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Spectromagnetic investigation of the active species in the oxidation of propenoidic phenols catalysed by [*N*,*N′*-bis(salicylidene)-ethane-1,2-diaminato]cobalt(II) *

Ezio Bolzacchini,[a] **Carmen Canevali,**[b] **Franca Morazzoni,**[b] **Marco Orlandi,**[a] **Bruno Rindone**[a] **and Roberto Scotti**[b]

[a] *Dipartimento di Scienze Ambientali, Università di Milano, Polo di Pirelli-Bicocca,*
Via Emanueli 15, 20126, Milano, Italy
[b] *Dipartimento di Scienza dei Materiali, Università di Milano, Polo di Pirelli-Bicocca,*
Via Emanueli 15, 20126, Milano, Italy

The oxidation of propenoidic phenols by molecular oxygen, catalysed by [*N*,*N′*-bis(salicylidene)ethane-1,2-diaminato]cobalt(II) [Co(salen)], was studied in different solvents and for variously substituted phenols to find processes alternative to those reported for the removal of polyphenols from waste waters in the paper industry. The reaction of methyl *E*-4-hydroxy-3-methoxycinnamate (*E*-methyl ferulate) selectively gave the corresponding 4-hydroxybenzoic acid and 4-hydroxybenzaldehyde; yields are highest in chloroform, good in methanol and very low in pyridine. Conversion was high with *E*-methyl ferulate, lower with methyl *E*-4-hydroxycinnamate, while the other phenols, methyl *E*-3-hydroxy-4-methoxycinnamate (*E*-methyl isoferulate) and methyl *E*-3-chloro-4-hydroxycinnamate, did not react. An EPR investigation of the reaction mixtures, performed on samples taken at different reaction times, demonstrated that the most probable mechanism involves reactions (i)–(iii). The

$$[\mathrm{Co^{II}(salen)}] + \mathrm{ROH} + \mathrm{O_2} \rightleftharpoons [\mathrm{Co^{III}(salen)(ROH)(O_2)}]^- \qquad \text{(i)}$$

$$[\mathrm{Co^{III}(salen)(ROH)(O_2)}]^- + \mathrm{ROH} \rightleftharpoons [\mathrm{Co^{III}(salen)(ROH)(RO^{\bullet})}] + \mathrm{HO_2}^- \qquad \text{(ii)}$$

$$[\mathrm{Co^{III}(salen)(ROH)(RO^{\bullet})}] + \mathrm{HO_2}^- \rightleftharpoons [\mathrm{Co^{III}(salen)(RO^-)(RO^{\bullet})}] + \mathrm{H_2O_2} \qquad \text{(iii)}$$

superoxocobalt radical, $[\mathrm{Co^{III}(salen)(ROH)(O_2)}]^-$, and the phenoxy cobalt radical, $[\mathrm{Co^{III}(salen)(RO^-)(RO^{\bullet})}]$, are the EPR-active species; $\mathrm{RO^{\bullet}}$ is suggested easily to dissociate from $[\mathrm{Co^{III}(salen)(RO^-)(RO^{\bullet})}]$ and, reacting with O_2 at the β-carbon of the allyl substituent, probably gives a dioxethane. This decomposes to aldehyde and acid. The phenol electron-donor properties promote the formation of the superoxocobalt derivative and consequently favour the formation of the phenoxy cobalt radical; a too high stability of this radical does not favour its evolution into oxidation products.

Propenoidic phenols are constituents of lignin, the most abundant natural polymer after cellulose. Waste waters from the paper industry, agroindustrial activities, *etc.* contain a high concentration of polyphenols. These compounds are usually removed by oxidation with nitroaromatics,[1] by oxidation with air at high temperatures in alkaline solution,[2] or by electrochemical oxidation.[3] As an alternative to these processes we recently proposed the oxidation with dioxygen in the presence of [*N*,*N′*-bis(salicylidene)ethane-1,2-diaminato]cobalt(II) [Co(salen)] as catalyst.[4] Two main degradation products were obtained: the 4-hydroxybenzoic acid and the commercially important 4-hydroxybenzaldehyde. These results prompted us further to investigate the activation of dioxygen by [Co(salen)] in this particular reaction, and to attempt direct detection of the possible intermediates, *e.g.* the superoxo-derivative of [Co(salen)] and the phenoxy radical, suggested as active intermediates in the oxidation of phenols.[5] Monitoring of the reaction was mainly performed by EPR spectroscopy.

Experimental

Reagents

The complex [Co(salen)] (99%) was from Aldrich. Methyl *E*-4-hydroxy-3-methoxycinnamate (*E*-methyl ferulate) **1**, methyl *E*-4-hydroxycinnamate **3** and methyl *E*-4-methoxycinnamate **5** were obtained from a mixture of the corresponding acids (Fluka) (4 g) and Dowex 50 W (8200 4) (0.4 g) in absolute methanol (25 cm^3). The mixture was heated under reflux overnight, filtered and evaporated under reduced pressure to obtain the product (97% yield).[6]

***E*-Methyl isoferulate 2 and methyl *E*-3-chloro-4-hydroxycinnamate 4.** Malonic acid (Fluka) (1.64 g, 15.8 mmol) was dissolved in anhydrous pyridine (4 cm^3) and mixed with the appropriate benzaldehydes.[6] The solution was refluxed for 3 h, cooled to room temperature and poured into a mixture of ice with concentrated HCl. The solid acid precipitated, was filtered off and methylated as above.[7]

Phenol oxidations

A solution (40 cm^3) of substrate (0.06 M) and [Co(salen)] (0.006 M) was put in a glass vessel (100 cm^3) and then inserted into an autoclave (250 cm^3). The autoclave was charged with dioxygen (1 MPa) and left at 25 °C for the required time. The solvent was then evaporated under reduced pressure and the residue resolved on a silica gel column with ethyl acetate–hexane (1 : 1) as eluent. Each reaction product was recognized by comparison with authentic samples. Quantitative analyses were performed by dissolving the residue in acetone (20 cm^3) and dimethyl sulfate (0.3 cm^3), then K_2CO_3 (435 mg) was added. After refluxing

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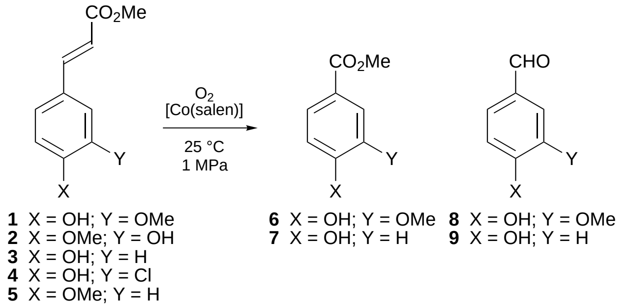
* *Non-SI unit employed*: G = 10^{-4} T.

Table 1 Conversion at different reaction times and selectivity after 48 h for the oxidation of: *E*-4-methyl ferulate (1), *E*-4-hydroxy methyl cinnamate (3).

		Conversion (%)			Selectivity (%) after 48 h	
Substrate	Solvent	1 h	5 h	48 h	Benzoic acid derivative	Benzoyl aldehyde derivative
1	Pyridine	0	2	14	**6** 10	**8** 4
	Methanol	38	55	80	**6** 36	**8** 44
	Chloroform	84	88	100	**6** 61	**8** 39
3	Pyridine	1	6	8	**7** 8	**9** 0
	Methanol	0	2	10	**7** 10	**9** 0
	Chloroform	6	37	60	**7** 17	**9** 43



Scheme 1

for 2 h the solid was filtered out, the solvent evaporated under reduced pressure and the residue dissolved in CH_2Cl_2 and analysed by GLC-mass spectrometry using biphenyl as internal standard.

Spectroscopic investigations

Deoxygenated solutions were prepared by dissolving [Co(salen)] (6×10^{-3} M) in solvents, previously outgassed in a nitrogen stream; when required, the substrate (6×10^{-2} M) was added. Solutions at 0.1 MPa oxygen pressure were obtained by bubbling oxygen for 15 min into the deoxygenated solutions. At reaction conditions (1 MPa oxygen pressure), aliquots of the solution containing [Co(salen)] (6×10^{-3} M) and the substrate (6×10^{-2} M) were taken at the following reaction times (expressed in minutes): 5, 10, 15, 20, 25, 30, 45, 65, 80, 95, 110, 125, 155, 185, 215, 245, 275 and 305, and immediately cooled in liquid nitrogen in order to slow down the reaction. The EPR spectra were recorded at −150 °C on a conventional Varian E-109 apparatus working at X-band frequency, equipped with a Varian automatic temperature controller. The *g* values were measured by standardization with diphenylpicrylhydrazyl (dpph). The amounts of the paramagnetic species were calculated by double integration of the resonance line areas. Spectra in the near-infrared region were recorded on a UV/VIS/NIR JASCO V-570 spectrophotometer with samples which had reacted for 15 min.

Results

Compounds **1**–**5** were investigated (Scheme 1). Table 1 reports the results. In particular, compounds **2** and **5** did not react showing that the phenolic group in position 4 is necessary for the reaction. The conversion of **4** was negligible under these conditions. With *E*-methyl ferulate **1**, conversions were highest in chloroform, good in methanol and very low in pyridine. The same reactivity but at a minor extent was obtained with methyl *E*-4-hydroxycinnamate **3**. Reaction products were the benzoic acid derivatives **6** and **7** and the corresponding aldehydes **8** and **9**.

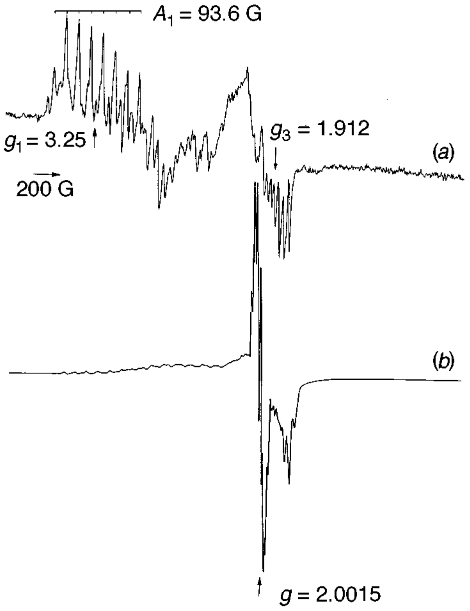


Fig. 1 The EPR spectrum, recorded at 123 K, of chloroform solutions of (*a*) [Co(salen)] (6×10^{-3} M), (*b*) [Co(salen)] (6×10^{-3} M)–*E*-methyl ferulate (6×10^{-2} M), after 15 min contact with O_2 at 0.1 MPa pressure

EPR Investigation

The EPR spectra of the reaction mixture in three different solvents (chloroform, methanol, pyridine) were recorded at −150 °C on samples taken at different reaction times by cooling aliquots in liquid nitrogen in order to slow down the reaction. Blanks (the catalyst alone and the zero-time solutions in a nitrogen atmosphere) were measured under the same conditions.

Chloroform solutions. Table 2 summarizes the EPR data related to [Co(salen)] in different solvents, reacting with oxygen and different substrates.

[*Co*(*salen*)].—The EPR parameters of the spectrum of a deoxygenated solution recorded at −150 °C are difficult to obtain, due to the contemporary presence of several paramagnetic centres [Fig. 1(*a*)]. It is well known that chloroform does not form good glasses and some of the metal centres are aligned in certain orientations,[8] in considerably large grains of chloroform crystals. This leads to selected orientations of the same paramagnetic centre with respect to the magnetic field. Some parameters of the predominant paramagnetic species can be determined ($g_1 = 3.250$, $g_3 = 1.912$, $A_1 = 93.6$ G, $A_3 \leqslant 30$ G), and are very similar to those reported for the planar form of [Co(salen)].[9] In the presence of oxygen, 0.1 MPa pressure, the spectrum remains unchanged. Under reaction conditions (1 MPa dioxygen) no EPR resonances were detected. As the formation of a [Co(salen)] superoxo-adduct is excluded by the absence of co-ordinated base (see later), it is probable that the resonances of planar [Co(salen)] are quenched because of the magnetic coupling with the paramagnetic oxygen molecules, intercalated between the cobalt centres.[10]

[*Co*(*salen*)]–*E-methyl ferulate* **1** (1 : 10 *molar ratio*).—The spectrum of the deoxygenated solution is identical to that in the absence of substrate. If contact is made with O_2 at 0.1 MPa pressure, for 15 min, a new signal appears at $g = 2.0015$, beside the resonance lines of [Co(salen)] [Fig. 1(*b*)]. This suggests that [Co(salen)] reacts only when both oxygen and substrate are present. After contact with O_2 at 1 MPa pressure (reaction conditions), aliquots of the solution taken at regular intervals gave the following results.

(*i*) Five minutes after the oxygen contact the signals of [Co(salen)] are no longer observable and two superimposed signals appear [Fig. 2(*a*)]. One is very similar to the signal

Table 2 The EPR and electronic data for [Co(salen)] (6.0×10^{-3} M)–substrate (6.0×10^{-2} M) solutions in $CHCl_3$

Substrate	Atmosphere	g	A/G	Paramagnetic species	Absorption at 1200 nm
Absent	N_2, O_2 (0.1 MPa)	$g_1 = 3.250$ $g_3 = 1.912$	$A_1 = 93.6$ $A_3 \approx 30$	Planar [Co(salen)]	Seen
E-Methyl ferulate **1**	N_2	$g_1 = 3.250$ $g_3 = 1.912$	$A_1 = 93.6$ $A_3 \approx 30$	Planar [Co(salen)]	Seen
	O_2 (0.1 MPa)	As under N_2 $g = 2.0015$	As under N_2 $A = 18.7$	Planar [Co(salen)] Phenoxy cobalt radical	Seen
	O_2 (1 MPa)	$g_1 = 2.087$ $g_1 = 2.0015$	$A_1 = 20.7$ $A = 18.7$	Superoxocobalt derivative Phenoxy cobalt radical	Undetected
E-Methyl isoferulate **2**	O_2 (1 MPa)	$g_1 = 2.087$ $g = 2.003$	$A_1 = 20.7$ $A = 18.0$	Superoxocobalt derivative Phenoxy cobalt radical	Undetected
Methyl *E*-4-hydroxycinnamate **3**	O_2 (1 MPa)	$g = 2.000$	$A = 16.2$	Phenoxy cobalt radical	Undetected
Methyl *E*-3-chloro-4-hydroxycinnamate **4**	O_2 (1 MPa)	$g = 2.005$	$A = 18.6$	Phenoxy cobalt radical	Undetected

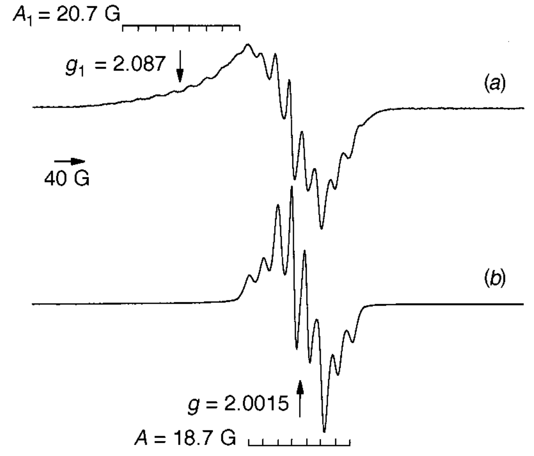


Fig. 2 The EPR spectra, recorded at 123 K, of a chloroform solution of [Co(salen)] (6×10^{-3} M)–*E*-methyl ferulate (6×10^{-2} M) (*a*) after a 5 and (*b*) a 15 min contact with O_2 at 1 MPa pressure

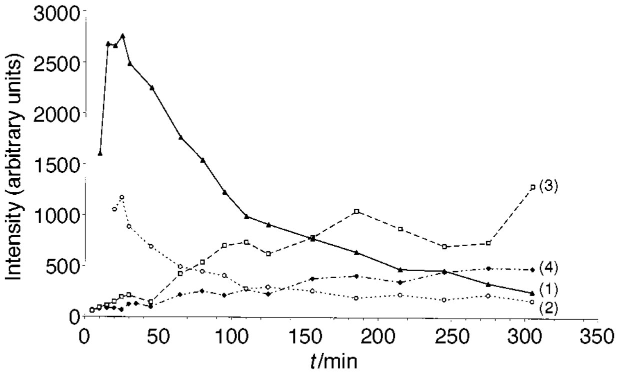


Fig. 3 Trends of intensity (arbitrary units) of resonances *vs.* time of the phenoxy cobalt radicals, in chloroform solutions at 123 K of [Co(salen)] (6×10^{-3} M) and *E*-methyl ferulate (6×10^{-2} M) (line 1), *E*-methyl isoferulate (6×10^{-2} M) (2), *E*-4-hydroxymethylcinnamate (6×10^{-2} M) (3) and methyl *E*-3-chloro-4-hydroxycinnamate (6×10^{-2} M) (4)

reported for the superoxocobalt complex [Co(salen)B(O_2)] (B = additional axially co-ordinated base ligand),[11] although only the low-field component of the magnetic tensors could be clearly distinguished ($g_1 = 2.087$, $A_1 = 20.7$ G). The other, already observed at 0.1 MPa oxygen pressure after 15 min, has eight resonance lines centred at $g = 2.0015$, due to the hyperfine interaction with the ^{59}Co ($I = \frac{7}{2}$) nucleus. The low value of the hyperfine coupling constant ($A = 18.7$ G) suggests that the unpaired electron is mainly located on the ligand [Fig. 2(*b*)]. This signal is very similar in g and A tensor values to that of a phenoxy radical co-ordinated to cobalt.[12]

(*ii*) After 10 min the superoxide signal becomes very weak and the signal of the cobalt phenoxy radical dominates. The trend of the amount of the latter radical (as integrated signal area) *vs.* reaction time is shown in Fig. 3, line 1. The absolute amount of the radical ranges between 20 and 2% of the total [Co(salen)]. It is important to observe that neither the signals of [Co(salen)B(O_2)] nor those of the phenoxy radical fixed on cobalt are quenched by the high oxygen pressure. Instead, unchanged [Co(salen)], if any, cannot be observed at high oxygen pressure.

[*Co*(*salen*)]–*E-methyl isoferulate* **2** (1 : 10 *molar ratio*).—Also in this case, the spectrum in the absence of oxygen is identical to that observed for [Co(salen)]. Unlike the case of *E*-methyl ferulate **1**, the signal attributable to the superoxocobalt complex appears after 15 min of reaction with O_2 also at 0.1 MPa pressure. The EPR spectra taken at regular intervals show at the beginning the contemporary presence of two signals: one is that of the superoxocobalt complex, better resolved than in the case of *E*-methyl ferulate, with easily accessible tensor components ($g_1 = 2.087$, $A_1 = 20.7$ G). The intensity of this signal decreases with time, even if less rapidly than in the case of *E*-methyl ferulate. The other signal, which becomes dominant after 20 min of reaction, corresponds to the spectrum of the cobalt phenoxy radical (eight resonance lines with $g = 2.003$ and $A = 18.0$ G). The trend of the cobalt phenoxy radical at different reaction times is shown in Fig. 3, line 2.

[*Co*(*salen*)]–*methyl E*-4-*hydroxycinnamate* **3** *and –methyl E*-3-*chloro*-4-*hydroxycinnamate* **4** (1 : 10 *molar ratio*).—During the reaction the cobalt phenoxy radicals are similar to those observed in the case of *E*-methyl ferulate, but their amounts have different trends (Fig. 3, lines 3 and 4) with respect to the substrates previously described. Moreover the amount in the first 30 min of reaction is low and cobalt superoxide was never detected.

[*Co*(*salen*)]–*methyl E*-4-*methoxycinnamate* **5**.—No EPR signal was observed.

Methanol solutions. [*Co*(*salen*)].—In deoxygenated solution the observed signal is attributable to an axially co-ordinated methanol adduct, probably a five-co-ordinated one, in which the fifth site is occupied by the methanol (Fig. 4). The spectrum is very similar to that of the inactive form of [Co(salen)] in which the cobalt atom is five-co-ordinated by interaction with the oxygen of the salen ligand of another [Co(salen)] molecule.[13] The signal has roughly rhombic symmetry, but not all the magnetic tensor components could be precisely determined, only the high-field component having $g_3 = 2.010$ and $A_3 = 124.0$ G. In the presence of oxygen at 0.1 MPa pressure the signal completely disappears, probably by oxidation of Co^{II} to Co^{III}, without formation of the superoxo-derivative [Co(salen)]-(MeOH)(O_2)] (see later).

[*Co*(*salen*)]–*E-methyl ferulate* **1** (1 : 10 *molar ratio*).—In deoxygenated solution the spectrum is the same as in the

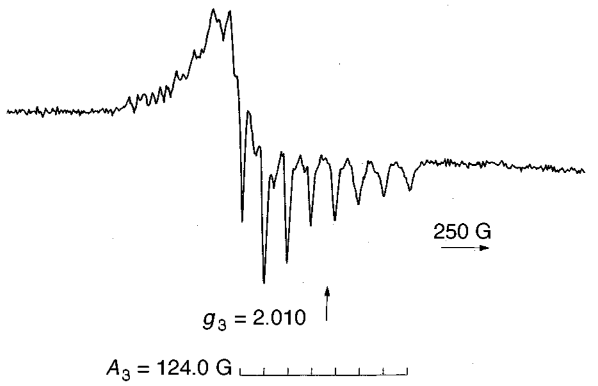


Fig. 4 The EPR spectrum, recorded at 123 K, of [Co(salen)] (6×10^{-3} M) in methanol solution under a nitrogen atmosphere

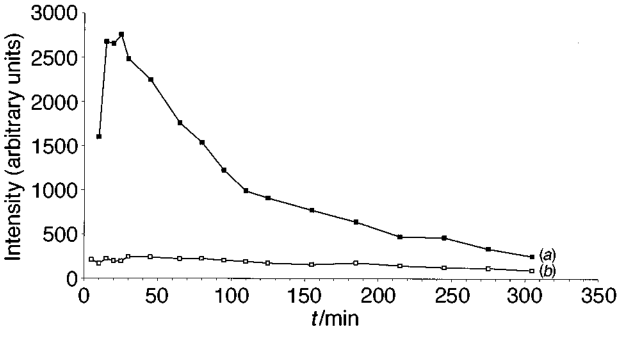


Fig. 5 Trends of intensity (arbitrary units) of resonances *vs.* time of the phenoxy cobalt radicals, taken at 123 K, for solutions of [Co(salen)] (6×10^{-3} M)]-*E*-methyl ferulate (6×10^{-2} M) **1**, (*a*) in chloroform, (*b*) in methanol

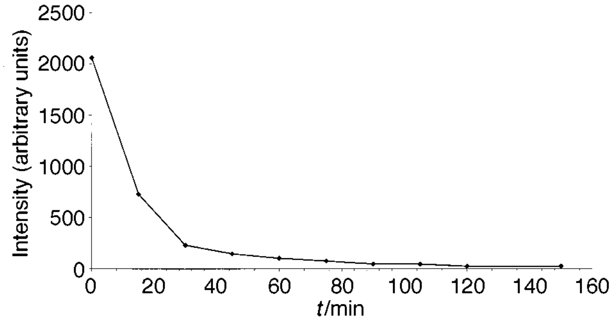


Fig. 6 Trend of intensity (arbitrary units) of resonances *vs.* time of [Co(salen)(py)(O_2)] taken at 123 K in a pyridine solution of [Co(salen)] (6×10^{-3} M)-*E*-methyl ferulate (6×10^{-2} M)

absence of the substrate. After contact with oxygen at 0.1 MPa pressure the signal of [Co(salen)] disappears. At 1 MPa pressure (reaction conditions) the EPR spectra of aliquots taken at regular intervals, cooled and recorded at −150 °C showed symmetric resonance lines very similar to those observed in chloroform and attributed to the phenoxy radical fixed on cobalt. The superoxo-derivative of [Co(salen)] did not appear. The trends in resonance lines for the reactions in methanol and in chloroform are compared in Fig. 5; in methanol a lower amount of radical was observed at any reaction time and the relative ratio between chloroform and methanol ranged from 10 to 2:1, depending on the reaction time (Fig. 5).

Pyridine (py) solutions. [*Co*(*salen*)].—In deoxygenated solutions the well known resonance lines of [Co(salen)(py)] appeared,[13] although the signals are very broad. In the presence of oxygen (both at 0.1 MPa and under reaction conditions), a signal ($g_1 = 2.082$, $g_2 = 1.996$, $A_1 = 19.6$) identical to that reported for the superoxide adducts of [Co(acacen)-(py)] [H_2acacen = 4,4′-ethylenedinitrilobis(pentan-2-one)] was observed.[11]

[*Co*(*salen*)]-*E-methyl ferulate* **1** (1:10 *molar ratio*).—In deoxygenated solution the substrate causes no changes in the EPR spectra. At 0.1 MPa oxygen pressure and under reaction conditions the cobalt phenoxy radical never forms and the superoxo-adduct [Co(salen)(py)(O_2)] is the only observed species: it rapidly decreases with time (Fig. 6), probably because of the dimerization reaction leading to a diamagnetic μ-peroxo-complex.[14]

All other substrates have the same behaviour.

Electronic investigation in the near-infrared region

The results are summarized in Table 2. The presence of the absorption band in the near-infrared region at 1200 nm indicates a planar configuration of [Co(salen)].[9] Co-ordination of a fifth (methanol, pyridine, phenol) and sixth (molecular oxygen) ligand in axial position leads to disappearance of this absorption. The absorption could not be detected also in the case of planar [Co(salen)] in the presence of high oxygen pressure, as it was obscured by the strong oxygen absorption bands in the visible region.

Discussion

Drago *et al.*[5b] studied the oxidation of isoeugenol catalysed by [bis{3-(salicylideneaminato)propyl}methylamine]cobalt(II). By analogy with their previous studies on the oxidation of variously substituted phenols with the same catalyst,[5a] these authors proposed that the phenolic group of isoeugenol [MeO-C_6H_3(CH=CHMe)OH] is first converted into a phenoxy radical through interaction with the superoxo-derivative of the cobalt catalyst; unpaired electron delocalization in the radical then leads to a π-allyl type substituent. Further oxygen attack at the β-carbon of the allyl substituent in the isoeugenol phenoxy radical was supposed to give dioxethane which decomposes into vanillin and acetaldehyde. They also investigated the role of the superoxocobalt adduct by monitoring its amount during the oxidation, through EPR spectra recorded at reaction temperature (25 °C): as the reaction progressed, the signal intensity of this derivative decreased and so did the rate of the reaction. However, no direct evidence for the isoeugenol phenoxy radical was ever obtained.

Very recently Elder and Bozell[15] performed molecular orbital calculations in order to rationalize the differences in the oxidation of variously substituted phenols, catalysed by cobalt(II) Schiff-base complexes. These authors based their conclusions essentially on the mechanism proposed by Drago and no interaction between the cobalt centre and the phenol or phenoxy radical was suggested.

Our results require the discussion of the following issues: (*i*) the co-ordination of propenoidic phenol (ROH) to [Co(salen)], in the presence of O_2 and the formation of the superoxocobalt derivative [Co(salen)(ROH)(O_2)]; (*ii*) the basicity of the co-ordinated oxygen and its radical reactivity; (*iii*) the stability of the phenoxy radical bound to cobalt.

(*i*) The results show that if the substrate cannot co-ordinate to [Co(salen)] neither the superoxocobalt derivative nor the cobalt phenoxy radical forms. In fact in $CHCl_3$ and in MeOH when the hydroxyl group is substituted by a methoxy group, as in substrate **5**, those species were not observed. Moreover, the amount of cobalt phenoxy radical is much lower in methanol than in chloroform, because methanol partially competes with phenol in the co-ordination to cobalt. In pyridine the co-ordination of phenol is not possible since pyridine, which has stronger basicity, successfully competes with phenol for the formation of [Co(salen)(py)(O_2)]. This probably undergoes further evolution into the peroxo diamagnetic dimeric derivative [{Co(salen)(py)}$_2O_2$].[14] These observations suggest that the first step of the oxidative process is the formation of a six-co-ordinated cobalt adduct, [Co(salen)(ROH)(O_2)], with O_2 and ROH in *trans* position.

The tendency of [Co(salen)] to form [Co(salen)(ROH)(O_2)] depends on the electron-donor character of the phenol ligand which is expected to lie in the order *E*-methyl ferulate **1** $\approx$ *E*-methyl isoferulate **2** > methyl *E*-3-chloro-4-hydroxycinnamate **4** $\geqslant$ methyl *E*-4-hydroxycinnamate **3**.[16] In fact, we did not observe [Co(salen)(ROH)(O_2)] in the case of substrates **3** and **4**. The results previously reported suggested that the ability of phenols to co-ordinate [Co(salen)] plays an important role in the following oxidation.

(*ii*) The co-ordination of O_2 to cobalt should involve the spin-pairing model proposed by Drago and co-workers.[17] Thus the negative charge on the co-ordinated oxygen is expected to increase with the ligand-field strength of the axially co-ordinated basic ligand, in the order: py $\geqslant$ **1** $\approx$ **2** > **4** $\geqslant$ **3**. Moreover while it is expected that [Co(salen)(py)(O_2)] undergoes dimerization through a peroxo bridge, the more electron releasing the co-ordinated phenol the better one might expect the superoxo ligand to abstract a hydrogen atom from ROH.[18] Reactions (1)–(3) could be suggested to account for the interaction of [Co(salen)] with oxygen in the presence of the phenolic substrate. The first step is the formation of the EPR-active superoxo-derivative. The second step leads to production of a cobalt(III) phenoxy radical, which is still an EPR-active species, through a more complicated process than was reported; in fact at least hydrogen abstraction, HO_2^- dissociation and RO$^\bullet$ co-ordination to cobalt should be involved. The sequence of the second step is favoured in the case of substrates **1** and **2**, because of the stronger base character of the corresponding [Co^{III}(salen)(ROH)(O_2)]$^-$ derivative.

$$[\mathrm{Co^{II}(salen)}] + \mathrm{ROH} + \mathrm{O_2} \rightleftharpoons [\mathrm{Co^{III}(salen)(ROH)(O_2)}]^- \quad (1)$$

$$[\mathrm{Co^{III}(salen)(ROH)(O_2)}]^- + \mathrm{ROH} \rightleftharpoons [\mathrm{Co^{III}(salen)(ROH)(RO^\bullet)}] + \mathrm{HO_2}^- \quad (2)$$

$$[\mathrm{Co^{III}(salen)(ROH)(RO^\bullet)}] + \mathrm{HO_2}^- \rightleftharpoons [\mathrm{Co^{III}(salen)(RO^-)(RO^\bullet)}] + \mathrm{H_2O_2} \quad (3)$$

(*iii*) The hypothesized [Co^{III}(salen)(RO$^-$)(RO$^\bullet$)] species is a radical very similar to those identified by Steenken and co-workers[19] for Fe^{III} and obtained by a strong oxidation of iron(III) bis(phenolato) complexes. For these metal phenoxy radicals an easy decomplexation of the phenoxy radical from Fe^{III} was also suggested.[19] The cobalt(III) phenoxy radical should have different stability depending on the ability of the phenol to delocalize the unpaired electron. A propenoidic chain *para* to the phenolic group, as in *E*-methyl ferulate, stabilizes it; the amount of radical found in the case of phenol **1** is much higher than in the case of **2**. In the case of phenols **3** and **4** the lower basicity does not assist the formation of [Co(salen)-(ROH)(O_2)], consequently the cobalt phenoxy radical is formed in minor amount. On the other hand, the low amount of radical increases with reaction time and suggests a higher radical stability in the case of phenols **3** and **4**. This is consistent with the expected trend of the reduction potentials:[18] **1** $\approx$ **2** $\ll$ **3** < **4**. The decomplexed radical RO$^\bullet$, according to its ability, can undergo further attack by O_2 at the β-carbon of the allyl substituent leading to dioxethane formation. This decomposes to aldehyde and acid. The radical reaction with O_2 is assessed by the disappearance of the EPR radical signal (Fig. 3), being faster the lower the reduction potential of ROH.[18]

The amount of [Co^{III}(salen)(RO$^-$)(RO$^\bullet$)] parallels both conversions and selectivities reported in Table 1.

The points previously discussed suggest that the phenol oxidation reaction involves the formation of the superoxo-derivative of [Co(salen)], followed by phenol dehydrogenation, leading to the phenoxy radical. The first step is controlled by the electron-donor properties of the phenols. The radical stability affects the subsequent reaction to final products.

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