carried out in presence of  $\text{H}_2^{18}\text{O}$ , using  $\text{H}_2\text{O}_2$  as terminal oxidant. The compositions of cyclohexanol were determined from the relative abundances of the peaks at  $m/z=100$  ( $^{16}\text{O}$ ) and  $102$  ( $^{18}\text{O}$ ) in GC-MS. After a 5 min. reaction time 34% of the cyclohexanol product contains  $^{18}\text{O}$ -labeled. Secondly, when the oxidation was done with  $\text{H}_2^{18}\text{O}_2$  a 42% of the oxygen atoms in the cyclohexanol were  $^{18}\text{O}$ -labeled. The results support the mechanism where the iron-oxo species are formed via water-assisted homolysis of O–O bond, and the carbonyl bond formed via either the oxygen from  $\text{H}_2\text{O}_2$  or the oxygen from  $\text{H}_2\text{O}$ .<sup>[14]</sup>

We studied the kinetic isotopic effect (KIE) using cyclohexane ( $c\text{-C}_6\text{H}_{12}$ ) and  $\text{D}_{12}$ -cyclohexane ( $c\text{-C}_6\text{D}_{12}$ ) as substrates to gain further insight into the mechanism of the reaction and nature of an active species.

**Table 2.** Aliphatic alkanes substrates for selectivity studies.<sup>a</sup>

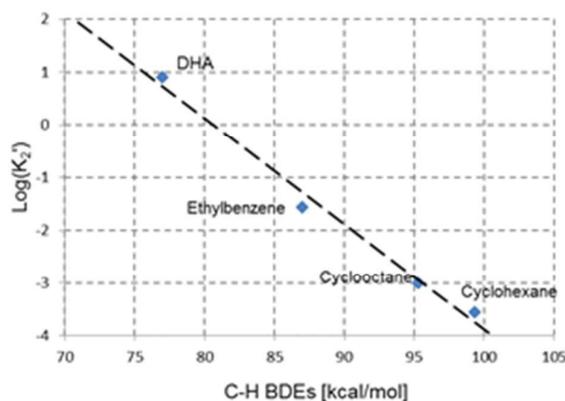
Entry	Substrate	products yields	Yield [%] <sup>b</sup>
15		22%	33
16		8% 10% 18%	36
17		53% 2% 4%	59
18		10% 33%	43
19		30%	30
20		25% 28% 7% 13%	73
21		6% 16% 63%	85

<sup>a</sup>) Reaction conditions: substrate 2.0 mmol, iron(III) chloride 5 mol%, THA 10mol%,  $\text{H}_2\text{O}_2$  6.5 mmol (30% in water), MeCN 1 mL and temperature  $60^\circ\text{C}$ .  
<sup>b</sup>) The results were collected via  $^1\text{H}$  NMR using dichlorobenzene as an internal standard and GC-MS (all experiments were repeated at least 3 times) and all products were identified by comparison of their analytical data with those of previous reports or commercial materials.



**Figure 1.** FTIR spectra recorded after the interaction of the in-situ prepared complex with  $\text{H}_2\text{O}_2$  in a 3 hour interval.

The oxidation rate of  $\text{C}_6\text{D}_{12}$  is significantly lower relative to  $\text{C}_6\text{H}_{12}$  indicating that H-atom abstraction is an important component of a rate determining step (see supporting information). The pseudo-first-order rate constants ( $k_{\text{obs}}$ ) for  $c\text{-C}_6\text{H}_{12}$  and  $c\text{-C}_6\text{D}_{12}$  are  $2.26 \times 10^{-2}\text{ s}^{-1}$  and  $1.15 \times 10^{-2}\text{ s}^{-1}$ , respectively. The KIE obtained ( $k_{\text{obsH}}/k_{\text{obsD}}$ )  $1.9 \pm 0.4$ , is in good agreement with the value of  $2.2 \pm 0.4$  from competition experiments (see Figure S3 and Table 3 in SI). A series of substrates used in excess shows that the catalyst decay follows first-order kinetics.  $k_{\text{obs}}$  values were linearly dependent on substrate concentration in all cases. This permits us to define the comparable second-order rate constants  $k_2$  (Figures S1-4 in SI). The linear plot of  $k_2'$  (calculated based on the number of equivalent target C–H bond of the substrate) against the C–H bond dissociative energy (BDE) of different alkanes (Figure 2). The kinetic study strongly suggests that reactions proceed through the iron-oxo assisted H-atom abstraction mechanism.<sup>[14]</sup>



**Figure 2.** Plot of  $k_2'$  against C-H BDE of alkanes (DHA=Dihydroanthracene) in MeCN at 296 K.  $k_2'$  values are calculated based on the number of equivalent target C-H bonds of substrates. BDE's for C-H bonds are from reference 3.

In conclusion, in the presence of thymine-1-acetate ligand high-valent iron-peroxo species are generated from low spin Fe(III) complex with  $H_2O_2$  as a terminal oxidant. A rapid exchange of FeOOH oxygen atom with  $H_2^{18}O$  follows mechanism in which an exogenous water molecule assists the hydrogen transfer from the coordinated water molecule to the oxo group. The results support the mechanism where the iron-oxo species are formed via water-assisted heterolysis of O-O bond, and the carbonyl bond is formed via the oxygen either from  $H_2O_2$  or  $H_2O$ .

The iron/THA catalyst is capable of oxidizing alkanes with different steric and electronic properties. The catalyst may prefer tertiary C-H bonds over secondary ones, but the presence of steric congest can alter the order. Without tertiary C-H bonds the oxidation occurs selectively on secondary C-H bonds at the  $C_4$  and  $C_2$  positions as shown with the substituted cyclohexane substrates. Because of easy catalyst preparation, high activity and predictable selectivity, the Fe(III)/THA catalyst enables oxidative C-H activation of alkanes as an attractive strategy in various synthesis applications. Further studies on Fe(III)/THA catalyzed transformations and the mechanistic studies are currently under investigation.

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