

Oxidation of propenoidic phenols catalysed by *N,N'*-ethylenebis(salicylideneiminato)cobalt(II) [Cosalen]: reactivity and spectroscopic studies

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Abstract

Three propenoidic phenols, *E*-methyl ferulate, *E*-4-hydroxycinnamic acid methyl ester and *E*-3-chloro-4-hydroxycinnamic acid methyl ester, were oxidized with dioxygen, in the presence of *N,N'*-ethylenebis(salicylideneiminato)cobalt(II) [Cosalen]. The yields of conversion to oxidized products depended on the reaction solvent and on the substituents on the phenyl ring. EPR and electronic investigations suggest that an organometallic radical acts as the intermediate active species.

Keywords: Cosalen; Phenol; Oxidation; EPR study

1. Introduction

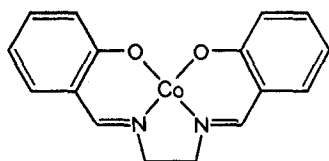
Catalytic oxidation of propenoidic phenols is becoming a good alternative to the incineration of polyphenol rich wastewaters [1]. Cobalt(II) derivatives are known to promote the reduction of dioxygen; for this reason Schiff base complexes of cobalt were extensively used as catalysts in several oxidation processes [2].

Here we report the study of the catalytic oxidation of two propenoidic phenols with molecular oxygen catalysed by *N,N'*-ethylenebis(salicylideneiminato)cobalt(II) [Cosalen] (Scheme 1).

2. Results and discussion

Chloroform and pyridine solutions of Cosalen (0.0144 M) and *E*-methyl ferulate (**1**) (0.144 M) were treated at 25°C with dioxygen at a pressure of 10 bar. At different reaction times the reaction mixture was separated and the components quantified.

In both solvents, after 48 h, two major products of oxidative degradation were obtained: 4-hydroxy-3-methoxybenzoic acid (**2**) and 4-hydroxy-3-methoxybenzaldehyde (vanillin) (**3**). Conversions, referred to *E*-methyl ferulate and taken at different reaction times, were much



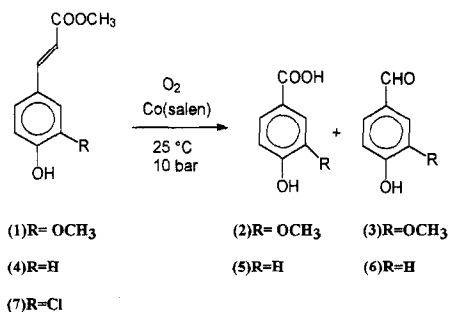
Scheme 1. Cosalen molecular structure.

higher in chloroform than in pyridine. Specifically in chloroform, after one hour, the conversion was 84% of the original *E*-methyl ferulate (Table 1). These reaction products derived from the loss of two carbon atoms from the original propenoidic chain (Scheme 2). No reaction was observed in pyridine.

Unexpectedly, solvents which usually cause desorption of O₂ from Cosalen (e.g. chloroform) [3] promoted the oxidative degradation of *E*-methyl ferulate, while no promotion was observed for solvents which usually activate the addition of O₂ to Cosalen (e.g. pyridine) [3].

In order to test the influence on the reactivity of the substituents on the aromatic ring, the reaction was carried out by using *E*-4-hydroxycinnamic acid methyl ester (4) and *E*-3-chloro-4-hydroxycinnamic acid methyl ester (7) under the same experimental conditions. Again, products deriving from the loss of two carbon atoms from the side chain were obtained. They were 4-hydroxybenzoic acid (5) and 4-hydroxybenzaldehyde (6). The yields were lower than with *E*-methyl ferulate (1). In the case of the chloro-derivative no conversion at all was observed (Table 1).

The interaction of oxygen with Cosalen in



Scheme 2. Cosalen-catalyzed oxidation of propenoidic phenols.

the presence of propenoidic phenols was also investigated by EPR, because of the EPR activity of Cosalen and of its adducts with base molecules and O₂ [3,4].

The EPR spectra of chloroform and pyridine deoxygenated solutions containing Cosalen (0.0144 M) and *E*-methyl ferulate (0.144 M) were respectively identical to those reported in the literature for Cosalen · *n*CHCl₃ and Cosalen(py) [3,4]. These latter adducts were described as very different in the ligand field symmetry and in the electronic properties of cobalt centres. The differences in the coordination geometry between the planar Cosalen · *n*CHCl₃ [5] and the pentacoordinated Cosalen(py) are responsible for strong energy differences in the electronic states of cobalt centre [3,4].

When chloroform and pyridine solutions of Cosalen and *E*-methyl ferulate were exposed to oxygen and left for 15 min at 25°C under 10 bar pressure, the EPR spectrum of the pyridine solution showed the presence of the Cosalen(py)O₂

Table 1

Conversion at different reaction times and selectivity after 48 hours of Cosalen-catalyzed oxidation in two different solvents of: *E*-methyl ferulate (1), *E*-4-hydroxycinnamic acid methyl ester (4)

Phenol	Solvent	Conversion (%) after:			Selectivity (%) after 48 h	
		1 h	5 h	48 h	4-hydroxy benzoic acid derivatives	4-hydroxy benzoyl aldehyde derivatives
<i>E</i> -methyl ferulate (1)	pyridine	0	2	14	10 (2)	4 (3)
	chloroform	84	88	100	61 (2)	39 (3)
<i>E</i> -4-hydroxycinnamic acid methyl ester (4)	pyridine	1	6	8	8 (5)	0 (6)
	chloroform	6	37	60	17 (5)	43 (6)

n.c. = not converted.

superoxide derivative [6], while that of the chloroform solution showed a new radical species (Fig. 1). The radical has eight resonance lines centred at $g = 2.0028$, due to the hyperfine interaction with ^{59}Co nucleus ($I = 7/2$) of 10 Gauss. The spectrum allows to detect also a superhyperfine splitting of about 3 Gauss. The value of the Co hyperfine interaction indicates that the unpaired electron is mainly located on the ligand and that another nucleus, probably ^1H ($I = 1/2$), interacts with it.

On prolonging the contact with oxygen under pressure, the amount of the radical decreased: after 5 h it was one tenth of the initial amount, remaining unchanged thereafter.

The substitution of $-\text{OCH}_3$ with $-\text{H}$ lowered the radical amount to about one tenth at all reaction times, while in the case of the chloroderivative no signal at all was observed.

The electronic spectra taken in the region of near infrared and UV–visible frequencies on the same deoxygenated chloroform solutions as the EPR spectra, showed the absorption bands of $\text{Cosalen} \cdot n\text{CHCl}_3$ (Fig. 2 line 1) [3]. After exposure to oxygen for 15 min at 25°C under 10 bar pressure, the spectra showed relevant changes (Fig. 2 line 2).

The discussion was aimed to answer two main questions:

- (i) Which is the cobalt ligand field in the new radical species?
- (ii) Does the radical play a role in the oxidative degradation of propenoidic phenols, and why is this reaction favoured in CHCl_3 ?

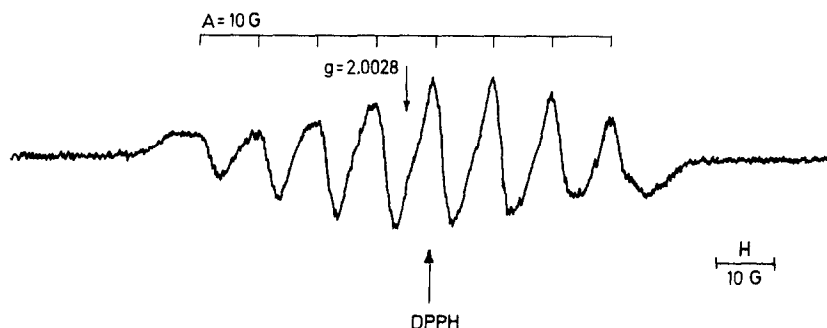


Fig. 1. EPR spectrum, recorded at room temperature, of a CHCl_3 solution of Cosalen (0.0144 M) and *E*-methyl ferulate (0.144 M) taken after 15 min of oxygen contact.

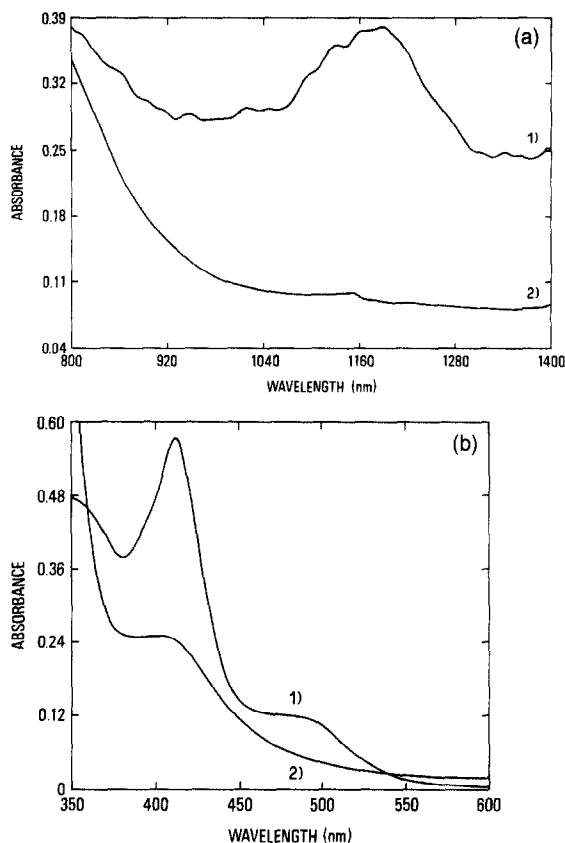


Fig. 2. Electronic spectra in the near infrared (a) and UV–visible region (b) of a CHCl_3 solution of: (line 1) deaerated Cosalen or Cosalen and *E*-methyl ferulate in a 1/10 molar ratio; (line 2) the same taken after 15 min of dioxygen contact.

With regard to the question (i), it would seem that the new radical species depends both on dioxygen and phenol, the $\text{Cosalen} \cdot n\text{CHCl}_3$ spectra changing if O_2 and propenoidic phenol are both present. The coordination around cobalt has cubic symmetry field (isotropic g value).

Both EPR and UV–visible spectra are strongly similar to those of the hexacoordinated Cosalen(3,5 di-*tert*-butyl-*o*-benzosemiquinone) [7]. The electronic spectra in the near infrared frequency region confirm that the planar coordination of Cosalen $\cdot n\text{CHCl}_3$ changed in the presence of both *E*-methyl ferulate and oxygen; in fact the absorption at about 1200 nm unique to planar Cosalen [3] disappeared. The superhyperfine coupling seen in the *E*-methyl ferulate cobalt derivative in the presence of oxygen was tentatively ascribed to cobalt interaction with a hydrogen of the phenol ring. This suggests that cobalt interacts with the propenoidic phenol. At this stage we were unable to indicate a form of coordinated oxygen, if any.

As for the second question, we suggest that the cobalt radical observed in CHCl_3 acts as an intermediate in the oxidation of propenoidic phenols and that Cosalen catalyzes the reaction. In fact, the formation of the superoxide derivative Cosalen(py) O_2 in pyridine hindered the formation of cobalt radical and any oxidation of the propenoidic phenols. The substitution of $-\text{OCH}_3$ with $-\text{H}$ or with $-\text{Cl}$ also caused a decrease in the amount of the produced radical and the conversion yields of the phenols decreased in a parallel way.

The span of the potential of our results ranges from reaction studies on oxygen to the modeling of the biological cycle of lignin. Furthermore our findings should stimulate further work on Cosalen catalyzed wastewater treatments [8] leading to the recovery of organic carbon from lignin oligomers [9].

3. Experimental

3.1. Reagents

E-Methyl ferulate and *E*-*para*-hydroxymethylcinnamate were obtained by treatment of the corresponding acids (Fluka) with methanol and gaseous hydrogen chloride. Cosalen was purchased from Aldrich. *E*-3-chloro-4-hydroxy-

methylcinnamate was obtained by reacting 3-chloro-4-hydroxybenzaldehyde [10] with malonic acid [11] and methylating as above.

3.2. Phenol oxidations

A 40 ml solution of propenoidic phenol (0.144 M) and Cosalen (0.0144 M) were put in a 100 ml volume glass linear and then inserted into a 250 ml autoclave. The autoclave was charged with dioxygen (10 bar) and left at 25°C for the required time. The solvent was then evaporated under reduced pressure and the residue was resolved on silica column with ethyl acetate and hexane as eluents. Each product was recognized by comparison with authentic samples. When conversion and selectivity had to be determined, the residue was dissolved in acetone (20 ml) and dimethyl sulphate (0.3 ml); then K_2CO_3 (435 mg) was added. After refluxing for 2 h, the solid was filtered out, the solvent was evaporated under reduced pressure and the residue was dissolved in CH_2Cl_2 and analyzed in GLC–MS using biphenyl as internal standard.

3.3. Apparatus

EPR spectra were recorded at room temperature and when required at -150°C on a conventional Varian E 109 apparatus working at the X-band frequency. The g values were measured by standardization with DPPH. The ratios between the amounts of radical were calculated by double integration of the resonance line area.

Electronic spectra were recorded in the region of UV–visible frequencies on a HP 8452A diode array spectrophotometer and in the near infrared region on a Varian 2390 spectrophotometer.

Acknowledgements

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