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Oxidation activity and stability of homogeneous cobalt-sulphosalen catalyst Studies with a phenolic and a non-phenolic lignin model compound in aqueous alkaline medium

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Abstract

Oxidation activity and stability of cobalt-Schiff base complex catalyst, Co-sulphosalen, were studied in aqueous alkaline medium. The 4-coordinated Co-sulphosalen was shown to be an active catalyst, with molecular oxygen increasing the initial oxidation rates of both a phenolic (guaiacol) and a non-phenolic (veratryl alcohol) lignin model compounds. Studies with a visible absorption spectrometer showed that 4-coordinated Co-sulphosalen forms a new complex with pyridine, which attaches as axial ligand. The activity of Co-sulphosalen complex was not increased, however, but instead was slightly decreased by the addition of pyridine. With a newly developed HPLC method, it was shown that Co-sulphosalen is not stable but decomposes as a function of time. The decomposition of the catalyst through hydrolysis of its imine structures was independent of the oxidation of the model compound. The decomposition rate of Co-sulphosalen increased with increasing pH and was higher in the absence of oxygen. The presence of pyridine had virtually no effect on the stability of the catalyst.

Keywords: Oxidation; Schiff base catalyst; Coordination state; Kinetics; Stability

1. Introduction

Traditionally, residual lignin has been oxidatively degraded to soluble fragments by chlorine-containing chemicals. The oxidative degradation of lignin by molecular oxygen instead of chlorine-containing chemicals is an attractive alternative, not only for environmental reasons but because of the lower chemical costs. Unfortunately, oxygen is a far less selective bleaching agent than chlorine chemicals [1]. The selectivity of the oxygen-based methods conceivably might be increased by adding a catalyst. Polyoxometalates, metalloporphyrins and cobalt-Schiff base complexes are the most important groups of homogeneous catalysts reported to be active in bleaching reactions with oxygen [2–12]. However, no catalytic oxygen bleaching method has yet been introduced commercially.

The activity and stability of Co-Schiff base catalysts are reported to be strongly dependent on the coordination state of the complex, the reaction medium and pH. In a non-aqueous reaction medium, the catalytic activity of 5-coordinated Co-Schiff bases was higher than the activity of 4-coordinated Co-Schiff bases in

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the oxidation of several phenolic compounds [13,14]. In our previous study [12], and in studies of Fullerton and Ahern [8,9] and Meguro and co-workers [10,11], 4-coordinated Co-Schiff bases catalysed the oxidation of lignin model compounds and pulp in an aqueous alkaline reaction medium. Unfortunately, the catalytic activity of Co-Schiff bases decreases rapidly at pH higher than 10 [8,9,12]. Fullerton and Ahern proposed that this drop in activity is caused by the instability of Co-Schiff base complexes at high alkalinity.

In this work, we studied the oxidation of lignin model compounds in the presence of sulphonated Co-Schiff base catalyst, Co-sulphosalen. An attempt was made to improve the activity of 4-coordinated Co-sulphosalen by increasing the coordination state of the complex to five through the addition of axial ligand, pyridine. In addition, we studied the stability of both 4- and 5-coordinated Co-sulphosalen. Our findings are used to decide whether Co-sulphosalen could be useful as a catalyst for pulp bleaching.

2. Experimental

2.1. Materials

Guaiacol (2-methoxyphenol, >99%) was purchased from Merck and veratryl alcohol (3,4-dimethoxybenzyl alcohol, 96%) was from Aldrich. Oxygen (AGA, 99.5%) was used as oxidant and nitrogen (AGA, 99.5%) was used in the reference experiments carried out in the absence of oxygen. Buffer solutions (Merck Titrisol^{TM} ampoules) for pH 9–12 were used as solvent. The pH values referred to later in the paper correspond to the pH of the buffer solution used as solvent. All other materials were of p.a. grade (if not otherwise stated) and were used as received.

2.2. Catalysts

The catalyst, Co-sulphosalen (bis[(5-sulphonatosalicylaldehyde)ethylenediiminato] cobalt(II)disodium salt) hexahydrate, was synthesised at the University of Helsinki. The preparation of the ligand, bis(5-sulphonatosalicylidene)-1,2-ethylenediamine disodium salt, was carried out according to Langenbeek and Oehler [15]. Both the synthesised ligand and the intermediate of the ligand preparation, 2-hydroxy-4-(sodium sulphonate)benzaldehyde, were used as reference compounds in study of the decomposition of Co-sulphosalen. The catalyst was prepared from the ligand and $Co(OAc)_2{\cdot}4H_2O$ according to the method of Mukherjee and Rây [16] as modified by Haikarainen et al. [17]. The synthesised product was characterised by ESI-TOF mass spectrometry (Jeol JMS-SX102). The details of the synthesis and the characterisation of Co-sulphosalen are given elsewhere [17]. A transition metal salt, cobalt(II) acetate tetrahydrate (Merck, 99%), was used as the reference catalyst.

2.3. Procedure

All the experiments were carried out in a semi-batch glass reactor (250 ml) equipped with a magnetic stirrer. In a typical catalytic oxidation experiment, the solvent, buffered alkaline water (90 ml), was placed in the reactor and heated to the reaction temperature. Oxygen was bubbled through at a rate (150 ml/h) low enough to avoid evaporation of the solvent. The catalyst, Co-sulphosalen, dissolved in 5 ml of the buffer solution, was added to the reactor. The reaction was started by adding the model compound (0.1 mmol) in the buffer solution (5 ml). Seven samples of 1 ml were withdrawn from the reaction mixture during reaction of 24 h. The samples were analysed with a gas (Hewlett-Packard HP 5890 GC) or a high performance liquid (Agilent 1100 Series HPLC) chromatograph. In the GC and HPLC analyses, the identification of compounds was based on the known retention times of the model and reference compounds. In addition, the main decomposition product of Co-sulphosalen was identified by HPLC-mass spectrometry (Agilent 1100 Series HPLC; Micromass Quattro II triple quadrupole MS equipped with an electrospray interface) at the Technical Research Centre of Finland. From the results of the analyses, conversions of the model compounds and the decomposition of Co-sulphosalen were calculated on a molar basis. The conversions referred to in this study are total conversions of the compounds. The initial oxidation rates were determined by calculating the derivatives at time zero for the functions presenting the concentration of the compounds as a function of time. The experimental procedure is explained in more detail elsewhere [12]. A UV-Vis spectrometer (Varian Cary 50) was used to study the effect of pyridine on the coordination of Co-sulphosalen.

3. Results

3.1. Oxidation of guaiacol

The activity of Co-sulphosalen in the oxidation of guaiacol was studied at 70 °C and pH 11. Guaiacol was fairly reactive with the active species formed from molecular oxygen, even in the absence of the catalyst (Fig. 1). However, no reaction at all was observed when the experiment of 24 h was carried out in the absence of both oxygen and the catalyst. Very low concentration (0.01 mmol/kg) of 4-coordinated Co-sulphosalen increased the initial oxidation rate of guaiacol by more than 100% (Fig. 1). The same concentration of the reference catalyst, Co(II) acetate, increased the initial oxidation rate by only 15%. In the presence of higher (0.1 mmol/kg) concentration of Co(II) acetate, the initial oxidation rate was even slightly lower than in the absence of the catalyst (Fig. 1).

The effect of the coordination state of Co-sulphosalen catalyst was studied by adding pyridine to the reaction mixture. Fig. 1 shows that addition of pyridine to the reaction mixture caused a slight decrease in the initial oxidation rate of guaiacol. The initial oxidation rate did not, however, depend on the concentration of pyridine; the rate was virtually the same with low (0.01 mmol/kg) and with high (1 mmol/kg) concentrations. The formation of 5-coordinated complex in situ, with pyridine as axial ligand, was assumed in

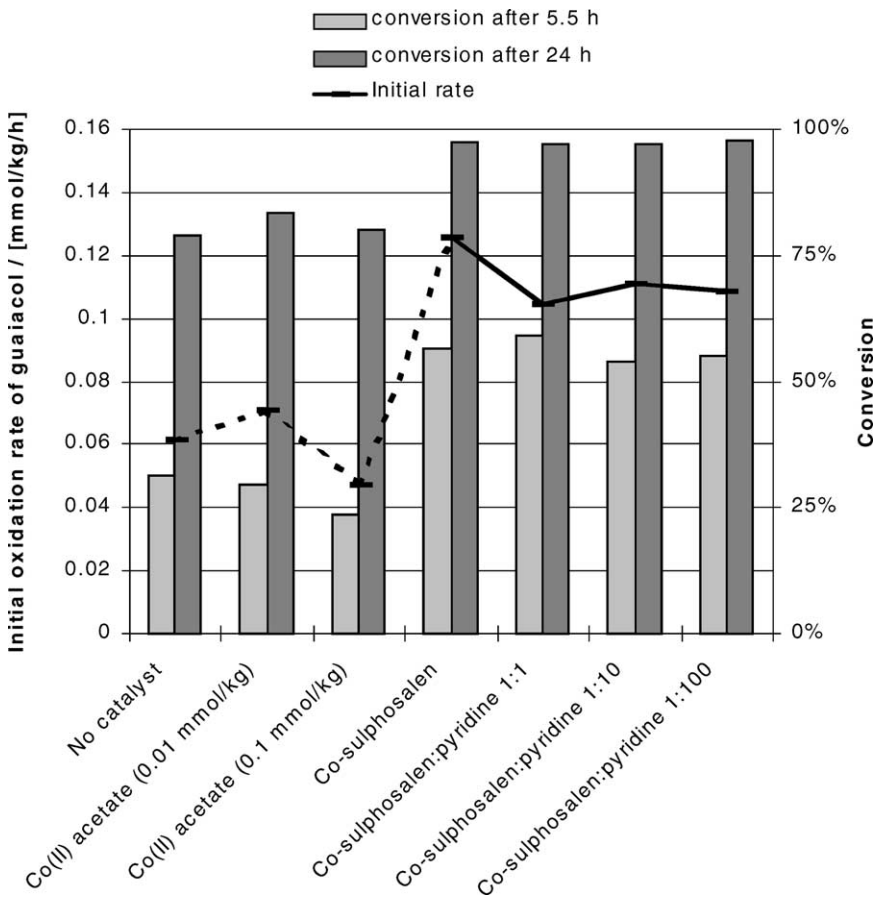


Fig. 1. Initial oxidation rate and conversions after reactions of 5.5 and 24 h in the oxidation of guaiacol as a function of the concentration of pyridine ($c_0 = 1$ mmol/kg, $c_{cat.} = 0.01$ mmol/kg, $T = 70$ °C, pH = 11, $p(O_2) = 1$ bar).

Table 1
Initial rate and conversion after reaction of 24 h in the oxidation of veratryl alcohol ($c_0 = 1$ mmol/kg, $T = 80\,^{\circ}$C, pH = 11, $p(O_2) = 1$ bar)

Catalyst	$c_{cat.}$ (mmol/kg)	c(pyridine)/$c_{cat.}$	Initial rate (mmol/kg/h)	Conversion (%) after 24 h
No catalyst	No catalyst	No pyridine	n.d.	<0.1
Co(II) acetate	0.1	No pyridine	n.d.	<0.1
Co-sulphosalen	0.01	No pyridine	0.0013	2.3
Co-sulphosalen	0.01	10	0.0013	1.9
Co-sulphosalen	0.1	No pyridine	0.0084	15.1
Co-sulphosalen	0.1	10	0.0079	14.0

these experiments. In a further experiment, pyridine was mixed with concentrated Co-sulphosalen (0.2 mmol/kg) solution to obtain 5-coordinated complex before the start of the reaction. The pre-mixing of pyridine and Co-sulphosalen had no effect on either the initial oxidation rate or the conversion after reaction of 24 h.

3.2. Oxidation of veratryl alcohol

The non-phenolic lignin model compound, veratryl alcohol, was scarcely reactive with oxygen under the aqueous alkaline (pH 11) reaction conditions at 70 °C, and therefore higher temperature (80 °C) was used in the oxidation of veratryl alcohol than in the oxidation of guaiacol. In the absence of the catalyst, the final conversion of veratryl alcohol after the reaction of 24 h was >0.1%. The activity of Co-sulphosalen in the oxidation of veratryl alcohol was noticeable; depending on its concentration, the final conversion achieved was between 1.9 and 15.1% (Table 1). From the mass balance, it was clear that the only reaction was the oxidation of veratryl alcohol to veratryl aldehyde. The reference catalyst, Co(II) acetate (0.1 mmol/kg), was not at all active in the oxidation of veratryl alcohol (Table 1).

The effect of pyridine on the oxidation of veratryl alcohol was similar to the effect of pyridine on the oxidation of guaiacol. The addition of pyridine had a slightly negative effect both on the initial oxidation rate and on the conversion after reaction of 24 h (Table 1).

In further studies with 4-coordinated Co-sulphosalen, it was shown that the initial oxidation rate of veratryl alcohol increased with increasing alkalinity (Fig. 2). At pH 12, the conversion after 24 h was lower than at pH 11, however.

3.3. Coordination of Co-sulphosalen

The ability of Co-sulphosalen to coordinate with pyridine was deduced from the change in its visible absorption spectra with the addition of the coordination compound. As shown in Fig. 3, the visible spectrum of Co-sulphosalen was clearly changed by the addition of pyridine. The increase of the absorption had a maximum at 440 nm and it was perceivable in the presence of pyridine even at lowest concentration (0.1 mmol/kg). According to Meguro and co-workers

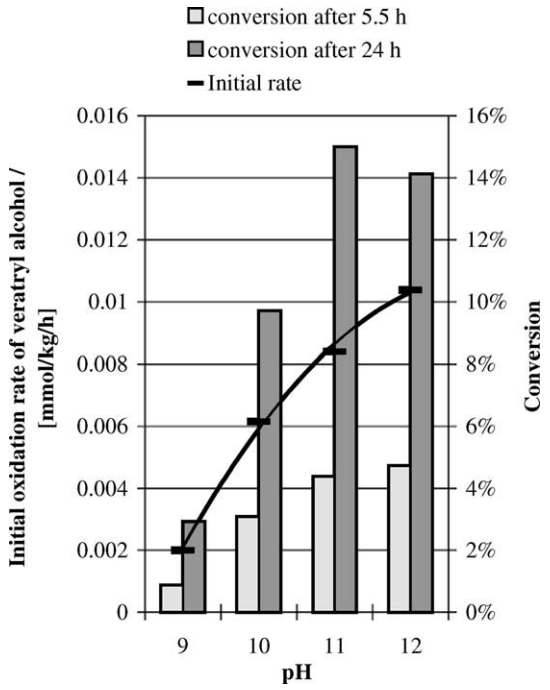


Fig. 2. Initial oxidation rate and conversions after reactions of 5.5 and 24 h in the oxidation of veratryl alcohol as a function of pH ($c_0 = 1$ mmol/kg, $c_{cat.} = 0.1$ mmol/kg, $T = 80\,^{\circ}$C, $p(O_2) = 1$ bar).

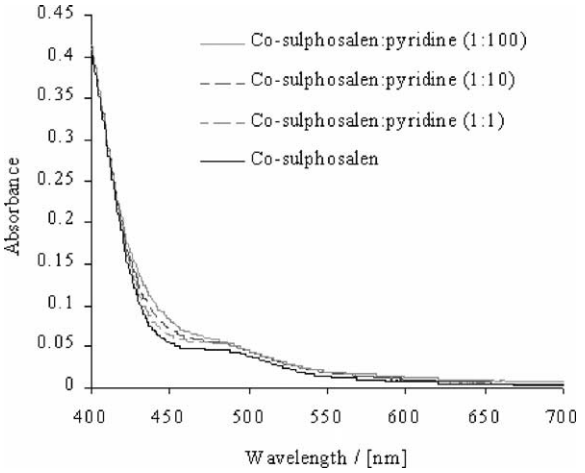


Fig. 3. Effect of pyridine on spectrum of Co-sulphosalen solution ($c_{cat.} = 0.1$ mmol/kg, pH = 11, $T = 25\,^{\circ}C$).

[10,11] and Drago and co-workers [18], the change in the visible spectrum indicates qualitatively that Co-Schiff base forms a new complex with the added component.

3.4. Stability of Co-sulphosalen

As mentioned earlier, the stability of the complex is an important factor when cobalt-Schiff base catalysts are used under highly alkaline oxidising conditions [8–11]. In this study, the decomposition of Co-sulphosalen was successfully followed by a new method of HPLC analysis (Fig. 4). Fig. 5 shows how the concentration of Co-sulphosalen complex decreased with time. The decomposition rate of Co-sulphosalen was virtually the same in the presence and the absence of the model compound, veratryl alcohol. Likewise, pyridine had no effect on the decomposition of Co-sulphosalen (Table 2). Studies with different alkalinities of the reaction mixture showed that the decomposition rate of Co-sulphosalen increased rapidly with increasing pH of the buffer solution (Fig. 6). In addition, Co-sulphosalen complex was observed to decompose in a further experiment carried out in non-buffered aqueous alkaline reaction medium. Finally, it was shown that the absence of oxygen increased the decomposition rate of Co-sulphosalen (Table 2).

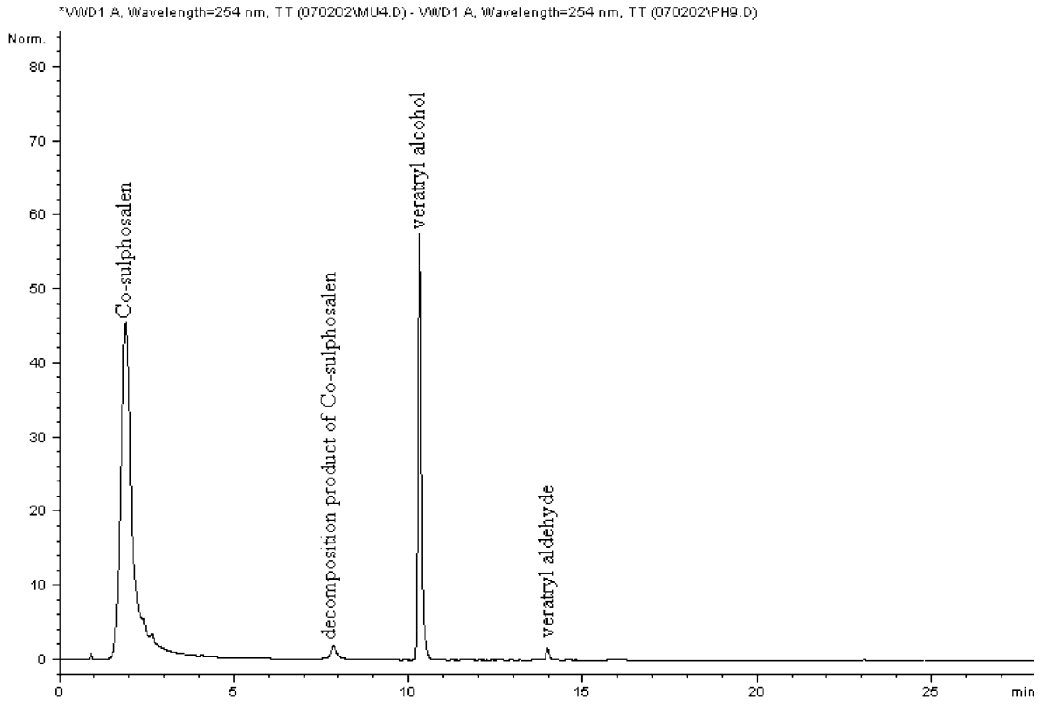


Fig. 4. HPLC chromatogram of a sample extracted during the oxidation of veratryl alcohol, showing peaks of Co-sulphosalen, the main decomposition product of Co-sulphosalen, veratryl alcohol and veratryl aldehyde.

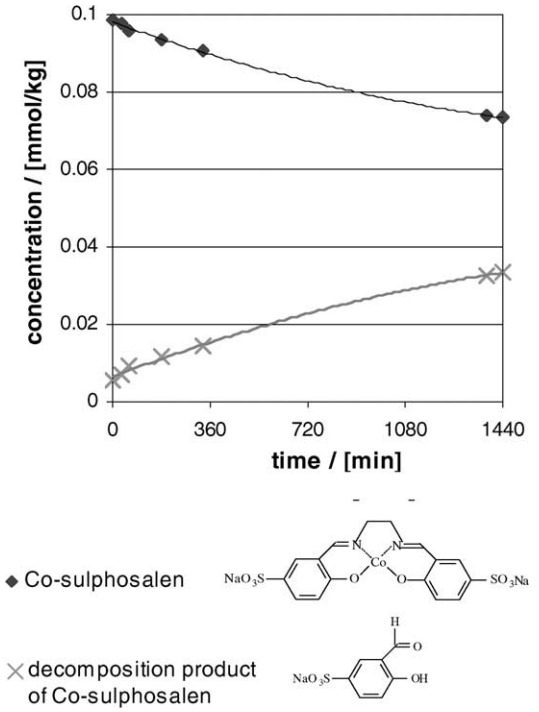


Fig. 5. Decomposition of Co-sulphosalen and formation of the main decomposition product (2-hydroxy-4-(sodium sulphonate)-benzaldehyde) as a function of time ($T = 80\,^{\circ}C$, pH = 11, $p(O_2) = 1$ bar, no veratryl alcohol).

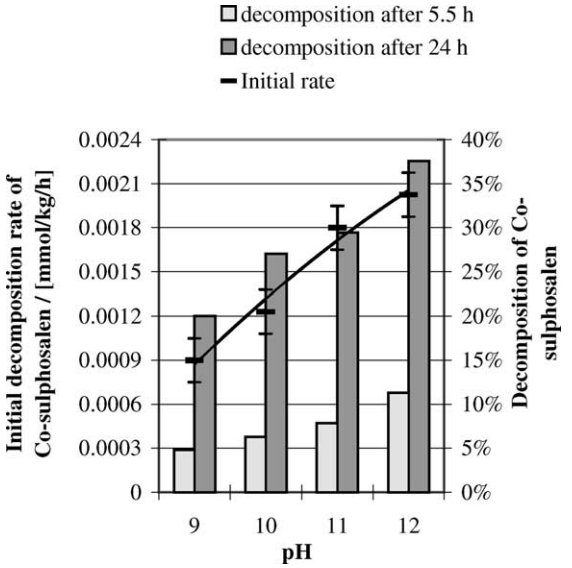


Fig. 6. Effect of pH on initial decomposition rate and conversions of Co-sulphosalen complex after reactions of 5.5 and 24 h in the oxidation of veratryl alcohol ($c_0 = 1$ mmol/kg, $c_{cat.} = 0.1$ mmol/kg, $T = 80\,^{\circ}C$, $p(O_2) = 1$ bar).

On the basis of the HPLC-MS analysis, 2-hydroxy-4-(sodium sulphonate)benzaldehyde (detected in the acid form) is deduced to be the main decomposition product of Co-sulphosalen (Fig. 7). As shown in Fig. 5, the concentration of this sulphonated salicylaldehyde increased with time. In each experiment, after 24 h, the molar amount of this decomposition product was 1.2 (±0.2) times the molar amount of the decomposed catalyst. Some other decomposition products of Co-sulphosalen were also detected but not identified.

4. Discussion

The presence of a phenolic group markedly enhances the reactivity of lignin model compounds [19]. In accordance with expectation, the phenolic model compound guaiacol readily reacted even in the absence of the catalyst. The non-phenolic veratryl alcohol, in turn, was almost non-reactive. With both model compounds, the activity of 4-coordinated Co-sulphosalen

Table 2
Initial decomposition rate and conversion of Co-sulphosalen after 24 h at 80 °C and pH 11(* ≥ $p(N_2) = 1$ bar)

c_0(catal.) (mmol/kg)	c_0(veratryl alcohol) (mmol/kg)	$p(O_2)$ (bar)	c(pyridine)/ c_0(catalyst)	Initial decomposition rate (mmol/kg/h)	Conversion (%) after 24 h
0.01	1.0	1	No pyridine	0.00013	31
0.01	1.0	1	10	0.00013	32
0.1	1.0	1	No pyridine	0.0018	31
0.1	1.0	1	10	0.0014	26
0.1	No	1	No pyridine	0.0014	25
0.1	No	0*	No pyridine	0.0027	40

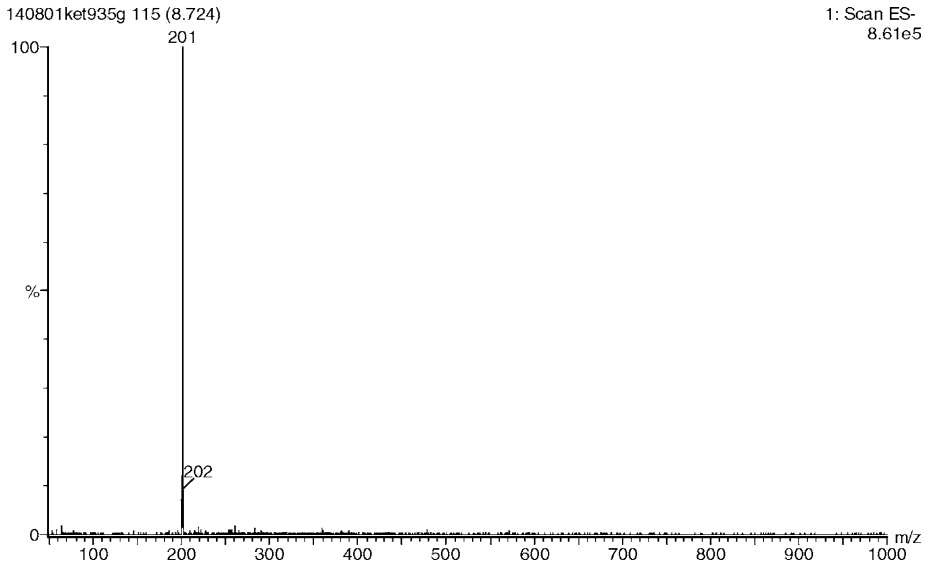
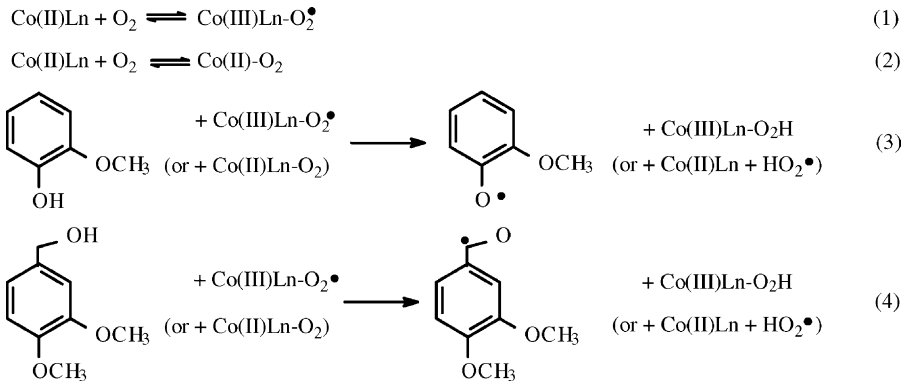


Fig. 7. MS-spectrum of the sulphonated salicylaldehyde.

was clearly demonstrated, however. The initial oxidation rates and the conversions achieved, both for guaiacol (Fig. 1) and for veraryl alcohol (Table 1), were noticeably higher even in the presence of the very low concentration (0.01 mmol/kg) of Co-sulphosalen than in the absence of the catalyst.

In the presence of oxygen, Co-Schiff bases form metal–O_2 complexes, such as oxygen–superoxo-cobalt(III) [14,20]and cobalt(II) Schiff base–oxygen [18,20] (Scheme 1, reactions 1–2). These Co-Schiff base/O_2 adducts have the ability to abstract hydrogen and therefore to initiate the oxidation reactions of guaiacol and veratryl alcohol (Scheme 1, reactions 3–4).

The very low concentration (0.01 mmol/kg) of the reference catalyst, Co(II) acetate, slightly increased the oxidation rate of guaiacol. In the presence of the higher concentration (0.1 mmol/kg) of Co(II) acetate, however, the rate was lower than in the absence of the catalyst. According to Yang [21], the catalytic activity of transition metal ions is due to their ability to promote the formation of hydroxyl radicals. Since the hydroxyl radical is one of the most active species



Scheme 1.

in oxygen bleaching, accelerated hydroxyl radical formation also has a positive effect on the oxidation rate of phenolic model compounds. In addition Yang [21] showed that at a certain concentration metal ions start to aggregate or to form hydroxy-bridged polynuclear complexes and that a maximum value in the oxidation rate of 4-methylguaiacol is obtained when the concentration of metal ions is about 0.003 mM.

The oxidation of veratryl alcohol with 4-coordinated Co-sulphosalen gave veratryl aldehyde as the sole reaction product. This is in agreement with the studies of Zhu and Ford [7], where no other reactions were observed when veratryl alcohol was oxidised in aqueous alkaline solution (under 1 bar oxygen pressure and at 85 °C) in the presence of relatively high concentration (0.8–2.5 mmol/kg) of a homogeneous metallophthalocyanine catalyst, cobalt phthalocyaninetetra(sodium sulphonate). The other homogeneous metallophthalocyanine catalysts that Zhu and Ford [7] tested were almost totally inactive in the oxidation of veratryl alcohol. From their results and the inactivity of our reference catalyst, Co(II) acetate, we can conclude that Co-sulphosalen has an especial ability to catalyse the oxidation of veratryl alcohol to veratryl aldehyde in aqueous alkaline medium (Table 1).

The catalytic activity of cobalt-Schiff base complexes appears to be related to the coordination state of the metal complex [13,14]. In this study, the effect of coordination state on the activity of Co-sulphosalen was studied by adding pyridine to the reaction mixture. The catalytic oxidation rates of both guaiacol and veratryl alcohol decreased slightly in the presence of pyridine as axial ligand. The effect of pyridine was more pronounced in the studies of Bozell et al. [14], where syringyl aldehyde reacted only in the presence of 4-coordinated Co-salen, but most of their other model compounds exhibited much higher reactivity in the presence of the 5-coordinated complex. Our spectral studies showed that the visible spectrum of Co-sulphosalen was changed upon the addition of pyridine. According to Meguro and co-workers [10,11] and Drago and co-workers [18], the change in the visible spectrum indicates qualitatively that Co-Schiff base forms a new complex with the added component. In our studies, the change in the visible spectra was more evident with high concentration (10 mmol/kg) of pyridine than in the presence of a stoichiometric (0.1 mmol/kg) concentration (Fig. 3). However, the concentration of pyridine did not affect the activity of Co-sulphosalen in the oxidation of guaiacol (Fig. 1). On the basis of the spectral and the oxidation studies, we can conclude that the activity of Co-sulphosalen is little affected by the formation of 5-coordinated complex with pyridine.

Although inadequate stability is reported to be a major problem with Co-Schiff base complex catalysts [9], their deactivation is poorly understood. In the conditions of the present study ($T = 80\,^{\circ}C$, pH 9–12 and $p(O_2) = 1$ bar), the concentration of Co-sulphosalen complex clearly decreased with time. The reaction associated with the decomposition was alkaline hydrolysis of the imine structures of Co-sulphosalen resulting in the formation of 2-hydroxy-4-(sodium sulphonate)benzaldehyde. The decomposition rate of the catalyst was virtually the same in the presence and the absence of veratryl alcohol, from which we can conclude that the hydrolysis reaction is independent of the catalytic oxidation reaction. The presence of oxygen stabilised Co-sulphosalen complex, lowering its decomposition rate. Relevant to this, Cole and Linck [22] concluded that imines complexed to metal ions are relatively stable to hydrolysis until the metal ion-imine bond breaks.

We demonstrated that both the initial oxidation rate of veratryl alcohol and the decomposition rate of Co-sulphosalen increase with increasing alkalinity. With the high decomposition rate of Co-sulphosalen at pH 12, the conversion of veratryl alcohol after reaction of 24 h reached a maximum at pH 11. In the studies of Fullerton and Ahern [9], Co-salen was the promising delignification catalyst at pH 8–10. Our studies showed that the activity of Co-sulphosalen at pH 9 is low but the initial decomposition rate is still about 50% of the value at pH 11.

5. Conclusions

We have shown that water-soluble Co-sulphosalen is an active catalyst with molecular oxygen in the oxidation of both phenolic and non-phenolic lignin model compounds. Studies with the visible absorption spectrometer showed that 4-coordinated Co-sulphosalen forms a new complex with pyridine, which attaches as an axial ligand. The activity of Co-sulphosalen complex was not increased by the addition of pyridine,

however, but instead slightly decreased. In addition, it turned out that Co-sulphosalen complex was not stable under the reaction conditions employed. The decomposition reaction, the hydrolysis of the imine structures of Co-sulphosalen, was independent of the oxidation of the model compound. Because of the instability of the complex, there will probably be very limited industrial use for Co-sulphosalen. Nevertheless, the methods developed to study the activity and the stability, together with the enhanced understanding of one Co-Schiff base catalyst (Co-sulphosalen), provide a good basis for finding more active and stable oxidation catalysts in the future.

Acknowledgements

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