

Oxidation of C₁–C₄ alcohols by iron- and ruthenium-sulfophthalocyanine precatalysts with hydrogen peroxide or mono-persulfate in water

Nicola d'Alessandro^a, Lolita Liberatore^a, Lucia Tonucci^a,
Antonino Morvillo^b, Mario Bressan^{a,*}

^a Dipartimento di Scienze, Università "G. d'Annunzio", Viale Pindaro 42, 65127 Pescara, Italy

^b Dipartimento di Chimica Inorganica, Università di Padova, Via Marzolo 1, 35131 Padova, Italy

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Abstract

A catalytic system consisting of iron- or ruthenium-sulfophthalocyanine and hydrogen peroxide or mono-persulfate was effective in the oxidation of simple primary and secondary alcohols as well as of simple ketones. The oxidation reactions were conducted in aqueous media with turnover rates, defined as moles of product per mole of catalyst per minute, up to 5. Primary alcohols, including methanol, were selectively oxidized into the corresponding carboxylic acids. Secondary alcohols were transformed into the corresponding ketones, which were found to undergo further oxidation to esters via Baeyer–Villiger reaction, followed by hydrolysis or alternatively in the case of acetone via direct oxidation to acetic acid and CO₂. Moreover, *t*-butyl alcohol was also found to be slowly oxidized into acetone and methanol. Analysis of the oxidation reaction of cyclobutanol indicated an ionic mechanism; no deuterium kinetic isotope effect was measured in the cases of methanol and ethanol. The mechanistic origin of the catalytic efficiency is also discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The oxidation of alcohols has been of great value in organic synthesis and represents an important entry to essential functional groups, such as ketones, aldehydes, and carboxylic acids. Many standard oxidation procedures have been available for this purpose [1–3]; nevertheless, reactions currently used to

oxidize alcohols employ toxic chromium oxide. Thus, there is a constant need to develop inexpensive oxidants, preferably under catalytic conditions, to minimize inevitable co-products, which represents an environmental problem. The designing of such oxidation system remains a challenge; ideal catalytic oxidation reactions should operate at room temperature in an environmental friendly solvent system, e.g. water, and use green co-oxidants, such as oxygen (air) or hydrogen peroxide.

Aqueous-phase oxidation catalysis by transition metal complexes finds potential applications

* Corresponding author. Tel.: +39-85-4537548;

fax: +39-85-4537545.

E-mail address: bressan@sci.unich.it (M. Bressan).

for the detoxification of pollutants in wastewater [4] and also enjoys significant biological and mechanistic interest [5,6]. Biomimetic models of methane-mono-oxygenase have been recently developed for the oxidation of alcohols by using di-iron complexes [7,8]. Use of water as a solvent often imposes a non-banal reformulation of oxidation catalysts, since the active species are metal complexes in high oxidation states, typically strongly coordinated by water and in competition with the less polar organic substrates. Air is obviously attractive as an oxidant, but reactions are often nonselective and no generally applicable methods exist so far, despite very recent and interesting results ([9,10] and references therein). Hydrogen peroxide oxidations are expected to be more suitable, but a large excess is generally needed because of competitive dismutation of the oxidant; since the pioneering studies of Mares et al. [11] and Trost and Masuyama [12], only a limited number of effective oxidations of alcohols by this oxidant have been reported in the literature ([13] and references therein).

In the recent years, we have been interested in using ruthenium complexes as precatalysts for the oxidation of a number of organic substrates, including alcohols with mono-persulfate [14]. The oxidation of alcohols by high oxidation state ruthenium compounds as catalysts has been recently and comprehensively reviewed [15], but use of hydrogen peroxide was found to be generally unsuitable because of its extensive dismutation in the presence of ruthenium salts and complexes. More recently, we achieved a substantial improvement by using the water-soluble ruthenium(II) derivative RuPcS (where PcS is sodium-2,3-tetrakisulfophthalocyaninate) to effect the oxidation of chlorophenols [16] and chloro-olefins [17] in an entirely aqueous media, and in the presence of hydrogen peroxide. Related metal-sulfophthalocyanines (M = Fe, Mn) have been successfully used by Meunier and coworkers for the oxidation of chlorophenols [18,19], chloroanilines [20] and catechols [21] with persulfate or hydrogen peroxide in aqueous acetonitrile.

In this contribution, we wish to report on the catalytic oxidation of simple alcohols and ketones in aqueous media by RuPcS and FePcS catalysts (Fig. 1) that use KHSO_5 or H_2O_2 as the oxidizing source. We will also present some mechanistic implication using cyclobutanol as the substrate.

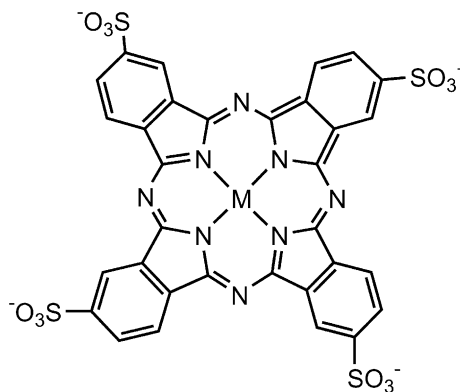


Fig. 1. Structure of MPcS complexes.

2. Experimental

2.1. Materials

RuPcS was prepared by a template synthesis starting from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, sodium-4-sulfophthalate, and urea [17]. We followed earlier reported general procedures for the synthesis of metal-sulfophthalocyanines [22]. FePcS, together with all reagent grade chemicals, was purchased from Aldrich.

2.2. Procedure for the catalytic oxidations

A water solution (10 ml) containing 0.5 mmol of the substrate and the metal catalysts (0.01 mmol) was stirred magnetically in a vial together with commercial Oxone[®], corresponding to a 0.5N concentration of active oxygen as KHSO_5 , or an equivalent amount of hydrogen peroxide, as determined by iodometric titrations. The reactions were carried out at 20°C and were not affected by the presence of air. Organic analyses were performed on an HP 6890 GLC instrument equipped with FID, using a 30 m HP-5 capillary columns (0.32 mm i.d.; 0.25 mm film thick) with the injection port kept at 250°C (carrier gas: He) on aliquots withdrawn with a microsyringe from the aqueous reaction mixtures either as such or diluted 1:10 with acetone. Commercial products were used for all gas chromatographic standardizations. The reaction mixtures were also treated by standard procedures with a 10:1 excess 2-methyl-1-butanol to analyze the possibility of dicarboxylic acids formed as

their isobutyl esters. The reactions were also followed by ^1H NMR by adding small amount of D_2O to the reaction mixtures. The ^1H NMR spectra were measured on a Bruker Avance 300 MHz instrument. The identity of each product was confirmed by comparison of the fragmentation pattern in the mass spectra obtained with an MD 800 Fisons mass spectrometer operating in the electron ionization mode at 70 eV.

3. Results and discussion

When excess persulfate or hydrogen peroxide was added to an aqueous solution of MPcS ($M = \text{Fe}, \text{Ru}$), an active species was immediately produced, as indi-

cated by the distinct fading of the intense color due to the MPcS complexes. These active species can be assumed to be oxygenated metal complexes in higher oxidation states; however, the fact that no detectable bands are observed in the 300–1200 nm region points to a profound transformation of the PcS macrocycle, for which the intense and diagnostic $\pi \rightarrow \pi^*$ transition(s) is/are expected to fall within the above range. This rather surprising result contradicts the common belief of the high resistance to the oxidation of the phthalocyanine ring; the destiny of the MPcS complexes in oxidizing media is being investigated.

The reactions were conducted at room temperature in a completely aqueous media containing an excess of the peroxidic oxidant (either mono-persulfate-oxone,

Table 1
Oxidation of alcohols and ketones by mono-persulfate catalyzed by MPcS complexes^a

Catalyst	[Cat]			0.1 mM	0.01 mM
	1 mM	Conversion in 24 h (%)	Products, % selectivity	Conversion in 24 h (%)	Conversion in 24 h (%)
Methanol					
RuPcS	100		Formic acid	29	5
FePcS	35			20	<1
Ethanol					
RuPcS	100		Acetic acid	100	10
FePcS	30			39	16
2-Propanol					
RuPcS	83		Acetone, 90; acetic acid, 9; methanol, 1; methyl acetate, tr; formic acid, tr	77	33 (19 ^b ; 3 ^c)
FePcS	75		Acetone, 91; acetic acid, 8; methanol, 1; methyl acetate, tr; formic acid, tr	58	44
2-Butanol					
RuPcS	99		MEK, 41; ethyl acetate, 24; acetic acid, 31; ethanol, 4	95	16 (10 ^c)
FePcS	92		MEK, 15; ethyl acetate, 38; acetic acid, 47; ethanol, 1	45	5
<i>t</i> -Butanol					
RuPcS	10		Acetone; methanol, tr	nd	nd
FePcS	15			nd	nd
Acetone					
RuPcS	22		Acetic acid, 87; methyl acetate, 11	nd	nd
FePcS	5		Methanol, 2	nd	nd
MEK					
RuPcS	80		Ethyl acetate, 43; acetic acid, 48; ethanol, 9	nd	nd
FePcS	55		Ethyl acetate, 48; acetic acid, 39; ethanol, 13	nd	nd

^a Reaction conditions: aqueous solutions, not buffered (pH ca. 2), of substrate 50 mM, KHSO_5 0.5N, and the catalysts; 20°C; conversions determined by ^1H NMR and/or GC; no detectable oxidation of the substrates in the absence of the catalysts, except otherwise stated; tr: trace amount; nd: not detectable.

^b RuPcS: 1 mM.

^c No catalyst.

pH ca. 2, or hydrogen peroxide, both in acidic pH ca. 2 by added H₂SO₄, and in neutral non-buffered media; typically 0.5N) and the substrates (50 mM). The MPcS catalysts (M = Fe, Ru) were added in a 0.02–2 mol% with respect to the substrates. The substrates examined were primary (methanol and ethanol) and secondary alcohols (2-propanol and 2-butanol) together with their corresponding ketones, acetone and methylethylketone, and *t*-butyl alcohol. In the absence of the catalysts, no reaction was observed: only with mono-persulfate, the secondary alcohols were slowly oxidized. Typical conversions, oxidation rates, and product distributions are shown in Tables 1 and 2. Yields depend upon the nature of both the substrate and of the catalyst, but a rationale was difficult to propose, possibly because of the strong changes in the polarity of the aqueous media induced by the various substrates: it is noteworthy that all the substrates

examined, including methanol but excluding *t*-butyl alcohol, are converted at comparable rates. The catalytic activity of RuPcS was definitely found to be higher than that of FePcS, particularly with the less reactive primary alcohols, and when lower concentrations of the catalysts were used. The initial rates of persulfate oxidations were maintained for extended periods of time and over 1000 cycles have been observed; however, oxidations after addition of further amounts of substrate to the reaction mixtures proceed at a rate significantly lower than the initial one, i.e. in the presence of fresh catalyst. This was a strong indication of a slow degradation of the initial catalytic species to a less active form.

Primary aliphatic alcohols gave rise to carboxylic acids, with no evidence of aldehydes as intermediate products; of particular interest was the facile oxidation of methanol, which was almost

Table 2
Oxidation of alcohols and ketones by hydrogen peroxide catalyzed by MPcS complexes^a

Catalyst	Conversion in 24 h (%)	Products, % selectivity
Methanol		
RuPcS	12 (13 ^b)	Formic acid
FePcS	24	
Ethanol		
RuPcS	4 (3 ^b)	Acetic acid; acetaldehyde, tr
FePcS	15	Acetic acid, 90; acetaldehyde, 10
2-Propanol		
RuPcS	12 (26 ^b)	Acetone; acetic acid and methanol, tr
FePcS	14 (10 ^c)	Acetone, 99; acetic acid, 1; methanol, tr
2-Butanol		
RuPcS	14 (24 ^b ; 1 ^c)	MEK
FePcS	34 (10 ^c)	MEK, 84; 3-hydroxy-2-butanone, 16
<i>t</i> -Butanol		
RuPcS	5	Acetone
FePcS	4	
Acetone		
RuPcS	25	Acetic acid
FePcS	22	
MEK		
RuPcS	10	Acetic acid
FePcS	10	Acetic acid, 64; 3-hydroxy-2-butanone, 36

^a Reaction conditions: aqueous solutions, not buffered (pH ca. 7), of substrate 50 mM, H₂O₂ 0.5N, and the catalysts 1 mM; 20°C; conversions determined by ¹H NMR and/or GC; no detectable oxidation of the substrates at MPcS 0.1 mM and below, except otherwise stated; tr: trace amount; nd: not detectable.

^b Acidic conditions, pH ca. 2 (H₂SO₄).

^c MPcS: 0.1 mM.

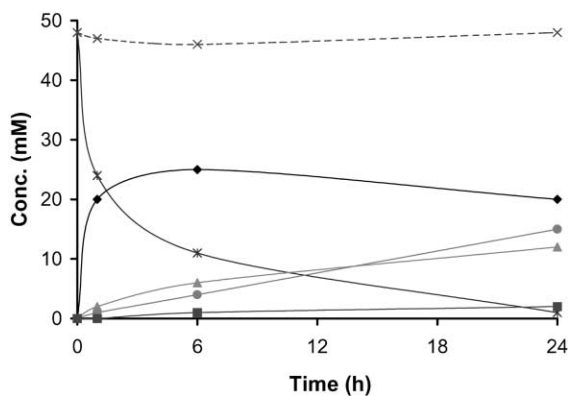


Fig. 2. Time course for 2-butanol oxidation in water (pH ca. 2). Conditions: substrate 48 mM, RuPcS catalyst 1 mM, KHSO_5 0.5N; 20°C. 2-Butanol (stars); MEK (rhombuses); ethyl acetate (triangles); acetic acid (circles); ethanol (squares); mass balance (crosses).

quantitatively transformed into formic acid in the presence of RuPcS (1 mM). Secondary alcohols were found to rapidly yield the corresponding ketones, but extensive over-oxidation of the latter substrates is observed, as demonstrated by control experiments carried out on acetone and methylethylketone under the same reaction conditions. Time course for the oxidation of 2-butanol (Fig. 2) clearly shows that MEK, which was rapidly formed in the initial reaction times, undergoes further oxidation to ethyl acetate, the expected product of a Baeyer–Villiger oxidation of the ketone; the reaction was further complicated by the facile hydrolysis of the ester into acetic acid and ethanol, and the possible oxidation of the latter, as illustrated in Fig. 3. No evidence of the other possible ester, i.e. methyl propionate, resulting upon the oxidative attack of methylethylketone at the $\text{CH}_3\text{-CO}$ moiety was found, thus pointing to high selectivity of the $\text{CH}_2\text{-CO}$ bond for the oxygen-insertion. 2-Propanol (and acetone) behaved similarly, except that acetic acid was the overwhelmingly major detected product, with only minor amounts of the ester (methyl acetate) and alcohol (methanol) (Fig. 4). The results suggested that the oxidation of acetone proceeded only partially via the Baeyer–Villiger mechanism; a direct oxidation of acetone to acetic acid and CO_2 can be envisaged, likely through pyruvic acid, the primary oxidation product of acetone which decarboxylated very easily and was indeed not found in the reaction mixtures.

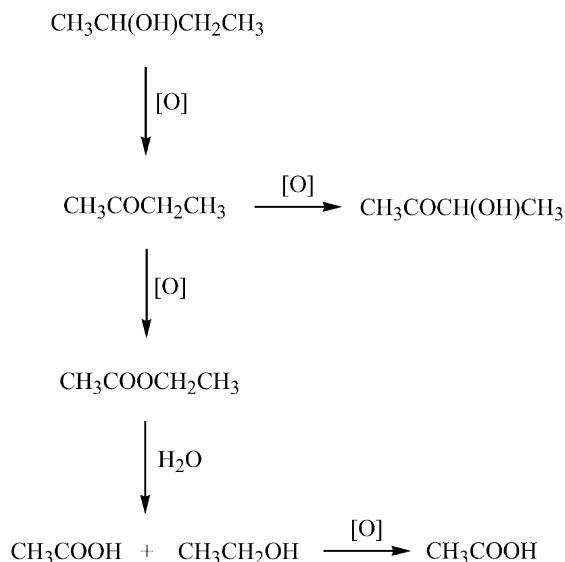


Fig. 3. Proposed reaction pathways for the oxidation of 2-butanol and MEK.

This reaction pathway was not operating in the case of 2-butanol, since no propionic acid was produced. *t*-Butyl alcohol was also slowly oxidized to acetone, implying that a H atom on the $\alpha\text{-C}$ of the alcohol was

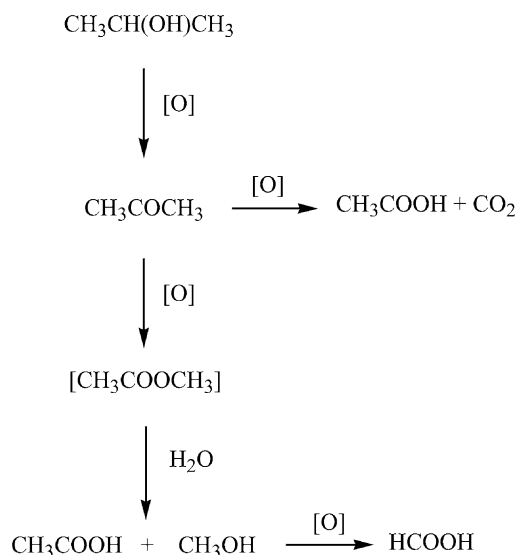


Fig. 4. Proposed reaction pathways for the oxidation of 2-propanol and acetone.

not necessary for the reaction to proceed; oxidation of tertiary alcohols has been reported to be either a one- or a two-electron process, resulting in a fragmentation reaction yielding ketones and carbon radicals [23].

Contrary to the experiments with mono-persulfate, where yields to the oxidant were very close to the calculated requirement, the catalytic oxidations conducted in the presence of H_2O_2 exhibited extensive dismutation of the oxidizing agent, even in acidic media. Although, initial rates were comparable with those measured with persulfate, dismutation considerably limits the overall yields and quantitative conversion can only be achieved by continuous addition of large excesses of hydrogen peroxide. Direct experiments showed that dismutation of H_2O_2 significantly slows down in the presence of the substrates, a clear indication of effective competition on the active metal sites. FePcS (0.1–1 mM) was found to cause the least amount of decomposition of H_2O_2 , with half-times for degradation between 12 and 24 h, depending upon the concentration of the metal complex. Therefore, the overall conversions for the H_2O_2 oxidations with FePcS were larger than RuPcS, despite the stronger intrinsic oxidizing properties of the active species derived from the latter, which was able to very

effectively oxidize hydrogen peroxide (half-times ≥ 1 h). The pattern of the oxidation products in the case of H_2O_2 oxidations was similar to that observed with mono-persulfate: the significant differences found in the amounts of the products coming from hydrolysis was likely due to the different pH at which the reactions were carried out, i.e. neutral for hydrogen peroxide and strongly acidic for mono-persulfate. Oxidation of MEK also gave 3-hydroxy-2-butanone, together with the products from the Baeyer–Villiger oxidation of the substrate: 3-hydroxy-2-butanone clearly was the result of hydroxylation of the $\alpha\text{-CH}_2$ group of MEK.

Oxidation rates with mono-persulfate were measured by varying catalyst concentrations in the 1–0.01 mM range for all the substrate–catalyst combinations, indicating a first-order dependence; however, the measured values were constantly found below 1 (between 0.3 and 0.7) for all substrate–catalyst combinations (Fig. 5). A plausible explanation was that in relatively concentrated solutions, significant stacking of the metal-catalysts and/or metal-precursors occurs, thus limiting the concentration of the active species. A first-order dependence was also measured for the substrates (2-propanol and ethanol in the 10–250 mM

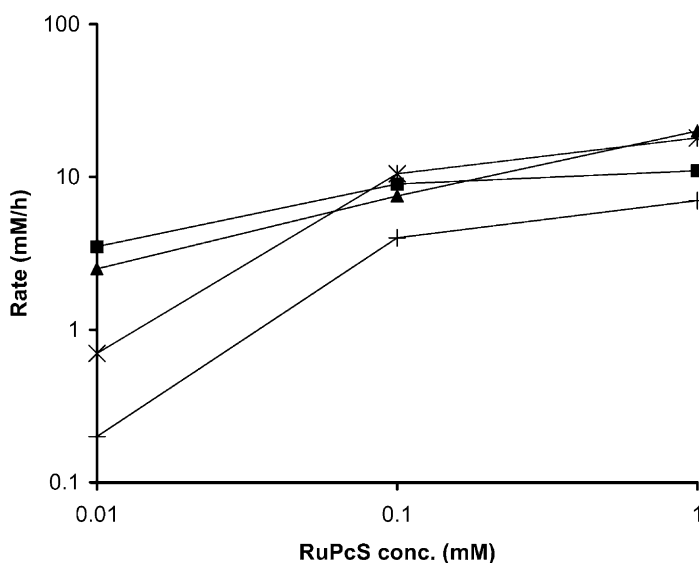


Fig. 5. Initial oxidation rates (substrate disappeared, mM/h) for methanol (crosses), ethanol (stars), 2-propanol (squares), and 2-butanol (triangles), 50 mM, by KHSO_5 0.5N in water (pH ca. 2) and in the presence of RuPcS catalyst at various concentrations; 20°C.

range in the presence of mono-persulfate and RuPcS, 0.1 mM). Finally, the absence of detectable kinetic isotope effects for alcohol oxidations (methanol- d_4 and ethanol- d_6 in the presence of RuPcS catalyst 1 and 0.1 mM) indicates that CH bond-breaking was relatively not important in the rate-limiting step.

We wanted to attempt to elucidate the mechanisms of oxidation with the first aspect of the redox processes, which might as involve the transfer of one or two electrons in the rate-determining step. The oxidation of cyclobutanol provided a useful and widely reported test to distinguish between different reaction mechanisms for the oxidation of alcohols: two-electron transfer agents are expected to selectively afford cyclobutanone [24], while one-electron transfer agent causes bond cleavage with noncyclic products being predominantly obtained [25]. The mono-persulfate–MPcS systems always led to the formation of cyclobutanone (together with minor amounts of γ -butyrolactone, up to 20%, arising from the persulfate oxidation of cyclobutanone itself), but without any evidence for noncyclic products after 24 h. Thus, the two-electron transfer mechanism appears to dominate.

4. Conclusion

In summary, we have discovered a novel and readily available catalytic system for the oxidation of primary alcohols, including methanol, to carboxylic acids, of secondary alcohols to ketones, and of ketones to various products, based on the oxidants mono-persulfate and hydrogen peroxide and working in water. Full conversions were observed at catalyst loading of less than 0.2%. Presently, we have no conclusive information on the nature of the active species derived from the MPcS precursors upon the facile oxidative degradation of the phthalocyanine macrocycle under very mild oxidizing conditions (<5% hydrogen peroxide at neutral pH). The outcome of cyclobutanol oxidation typically indicates the occurrence of a two-electron transfer, even if two-electron transfers on oxo-metal species are commonly characterized by large primary D-KIEs on the α -C [26]. The observed absence of detectable KIEs may indicate a concerted oxygen transfer from the oxidizing metal species to the alcoholic substrate coordinated to the metal through the oxygen atom [27,28].

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