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The effect of reaction conditions on the oxidation of veratryl alcohol catalyzed by cobalt salen-complexes

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Abstract

Cobalt salen-type [salen = N,N'-bis(salicylidene)ethylenediamine] complexes **1**–**6** were studied as catalysts for dioxygen activation in the oxidation of veratryl alcohol in basic aqueous conditions. The complexes Co(salen) (**1**), Co(αCH$_3$salen) (**2**) [αCH$_3$salen = N,N'-bis(αmethylsalicylidene)ethylenediamine], Co(4OHsalen) (**3**) [4OHsalen = N,N'-bis(4-hydroxosalicylidene)ethylenediamine], Co(sulfosalen) (**4**) [sulfosalen = N,N'-bis(5-sulfonatosalicylidene)ethylenediamine], Co(acacen) (**5**) [acacen = N,N'-bis(acetylacetone)ethylenediamine) and Co(N-Me-salpr) (**6**) [N-Me-salpr = bis(salicylideniminato-3-propyl)methylamine] were chosen to examine the influence of ligand structure on the catalytic activity. The effect of reaction conditions on the oxidation of veratryl alcohol was studied by varying temperature, pH, time or the nature and amount of the axial base needed to enhance the activity of complexes **1**–**5**. The catalytic behaviour of the studied complexes was shown to be very depended on the applied conditions and distinct differences could be observed among the complexes. In all reactions, veratraldehyde was the only product observed. The unsubstituted complex **1** was the most efficient catalyst in the studied system achieving turnover numbers of up to 28 at 80 °C and pH 12.5.

Keywords: Veratryl alcohol; Cobalt salen-complexes; Catalytic; Aqueous solution

1. Introduction

A controlled oxidation of organic compounds with molecular oxygen is a pursued approach in the development of environmentally benign and ecologically sustainable chemical processes. These processes can find their significance in the preparation of organic reagents [1], bleaching of pulp [2] or textiles [3], raw materials industry [4] and environmental catalysis. The problem in oxidation reactions, in general, is that high temperatures or high pressures are needed and therefore reagents are usually destroyed by radical reactions with oxygen. To enable a more specific reaction in milder conditions, a synthetic catalyst or an enzyme is needed, which can activate oxygen in such a way, that an organic substrate is oxidized selectively [5]. Many synthetic models of the active sites in enzymes have been prepared and studied to understand the mechanism of catalytic oxidation [3,5–10].

Elemental chlorine is no longer used in the pulp industry in Finland, but different compounds of chlorine are still important reagents in the bleaching sequence [11]. In these reactions several environmentally hazardous organochlorine compounds are possibly formed as side products. The use of molecular oxygen in pulp bleaching cycles is an attractive alternative to chlorine-based bleaching. The problems in totally chlorine free bleaching have been so far the need of expensive chemicals and the lower quality of the produced pulp. An efficient catalyst should enhance either the oxygen or the peroxide stage of the bleaching sequence targeting only certain functionalities in lignin and leaving the fibers untouched. Improving one of the

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stages considerably would also enable a shorter bleaching cycle and improve the quality of the recovered pulp. Catalytic transition metal complexes have more often been designed to activate the peroxide stage [2,12,13]. Dioxygen is, though, a highly desired oxidant as it is cheap and it enables clean processes with harmless side products [14]. The catalyst designed for this process should be cheap, stable in basic aqueous solutions and small, so that it can reach the sites to be oxidized in the lignin structure.

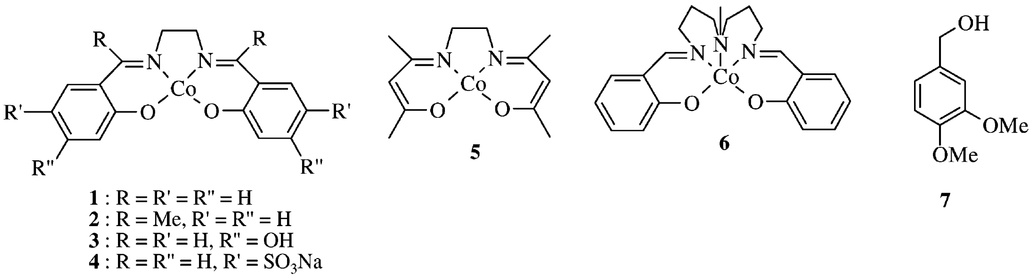
The salen-type complexes of cobalt have long been known to activate dioxygen [4,15–19]. Four-coordinated, square-planar cobalt salen-type complexes need an added base, which binds to the axial position of the coordination sphere of the central metal [4,20,21]. The trans axial ligand enhances the oxygen binding capability of the square-planar complexes and stabilizes the formed dioxygen adducts [20]. The most commonly utilized axial base in cobalt catalyzed oxidation systems is pyridine [4,21].

Co(salen) (**1**) and similar compounds react reversibly with oxygen to give an equilibrium mixture of a superoxo complex (Co:O_2 ratio 1:1) and a dimeric peroxo complex (Co:O_2 ratio 2:1) [4,9,15]. Variations in the reaction conditions or the ligand structure influence which of these species is favored [18,22]. Much of the observed effects of reaction conditions can be explained by the altered equilibrium of these two species. The formation of the superoxo complex is favored in the most polar solvents [20]. On the other hand, high temperatures favor the peroxo-bridged species [23,24].

The ability of cobalt salen-complexes to catalyze the oxidation of phenolic substrates is known [4,19,25–28], but examples of oxidation of benzylic type substrates are fewer [29]. In the present study, cobalt salen-type complexes **1**–**6** were used as catalysts to activate dioxygen for the oxidation of veratryl alcohol (**7**, Fig. 1), which was taken as a benzylic model compound for lignin substructures [30]. Veratryl alcohol was chosen as a substrate for several reasons: it contains moieties common to lignin, it is easily available, soluble in water, small and its oxidation with O_2 catalyzed by Co(salen) produces products, which are easy to analyze and therefore the observation of the effect of different reaction condition is simplified. It also has methoxy groups, so possible demethoxylation could be observed. These model reactions are important as the catalyst behaviour and activity must be monitored well before tests with more complicated substrates, e.g. pulp, can be performed. The model reactions will also help in determining the mechanism of the reaction.

Salentype complexes are easy to prepare and cheap. They are stable in water, even in higher pH and temperature, and they are small in size. Complexes **1**–**6** were chosen in order to study the influence of the ligand framework on the catalytic activity. Complex **1** has the unsubstituted salen ligand, while complex **4** has –SO_3H substituents in the ligand, which increase the solubility of the complex. Complexes **2** and **3** have electron donating substituents –CH_3 and –OH, respectively. The methyl group in the α-position (complexes **2** and **5**) should enhance the stability of the ligand. Complex **5** differs from complex **2** only by the absence of the aromaticity next to the alkoxy moiety. Complex **6** differs from the series by having an extra amine group in the bridge, otherwise resembling complex **1**.

The reactions were performed in alkaline water solutions to imitate the conditions in pulp bleaching sequences. Several reaction conditions were varied to study their effect on the oxidation activity of the



1 : R = R' = R'' = H
2 : R = Me, R' = R'' = H
3 : R = R' = H, R'' = OH
4 : R = R'' = H, R' = SO_3Na

5

6

7

Fig. 1. The structures of cobalt complexes **1**–**6** and veratryl alcohol **7**.

catalytic system. These variables include the added axial base, temperature, pH, time and solvent.

2. Experimental

The complexes **2**–**5** were prepared according to the literature methods [23,31–34]. The complexes **1** and **6** were purchased from Aldrich and used without further purification. The oxidations were performed in 25 ml two-neck flasks under oxygen gas at normal room pressure. In 10 ml of deionized water, veratryl alcohol and the axial base were added before the adjustment of pH with 2 M NaOH. The amount of cobalt complex used was the same in all experiments (0.15 mmol). The amount of veratryl alcohol used was 1.5–6 mmol. The reactions were performed at temperatures from 25 to 100 °C and allowed to proceed for approximately 20 h. The reactions were stopped by cooling to ambient temperature and adjusting the pH to 6–7 with 2 M HCl. After extraction with ethyl acetate, the solution was dried with sodium sulfate, filtered and the solvent was removed. The oxidation products were identified with IR (Perkin Elmer, Spectrum One)- and ^{1}H-NMR (Varian Gemini 2000)-spectroscopy and a few reaction products were also further examined by chromatographic methods (GC/MS, HP 5890/HP 5972 MSD) and mass spectrometry (EI-MS JEOL JMS-SX 102). If storage was needed between measurements, the oxidation products were stored at $-18\,^{\circ}$C.

3. Results and discussion

The percentages of the aldehyde conversions were determined by the ratio of the –CH_2 peak of the alcohol ($\delta = 4.55$) and the –CH peak of the formed aldehyde ($\delta = 9.78$) in the ^{1}H-NMR spectra. The GC measurements confirmed these percentages to be reliable and confirmed the absence of side products. The results are expressed as turnover numbers (TONs), which are calculated as the number of moles of substrate oxidized by 1 mol of the catalyst.

3.1. The effect of the axial base

The axial base has a significant effect on which species forms, superoxo or peroxo, and it also influences the bond length in the coordinated dioxygen [22]. In this study, it was noted that with complexes **1**–**5**, an axial base is needed for any oxidation to occur under the conditions used. Complex **6** with the base included in the ligand frame is significantly weaker as a catalyst (Figs. 3 and 4). The nature of the base has some effect as pyridine and diethylamine are almost equally efficient to enhance the oxidation, but bases such as ethylenediamine or imidazole inhibit the reaction. This indicates that the latter two bases bind to the cobalt center too strongly and either the dioxygen or the substrate cannot approach the active site. Thus, the mobility of the axial base might play an important role in the oxidation mechanism. The amount of added base has also been under discussion, and it has been suggested that too much of the base could inhibit the coordination of either the dioxygen [21] or the substrate [28]. In our experiments only the complex **5** needed stoichiometric amount of base to achieve higher conversions of the substrate. For other complexes studied, equimolar amount of base was necessary, but excess of it did not improve nor inhibit the reaction.

3.2. The effect of temperature

The minimum temperature needed for oxidation to proceed is 60 °C for catalytic systems involving complexes **1** and **5**, pyridine and water (Fig. 2). Best oxidation results for complexes **1** and **5** are obtained in the temperature range of 80–90 °C. In some extent, the effect of temperature can be related to the solubility of the complexes. The structure of the complexes affects their endurance of higher temperatures. The conversion percentages for complexes **1**–**5** at temperatures 80 and 100 °C are presented in Table 1. Contrary to the

Table 1
The oxidation of veratryl alcohol catalyzed by complexes **1**–**6** at temperatures 80 and 100 °C[a]

Complex	Conversion (%)	
	80 °C	100 °C
1	100	70
2	30	35
3	8	70
4	20	43
5	64	54

[a] The reactions were performed in water at pH 11 and using pyridine as the axial base. The results are expressed as the percentage of veratraldehyde formed. The amount of substrate in these reactions was 1.5 mmol.

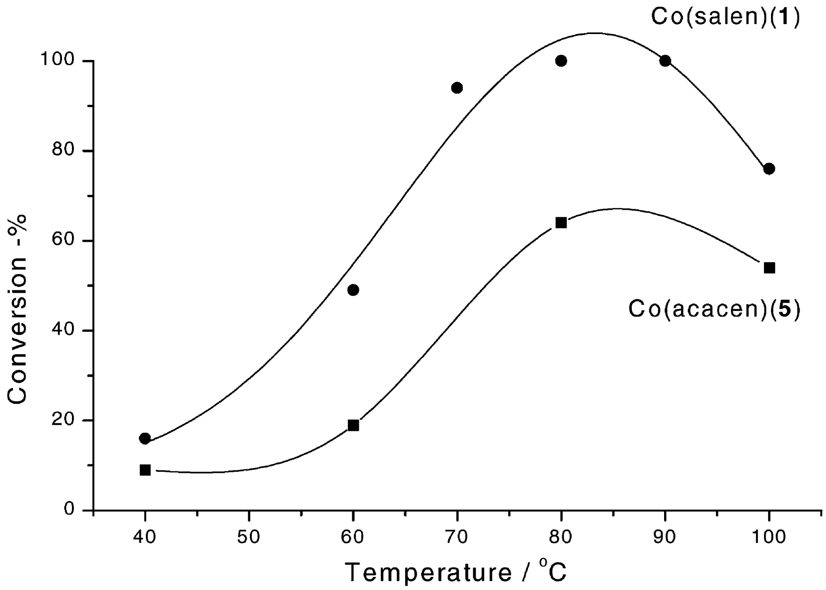


Fig. 2. The temperature needs to be over 60 °C for oxidation of veratryl alcohol to proceed well at pH 11 with complexes **1** and **5** as catalysts. Similar behaviour is observed for other complexes as well. The amount of veratryl alcohol in these experiments was 1.5 mmol.

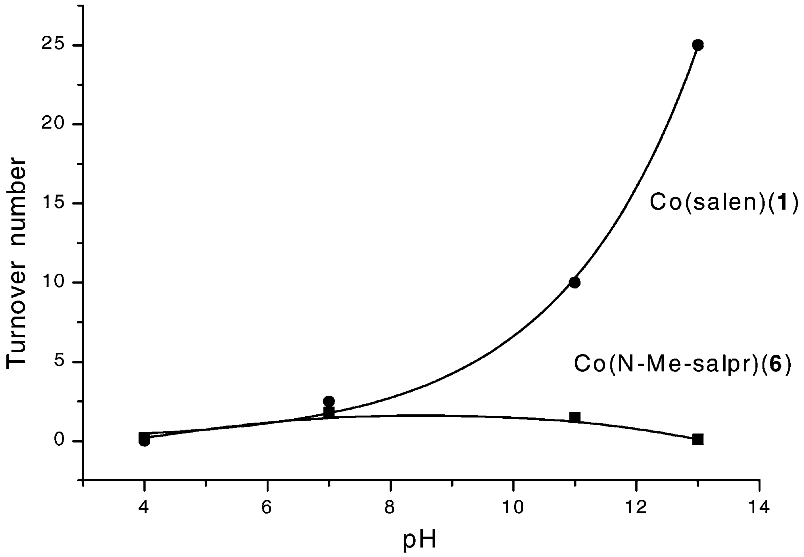


Fig. 3. The catalytic performance of complex **1** increases dramatically in higher pH values. Complex **6** shows low activity in the applied pH range. The amount of veratryl alcohol in these experiments was 6 mmol and the TON was calculated from the percentages of veratraldehyde formed.

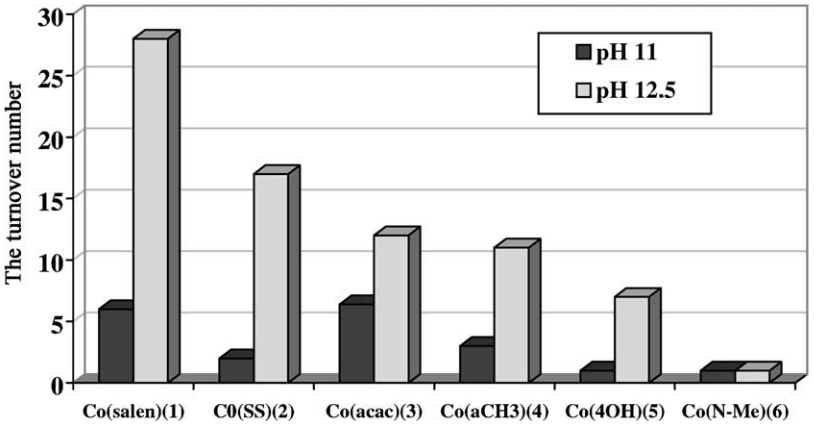


Fig. 4. The catalytic activity of the complexes **1**–**5** increases dramatically when raising the pH from 11 (left columns) to 12.5 (right columns). The amount of veratryl alcohol in these experiments was 6 mmol and the TON was calculated from the percentages of veratraldehyde formed.

behaviour of complexes **1** and **5**, the catalytic performance of complexes **3** and **4** improves with increasing temperature. The behaviour of complex **2** is similar at both temperatures. With complex **6** the conversions remain low even at higher temperatures.

3.3. The effect of pH

The variable which has a dramatic effect on the outcome of the oxidation reaction is pH. Changing the pH from 7–8 to 11 causes an enormous increase in catalytic activity for complexes **1**–**5**. Furthermore, increasing the pH to 12–13 more than doubles the conversion of alcohol to aldehyde (Fig. 3). The catalytic performance of complex **6** seems to be unaffected by changes in pH as it remains low in the pH range from 4 to 13. Fig. 4 shows how the TONs for catalysts **1**–**6** change when the pH of the reaction solution is raised from 11 to 12.5.

The complexes **1**–**5** retain their catalytic activity even in high pH values and high temperatures. When another portion of the substrate is added to the reaction solution after the initial 20 h period, the oxidation proceeds further, which indicates that the catalytic species remains active. The catalytic activity is not due to simple cobalt complexes produced in a decomposition of the complex, as in tests where cobalt(II)acetate or cobalt(II)chloride were used instead of complexes **1**–**6**, no oxidation products were obtained. Also reference experiments were performed in which no complex, no axial base or no oxygen was included, and these tests proved that this system is not active if any of the reaction components is missing.

4. Conclusions

Water is clearly an environmentally friendly solvent for large scale processes and it is the only solvent used in the pulp and paper industry. Therefore the catalytic system designed for bleaching cycles should stand aqueous and basic media. Our results show, that specific catalytic oxidation of lignin model compound veratryl alcohol can be achieved with molecular oxygen and cobalt salen-complexes in basic aqueous solutions. Catalytic oxidation has also been observed with these complexes in pulp bleaching conditions [11].

The tuning of reaction conditions proves to be important as notable differences are observed for each complex in different conditions. The most critical parameters were observed to be the nature of the axial base, temperature and pH. Changing one of the various parameters can affect dramatically the outcome of the oxidation reaction.

Based on the results above, Co(salen) (**1**) achieves its highest activity (TON 28) at 80 °C and pH 12.5. Complexes **1**–**5** show some common features, as their catalytic activity increases with raising the pH. The substituents in the salen ligand frame seem not to improve the catalytic behaviour of the cobalt complexes, as the most efficient catalyst in the oxidation of veratryl alcohol was the unsubstituted complex **1**. The structural differences do have some effect on how the complex stands reaction conditions. The substituents seem to enhance the thermal stability of these complexes. Complex **6** stands out from this group of compounds, as its catalytic behaviour is low in all of the studied environments, which might be caused by the rigidity of the axial base in the bridge.

The cobalt salen-complexes proved to be very selective in the oxidation of veratryl alcohol. These results indicate, that transition metal complexes can be an useful tool in the search of methods for improving the efficiency of the pulp bleaching cycle. Tests with other model compounds and modified ligand structures are under investigation.

Acknowledgements

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