

Catalytic oxidation of alcohols to carbonyl compounds with hydrogen peroxide using dinuclear iron complexes

Éva Balogh-Hergovich^a, Gábor Speier^{a,b,*}

^a *Research Group for Petrochemistry, Hungarian Academy of Sciences, 8200 Veszprém, Hungary*

^b *Department of Organic Chemistry, University of Veszprém, 8200 Veszprém, Hungary*

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Dedicated to Professor Josef Ziolkowsky on the occasion of his 70th birthday.

Abstract

Oxidation of primary and secondary alcohols has been studied in the presence of $[\text{Fe}(\text{ind})\text{Cl}]_2\text{O}$ (**1**) and $[\text{Fe}_2(\text{OMe})_2(\text{PAP})\text{Cl}_4]$ (**2**) (indH = 1,3-bis(2'-pyridylimino)isoindoline; PAP = 1,4-di(2'-pyridyl)aminophthalazine) as catalysts using hydrogen peroxide as primary oxidant. The complexes were found to be suitable catalysts for the oxidation of alcohols to the corresponding carbonyl compounds in acetone as solvent. The reactivity of the alcohols is in the order primary < secondary < cyclic secondary < aromatic. The reaction mechanism in the case of **1** probable involves an iron-based oxidant, while in the case of **2** a free-radical mechanism is suggested.

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1. Introduction

The catalytic conversion of primary and secondary alcohols into their corresponding aldehydes and ketones is an essential reaction in organic synthesis [1,2]. Traditional methods for performing such transformations generally involve the use of stoichiometric quantities of inorganic oxidants, e.g. Cr(VI), and generate large quantities of waste. The development of effective, more greener catalytic systems that use clean, inexpensive oxidants, such as molecular oxygen or hydrogen peroxide to convert alcohols to carbonyl compounds is an important challenge [3]. Transition metal-catalyzed oxidation of alcohols is of current interest, and various transition metal compounds and oxidant systems have been reported [4]. Ruthenium compounds have been extensively investigated as catalysts for alcohol oxidation in combination with various oxidants such as dioxygen [5], iodosobenzene [6], *t*-BuOOH [7],

and H_2O_2 [8]. Copper(I) salts and cobalt(III) complexes have been also shown to catalyze the oxidation of alcohols with molecular oxygen [9,10]. Hydrogen peroxide is a very attractive oxidant for industrial applications since water is the only by-product. Copper(II) complexes were developed as model systems for galactose oxidase (GO), which catalyzes the aerobic oxidation of primary alcohols to aldehydes and H_2O_2 [11,12]. Efficient Cu(II)-catalyzed oxidation of alcohols to the corresponding carboxylic acids in the presence of H_2O_2 has recently been described [13]. While oxidation of alcohols was accomplished by H_2O_2 utilizing catalytic amounts of Fe(III) salts [14,15], so far little effort has been devoted to the use of non-heme iron complexes as catalysts. The complex $[\text{Fe}(\text{Hdmg})_2(\text{py})_2]$ was found to be selective catalyst for the oxidative denitrication of nitroalkanes [16]. Feringa and coworkers [17] have reported a novel (μ -oxo)diiron(III) complex with a pentadentate ligand ($[\text{LFe}(\mu\text{-O})\text{FeL}]\text{ClO}_4$) (L = 2-({di(2-pyridyl)methyl}(2-pyridylmethyl)amino)methyl)phenol) which catalyze the oxidation of primary and secondary alcohols by the use of H_2O_2 . More recently we prepared new (μ -oxo)

* Corresponding author. Tel.: +36 88 422 0224657; fax: +36 88 427 492.
E-mail address: speier@almos.vein.hu (G. Speier).

diiron complexes, $[\text{Fe}(\text{ind})\text{Cl}]_2\text{O}$ (**1**) (indH = 1,3-bis(2'-pyridylimino)isoindoline) [18], and $[\text{Fe}_2(\text{OMe})_2(\text{PAP})\text{Cl}_4]$ (**2**) (PAP = 1,4-di(2'-pyridyl)aminophthalazine) [19] in order to modeling soluble methane monooxygenase (sMMO). The complexes exhibited monooxygenase-like activity utilizing hydrogen peroxide as the oxygen source and oxidized alkanes to alcohols and ketones in acetonitrile; however their use is limited due to their ability to dismutate H_2O_2 . This can be suppressed by working in acetone in which hydrogen peroxide reversibly forms 2-hydroxy-2-hydroperoxypropane. The latter compound gradually releases H_2O_2 as the reaction proceeds, maintaining a constant low oxidant concentration [20].

In this work we have studied the oxidation of primary and secondary alcohols with H_2O_2 as oxidant catalyzed by the non-heme dinuclear iron complexes **1** and **2**. The oxidation was carried out at room temperature in acetone. It was shown that alcohols are oxidized rapidly to the corresponding aldehydes or ketones with good selectivity. A tentative reaction mechanism is also proposed.

2. Experimental

2.1. Materials

All manipulations were carried out using standard Schlenk technique under purified argon [21]. Solvents were purified in the usual manner and stored under argon [22]. Cyclohexanol, 1-phenylethanol, 2-phenylethanol, H_2O_2 (35% aqueous), TBHP (*tert*-butylhydroperoxide, 70% aqueous), CPBA (3-chloroperoxybenzoic acid), 4-methylbenzyl alcohol, 4-methoxybenzyl alcohol, 4-chlorobenzyl alcohol, 4-nitrobenzyl alcohol and benzyl alcohol- d_7 (Aldrich), cyclopentanone, heptanol-4, and 2,2,4-trimethylpentanol-1 (Fluka) *n*-octanol (Biogal) were used without further purification. Commercial benzyl alcohol (Aldrich) was distilled and stored under argon. Complexes $[\text{Fe}_2\text{Cl}_2(\text{ind})_2\text{O}]$ [18], and $[\text{Fe}_2\text{Cl}_4(\text{PAP})(\text{OMe})_2]$ [19] were prepared by established procedures.

2.2. Analytical measurements

GC analyses were performed on a HP 5830A gas chromatograph equipped with a flame ionization detector and a 30 m (0.32 mm i.d., 1 μm FT) SP-1000 fused silica capillary column. Quantification of the products was achieved by using cyclopentanone as internal standard. GC–MS analyzes were performed on a HP 5890II/5971 GC/MSD apparatus equipped with a column identical to that used for GC analysis. Electronic spectra were recorded on a Shimadzu UV-160A spectrophotometer using quartz cells.

2.3. Oxidation procedure

Oxidation reactions were performed under an argon atmosphere at 25 °C. In a typical reaction the complex (35 μmol)

was dissolved in 8 cm^3 of acetone containing 3.5 mmol of substrate, then a solution of H_2O_2 (3.5 mmol in 2 cm^3 acetone) was added over a 15 min period. After stirring for another 15 min an internal standard (cyclopentanone) was added to the reaction mixture and the products were quantified by GC. The structures of the products were confirmed by GC–MS spectrometry and by comparison with authentic samples. For the estimation of kinetic isotope effect (KIE) the reaction was started by adding 0.35 mmol of hydrogen peroxide through a septum to a stirred solution of **1** (3.5 μmol), and benzyl alcohol or deuterated benzyl alcohol (0.35 mmol) in acetone (1 ml). In the competitive alcohol oxidation reactions a mixture of benzyl alcohol and another *para*-substituted derivative 4-XPhCH₂OH (where X = OMe, Me, Cl, and NO₂) were used following the procedure described above.

3. Results and discussion

The oxidation of primary and secondary alcohols catalyzed by the complexes $[\text{Fe}(\text{ind})\text{Cl}]_2\text{O}$ and $[\text{Fe}_2(\text{OMe})_2(\text{PAP})\text{Cl}_4]$ occurs readily to form the corresponding aldehydes and ketones as major products. The reactions were conducted at room temperature. Control experiments without catalyst under the same reaction conditions showed no oxidation.

The oxidation of benzyl alcohol was studied in more detail to optimize the reaction variables such as solvent, type of the oxidant, alcohol/oxidant molar ratio and length of reaction time. We checked first the activity of **1** in different solvents (MeOH, CH₃CN, acetone) with H_2O_2 as the oxidant. The best conversions have been observed in acetone. The effect of varying the oxidant was studied with **1** in acetone during the oxidation of benzyl alcohol. The results (Table 1) show that the best yields were obtained with H_2O_2 . When one equiv. of hydrogen peroxide was added to a solution of compound **1** and benzyl alcohol over 15 min and the mixture was stirred for 15 min oxidation occurred and benzaldehyde was formed in 52% yield, corresponding to 52 TN (turnover numbers (TN) = moles of product per mole of catalyst). A trace amount of benzoic acid was also obtained. Stirring the mixture for 60 min no more product could be obtained. Iodometric titration of the solution showed that 96–98% of the hydrogen peroxide was consumed. This suggests that more than stoichiometric amount of H_2O_2 is utilized in the reaction, which could be due to the thermal decomposition of H_2O_2 to dioxygen and water. Addition of another aliquot of H_2O_2 increased the amount of benzaldehyde, showing that the catalyst was stable under the conditions described in Table 1. In that case 68.7% of benzaldehyde and 4.6% of benzoic acid was formed.

The oxidation was extended to a variety of alcohols including primary and secondary, aromatic, aliphatic, cyclic and acyclic alcohols (Table 2). The presence of a benzene ring adjacent to the OH group in the alcohol appears to enhance the conversion. Cyclohexanol is oxidized relatively better than

Table 1
Oxidation of benzyl alcohol^a

Run	Complex	Oxidant		Time (min)	Conversion	Product distribution (%)	
		Type	(mmol)			Benzaldehyde	Benzoic acid
1	1	PhIO	3.5	120	4.8	69	31
2	1	TBHP	3.5	30	42.0	100	–
3	1	CPBA	3.5	30	39.1	100	–
4	1	H ₂ O ₂	3.5	30	53.0	98	2
5	1	H ₂ O ₂	3.5	60	53.5	96	4
6	1	H ₂ O ₂	7.0	60	73.3 ^b	94	6
7	1	H ₂ O ₂	3.5	30	50.4 ^c	96	4
8	2	H ₂ O ₂	3.5	30	15.3	99	1
9	2	H ₂ O ₂	3.5	120	22.3	98	3
10	2	H ₂ O ₂	3.5	120	9.0 ^c	99	1

^a Reaction conditions: benzyl alcohol 3.5 mmol, catalyst 35 μmol, acetone 10 cm³, Ar, 25 °C.

^b Addition of another aliquot of H₂O₂ after 30 min.

^c In the presence of 2,6-di-*tert*-butyl-4-methylphenol.

the secondary linear alcohol, heptanol-4 and better, than primary linear alcohols (compare entries 5, 7 and 9). Secondary oxidation products were also found when primary alcohols were used as substrates. For example, *n*-octanol (entry 9) forms *n*-octanoic acid too, besides its primary oxidation product, *n*-octanal. The presence of CH₃ groups near the carbon containing the OH group decreases the reactivity (compare entries 9 and 13 in Table 2). The relatively low yields could be due to the thermal decomposition of H₂O₂. When 5 equiv. of hydrogen peroxide was added to a solution of compound **1** and *n*-octanol over 60 min (entry 10) *n*-octanal was formed in 16.3% yield, however in that case 33.0% of *n*-octanoic acid was also formed. Similar results was obtained with 2,2,4-trimethylpentanol too (entry 14).

Complex **2**, containing the PAP ligand was also examined as catalyst for the oxidation of benzyl alcohol under the same reaction conditions. As shown in Table 1, the reaction of the latter afforded 15.2% benzaldehyde. Stirring the mixture for 120 min a total of 21.6 turnovers towards benzaldehyde could be achieved. The oxidation of other alcohols were also examined, but in these cases complex **2** was also less active, than complex **1** (Table 2). However, no overoxidation products were obtained with complex **2**.

Although the mechanism of the enhancing effect of iron in alcohol oxidation is not yet clear, some conclusions may be drawn. Analysis of the oxidation reaction of benzyl alcohol in the presence of complex **1** indicated an ionic mechanism, while with complex **2** a free-radical mechanism is

Table 2
Oxidation of alcohols^a

Run	Substrates	Complex	Time (min)	Products	Yield ^b (%)
1	1-Phenylethanol	1	30	2,2,4-Trimethylpentanal	29.0
2	1-Phenylethanol	2	120	2,2,4-Trimethylpentanoic acid	6.3
3	2-Phenylethanol	1	30	2,2,4-Trimethylpentanal	24.4
4	2-Phenylethanol	2	120	2,2,4-Trimethylpentanoic acid	7.7
5	Cyclohexanol	1	30	2,2,4-Trimethylpentanal	20.7
6	Cyclohexanol	2	120	2,2,4-Trimethylpentanal	9.0
7	Heptanol-4	1	30	Heptanal-4	9.4
8	Heptanol-4	2	120	Heptanal-4	5.2
9	<i>n</i> -Octanol	1	30	<i>n</i> -Octanal	11.8
				<i>n</i> -Octanoic acid	3.7
10	<i>n</i> -Octanol ^c	1	60	<i>n</i> -Octanal	16.3
				<i>n</i> -Octanoic acid	33.0
11	<i>n</i> -Octanol	2	120	<i>n</i> -Octanal	5.8
12	<i>n</i> -Octanol ^c	2	120	<i>n</i> -Octanal	8.5
13	2,2,4-Trimethylpentanol	1	30	2,2,4-Trimethyl-1-pentanal	6.1
				2,2,4-Trimethyl pentanoic acid	3.2
14	2,2,4-Trimethylpentanol ^c	1	60	2,2,4-Trimethyl-1-pentanal	13.0
				2,2,4-Trimethyl pentanoic acid	33.5
15	2,2,4-Trimethylpentanol	2	120	2,2,4-Trimethyl-1-pentanal	4.3
16	2,2,4-Trimethylpentanol ^c	2	120	2,2,4-Trimethyl-1-pentanal	5.3

^a Reaction conditions: substrate 3.5 mmol, catalyst 35 μmol, H₂O₂ 3.5 mmol, acetone 10 cm³, Ar, 25 °C.

^b Yields are based on substrate.

^c 17.5 mmol of H₂O₂ was added in 60 min.

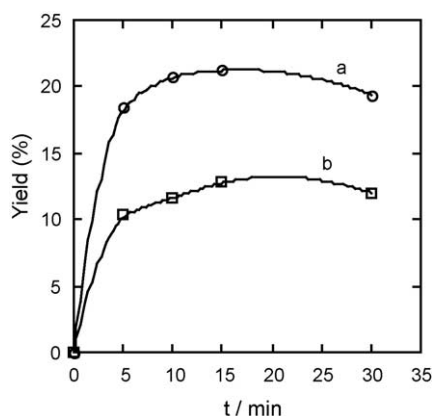


Fig. 1. Time course for benzyl alcohol (a) and benzyl alcohol-d₇ (b) oxidation. Conditions: substrate 0.35 mmol, H₂O₂ 0.35 mmol, complex **1** 3.5 μmol, acetone 1 cm³, 25 °C.

probable. To check the presence of radicals, we carried out inhibition experiments by the use of excess 2,6-di-*tert*-butyl-4-methylphenol. No significant lowering of the yield of benzyl alcohol was observed by complex **1** (entry 7). However, when the free-radical trap was added to the oxidation of benzaldehyde prior to H₂O₂ addition in the case of complex **2**, significant lowering of the oxidation product was obtained (entry 10), suggesting the involvement of free-radicals. Kinetic isotope effects (k_H/k_D) have been determined with benzyl alcohol-d₇ and the values of 1.8 and 1.6 were obtained for complexes **1** and **2**, respectively. Fig. 1 shows the time profile of the oxidation of alcohol (a) and benzyl alcohol-d₇ (b) with H₂O₂ in acetone. The observed KIE is similar to that reported for the oxidation of benzyl alcohol in the presence of a dinuclear iron complex [17]. However, large isotope effects were obtained for the alkane hydroxylations with iron complexes [23,24] for which hydrogen tunneling mechanisms were suggested. These results indicate that C–H bond breaking may occur in the rate-determining step in both systems.

Competitive reactions were also done for complex **1** with a series of *para*-substituted benzyl alcohol derivatives (4-XPhCH₂OH, where X = OMe, Me, Cl, and NO₂) in order to evaluate the influence of electronic factors on the reaction (Table 3). The relative reactivities show linear correlation with σ constants, the Hammett plot obtained is shown

Table 3
Relative (to hydrogen) reactivities for the oxidation of *para*-substituted benzyl alcohols^a

Run	Substrates	σ^b	k_{rel}^c
1	Benzyl alcohol	0	1.00
2	4-Methoxybenzyl alcohol	-0.28	1.24
3	4-Methylbenzyl alcohol	-0.14	1.21
4	4-Chlorobenzyl alcohol	0.24	0.32
5	4-Nitrobenzyl alcohol	0.81	0.034

^a Reaction conditions: substrates 3.5 mmol, complex **1** 35 μmol, H₂O₂ 3.5 mmol, acetone 10 cm³, Ar, 25 °C.

^b Values from Ref. [25].

^c Slopes from plots of ratios of product yields [XPhCHO]/[PhCHO] vs. ratios of initial concentrations of alcohols [XPhCH₂OH]/[PhCH₂OH].

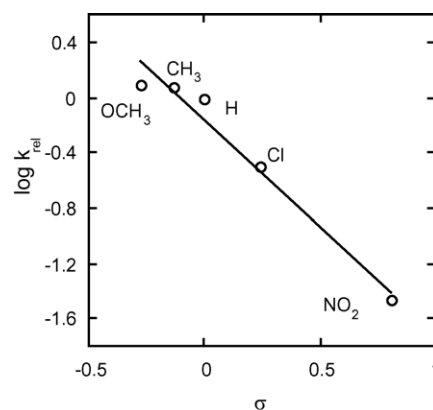


Fig. 2. Hammett plot for the oxidation of the *para*-substituted benzyl alcohols. Conditions: substrate 3.5 mmol, H₂O₂ 3.5 mmol, complex **1** 35 μmol, acetone 10 cm³, 25 °C.

in Fig. 2 ($R=0.98$). The reaction constant ρ was found to be large and negative ($\rho = -1.53$) demonstrating that electron-releasing substituents enhance the reaction rate. These results suggest that oxidation of alcohols with H₂O₂ catalyzed by complex **1** proceed through polar transition states with charge transfer from the substrate to the oxoiron species. Electron-releasing groups were found to promote the cleavage of the O–O bond in the homolysis of Fe^{III}(OOR) intermediates [26].

UV/Vis spectra of an acetone solution of [Fe(ind)Cl]₂O and benzyl alcohol recorded immediately after addition of H₂O₂ show drastic changes. The band at 390 nm, assigned to an oxo-to-iron charge transfer transition disappeared. In the case of [Fe₂(OMe)₂(PAP)Cl₄] only the intensities of bands at 210 and 361 nm decrease after addition of H₂O₂. The mixture of the freshly prepared catalyst with H₂O₂ was EPR-silent hinting to the absence of mononuclear iron species.

The mechanism of alcohol oxidation by oxometal complexes is attracting continuous interest, and various mechanistic pathways were suggested. In the hydride transfer (HT) mechanism proposed for the oxidation of alcohols by oxoruthenium complexes the oxometal complex abstracts a hydride from the alcohol forming an α -hydroxycarbon cation [27]. A hydrogen atom transfer (HAT) mechanism has been suggested for the oxidation of α -alkylbenzyl alcohols promoted by cytochrome P450 enzymes in which the active oxidant is believed to be an oxoiron(IV) radical complex [28]. Aromatic radical cation was proposed as key intermediate in the electron transfer (ET) mechanism [29]. Concerted hydride transfer (CHT) was suggested in the alcohol oxidation by dioxygen and aldehydes catalyzed by cobalt(III) complexes [10]. A hydrogen atom transfer or the hydride transfer mechanism is more in line with our results.

The mechanism of alcohol oxidation catalyzed by complex **1** may be viewed as an oxidative dehydrogenation involving the formation of high valent peroxoiron intermediate. The coordinatively unsaturated iron(III) activate H₂O₂

via an iron-peroxo species, the transient precursor of a metal-based oxidant. Our observations suggest that the reaction proceeds via heterolytic scission of the peroxide bond resulting in high-valent oxoiron intermediate ($\text{LFe}^{\text{V}}=\text{O}$), rather than via a homolysis. Accordingly, if the HAT mechanism is operating, the oxoiron species abstracts one hydrogen atom from the substrate and an α -hydroxy carbon radical ($\text{H}(\text{OH})\text{PhC}^\bullet$) is formed which undergoes fast oxygen rebound to form a gem-diol and then the expected aldehyde or ketone. In the case of the HT mechanism the oxoiron species abstracts a hydride from the alcohol forming an α -hydroxy carbon cation ($\text{H}(\text{OH})\text{PhC}^+$) and a hydroxoiron intermediate, which reacting with the cation produce the gem-diol and the product. However, from the results obtained we could not make distinction between the HT and HAT mechanisms. The reactivity of alcohols is in the order primary < secondary < cyclic secondary < aromatic, which agrees with the stabilization both of the α -hydroxy carbon radical and the α -hydroxy carbon cation suggested in the transition state. The correlation obtained between the relative reactivities and the electronic properties of the *para* substituents also support this suggestion. However, if an electron transfer mechanism is operating, in the case of α -alkylbenzyl alcohols an aromatic radical cation is formed which can be deprotonated by oxoiron species to produce a benzyl radical. The oxygen rebound step follows, as in the HAT mechanism. The radical cation may also undergo C–C bond cleavage and the formation of ketone can be accompanied by that of benzaldehyde. In the case of α -phenylethanol no traces of benzaldehyde were obtained, thus an ET mechanism appears to be unlikely. A concerted hydride transfer (CHT) mechanism and a nonsynchronous concerted (NSC) mechanism may be also excluded due to the Hammett correlation obtained.

In the case of complex **2** the results are consistent with a free-radical mechanism.

4. Conclusion

In summary the complexes $[\text{Fe}(\text{ind})\text{Cl}]_2\text{O}$ and $[\text{Fe}_2(\text{OMe})_2(\text{PAP})\text{Cl}_4]$ were found to be useful catalysts for the oxidation of alcohols using H_2O_2 in acetone as solvent. Presence of a benzene ring adjacent to the OH group in the alcohol appears to enhance the conversion. The reactivity of alcohols is in the order primary < secondary < cyclic secondary < aromatic. Complex **2** was less active than complex **1**, however no overoxidation products were obtained, even using large excess of H_2O_2 . The reaction mechanism in the case of **1** probable involves an iron-based oxidant and in the case of **2** a free-radical mechanism can be suggested.

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